Lecture: Advanced Statistical Physics

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Content

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Literature (Selection)

General

- Schwabl: *Statistical Mechanics*
- Landau,Lifshitz: *Theoretical Physics Vol V and IX*
- Chandler: *Introduction to Modern Statistical Mechanics*
- Chaikin/Lubensky: *Principles of Condensed Matter Physics*

Phase Transitions and Critical Phenomena

- Plischke/Bergersen: *Equilibrium Statistical Physics*
- Baker: *Quantitative theory of critical phenomena*
- Goldenfeld: *Lectures on Phase Transitions and the Renormalization Group*
- Binney, Dorwick, Fisher, Newman: *The Theory of Critical Phenomena*

Nonequilibrium Statistical Physics

- Kubo, Toda, Hashitsume: *Statistical Physics II*
- Zwanzig: *Nonequilibrium Statistical Physics*
- Babovsky: *The Boltzmann Equation*
- Paul/Baschnagel: *Stochastic Processes*
- van Kampen: *Stochastic Processes in Physics and Chemistry*
- Risken: *The Fokker Planck Equation*
- Oettinger: *Beyond Equilibrium Thermodynamics*
- Prigogine: *Non-equilibrium Statistical Mechanics*

Special Topics

- Wegner: *Supermathematics and its Applications in Statistical Physics*
- de Gennes: *Scaling Concepts in Polymer Physics*

Contents

Chapter 1

Brief Recapitulation: Thermodynamics and Statistical Physics

1.1 Thermodynamics

1.1.1 Basic Notions

Macroscopic systems are described by **macroscopic state variables**

- **Extensive** state variables: Proportional to N (particle number)
  If two systems are brought in contact, they add up.
- **Intensive** state variables: Independent of N
  If two systems are brought in contact, they strive to become equal

for example,					
	extensive	E, S	V	N	(M)
	intensive	T	P	μ	(H)

Stationary state: Does not change over time

Equilibrium: Stationary and no fluxes

Special status due to the "Zeroth law of thermodynamics"

> *If A is at equilibrium with B and B is at equilibrium with C, then A is at equilibrium with C.*

$\rightsquigarrow$ At equilibrium, intensive variables are constant throughout the whole system.

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[1] Prof. Dr. Friederike Schmid, Advanced Statistical Physics, University of Mainz, WS 2022/2023. Last change of PDF file on 21.12.2022.

Remark: This is the reason why one may introduce intensive variables such as temperature, chemical potential etc. : They can be defined based on suitable reference systems and one can construct prescriptions how to measure them.

At equilibrium, state variables can be connected by **equations of state**.

Examples: Van-der-Waals equation, Curie law ($M - CH/T = 0$).

Remark: One equation of state is usually not sufficient to fully describe a system. For example, the ideal gas law $PV = NRT$ does not provide sufficient information for deriving the internal energy of an ideal gas.

To fully characterize a thermodynamic system at equilibrium, one needs to know the **thermodynamic potentials**

1.1.2 Thermodynamic Potentials

1.1.2.1 Starting Point

The <u>fundamental</u> thermodynamic potential is the **Entropy** S

$S(E, V, N) \leftrightarrow E(S, V, N)$ contains all information on a system

S grows monotonously with E, i.e., $\frac{\partial S}{\partial E} > 0$.

Total differential: $\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu \mathrm{d}N$

- First derivatives: $\frac{\partial E}{\partial S}\big|_{V,N} = T$, $\frac{\partial E}{\partial V}\big|_{S,N} = -P$, $\frac{\partial E}{\partial N}\big|_{S,V} = \mu$
  → Equations of state
- Second derivatives: $\frac{\partial^2 E}{\partial V^2}\big|_{S,N} = -\frac{\partial P}{\partial V}\big|_{S,N} = \frac{1}{V}\frac{1}{\kappa_S}$ etc.
  → Response functions (compressibility, specific heat etc.)

However, typically, one is not interested in functional dependencies on the entropy, but rather in functional dependencies on the temperature $T = \frac{\partial E}{\partial S}$

⇒ Legendre transform, new thermodynamic potential:

Free energy $F(T, V, N) = \min_S \big(E(S, V, N) - TS\big)$

Differential: $\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu \mathrm{d}N$

Analogously, one can define

The **free enthalpy** or **Gibbs free energy** $G(T, P, N) = \min(F + PV)$
$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu \mathrm{d}N$

The **grand canonical potential** $\Omega(T, V, \mu) = \min(F - \mu N)$
$\mathrm{d}\Omega = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu$

The **general grand canonical potential** $\Delta(T, P, \mu) = \min(G - \mu N)$
$\mathrm{d}\Delta = -S\mathrm{d}T + V\mathrm{d}P - N\mathrm{d}\mu$

The choice of potential depends on the problem one wishes to study. For example, in experiments, one usually has constant pressure, therefore it is more convenient to work with G than with F.

1.1.2.2 Properties of thermodynamic potentials

- ⋆ Gibbs-Duhem relation

  E, S are extensive. ⇒ All thermodynamic potentials are extensive
  In particular: $\Delta(T, P, \mu)$ is extensive, i.e., $\Delta \propto N$,
  but does not depend explicitly on $N \Rightarrow\ \Delta \equiv 0$

  $$\Rightarrow\ G = \mu N, \quad F = \mu N - PV, \quad E = \mu N - PV + TS, \quad \cdots$$

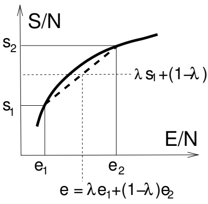
  $$\Rightarrow\ S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu = 0 \quad \text{or} \quad \frac{S}{N}\mathrm{d}T - \frac{V}{N}\mathrm{d}P + \mathrm{d}\mu = 0$$

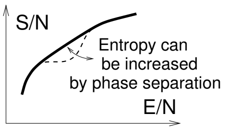
  (Gibbs-Duhem relation)

- ⋆ First derivatives → Equations of state
  Second derivative → Response functions

- ⋆ Convexity

  (i) Second law of thermodynamics: S is maximal
  $\Rightarrow\ S(E, V, N)$ concave ($\cap$)





(Mathematically: Given a system (E, V, N)
Consider potential subsystems (E_i, V_i, N_i) $(i = 1, 2)$
with $\sum_i N_i = N$, $\sum_i V_i = V$, $\sum_i E_i = E$
Define $e = E/N, v = V/N, e_i = E_i/N_i, v_i = V_i/N_i$
$s(e, v) = \frac{1}{N} S(E, V, N), s_i = s(e_i, v_i)$.
$\Rightarrow\ e = \lambda e_1 + (1-\lambda) e_2,\ v = \lambda v_1 + (1-\lambda) v_2$
with $\lambda := N_1/N$
Then, one must have: $s(e, v) \geqslant \lambda s_1 + (1-\lambda) s_2$!
(Otherwise, entropy can be increased by splitting up the system into the two subsystems!)
$\Rightarrow\ \frac{\partial^2 s}{\partial e^2} \leqslant 0,\ \frac{\partial^2 s}{\partial v^2} \leqslant 0,$
$\Rightarrow\ \frac{\partial^2 S}{\partial E^2}\Big|_{V,N} \leqslant 0,\ \frac{\partial^2 S}{\partial V^2}\Big|_{E,N} \leqslant 0$; Similarly: $\frac{\partial^2 S}{\partial N^2}\Big|_{E,V} \leqslant 0$.)

(ii) $\Rightarrow\ E(S, V, N)$ convex ($\cup$)

(Reason: According to (i), we have $s(e, v) \geqslant \lambda s_1 + (1-\lambda) s_2$
Insert $e = \lambda e_1 + (1-\lambda) e_2$; Consider inverse function $e(s, v)$
$\Rightarrow\ s(\lambda e_1 + (1-\lambda) e_2, v) \geqslant \lambda s_1 + (1-\lambda) s_2 =: \tilde{s} = s(e(\tilde{s}, v), v)$
$s(e, v)$ increases monotonically with e
$\Rightarrow\ e(\tilde{s}, v) \leqslant \lambda e_1 + (1-\lambda) e_2 \Rightarrow \frac{\partial^2 e}{\partial s^2} \geqslant 0, \quad \frac{\partial^2 e}{\partial v^2} \geqslant 0$
$\Rightarrow\ \frac{\partial^2 E}{\partial S^2}\Big|_{V,N} \geqslant 0,\ \frac{\partial^2 E}{\partial V^2}\Big|_{S,N} \geqslant 0$ etc.)

(iii) $\Rightarrow\ F(T, V, N)$: $\cup$ as a function of V
$\cap$ as a function of T $\quad \left(\frac{\partial^2 E}{\partial S^2} = -\frac{\partial T}{\partial S} > 0 \Rightarrow -\frac{\partial S}{\partial T} = \frac{\partial^2 F}{\partial T^2} < 0\right)$

General (except for S)
concave ($\cap$) as a function of intensive variables
convex ($\cup$) as a function of extensive variables

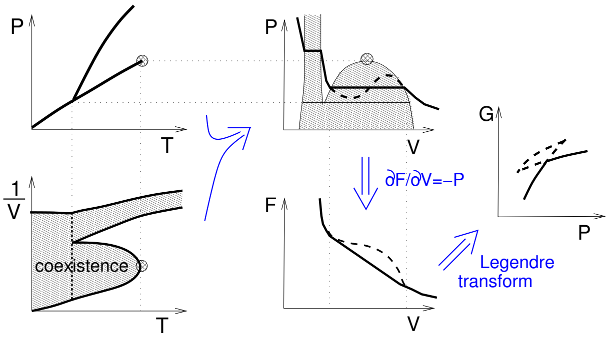
Consequences: Thermodynamic stability conditions
Positivity of compressibility and specific heat etc.

1.1.2.3 Thermodynamics of phase transitions

⋆ Examples:

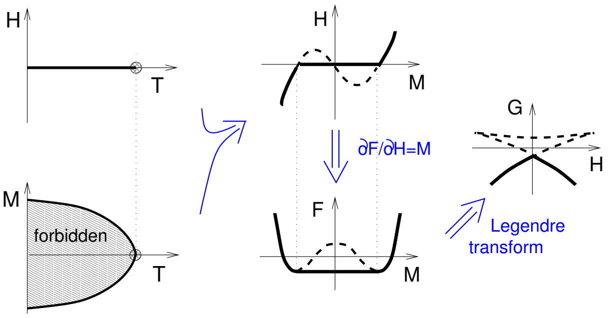
(a) Liquid-gas transition

Phase diagrams in the planes
$(P-T)$, $(V-T)$, $(P-V)$
Example of isotherm in $(P-V)$
$(P(V, T=T_0))$
Corresponding free energy curve
$(F(V, T=T_0))$
Corresponding Gibbs free energy
$(G(P, T=T_0))$



(b) Magnetism:

Phase diagrams in the planes
$(H-T)$, $(M-T)$, $(H-M)$
Example of isotherm in $(H-M)$
$(H(M, T=T_0))$
Corresponding free energy curve
$(F(M, T=T_0))$
Corresponding Gibbs free energy
$(G(H, T=T_0))$



Phase diagrams etc. have a similar topology than in the case of the liquid-gas transition

Main difference: No phase coexistence at equilibrium, because magnetization is not a conserved quantity ⇝ Spins can flip.

⇝ "Forbidden" regions instead of coexistence regions
(In real systems, however, nonequilibrium states where domains with different magnetization coexist are possible and even frequent).

⋆ General remarks:

At discontinuous phase transitions where phases may coexist:
– Intensive variables are equal (P, T, μ)
– Extensive variables "split up" $(V \to V_{(1)} + V_{(2)}, \cdots)$

⇝ Consequences for phase diagrams

Intensive variables, e.g., $P-T$ diagram
→ parametrized lines (in 2D) or surfaces (in 3D)

Extensive variables, e.g. $V-T$ diagram
→ at discontinuous transitions: Coexistence regions or forbidden regions (areas, volumes)
at continuous transitions: lines, parametrized surfaces etc.

Characterization of phases via "order parameter": Must be extensive
(must be able to distinguish between coexisting phases)

- ⋆ Gibbs phase rule

  Example, how general thermodynamic considerations can be used to deduce specific statements on phase transitions.

  Consider a simple one-component (NPT) system.
  Analyze coexistence lines in the ($P-T$) phase diagram.
  If m phases coexist, then the chemical potentials μ of all phases have to be equal $\mu_1(P,T) = \mu_2(P,T) = \cdots = \mu_m(P,T)$
  $\Rightarrow$ $(m-1)$ equations for two parameters (P and T)
  $\Rightarrow$ At most $\underline{m=3}$ phases can coexist (triple point).

  More generally: Consider n-component system,
  $\Rightarrow$ n chemical potentials have to be equal in all m phases
  $\Rightarrow$ $n \cdot (m-1)$ equations for $2 + m \cdot (n-1)$ unknown parameters (P, T and the concentrations of component i in phase j)
  $\Rightarrow$ $f = 2 + m(n-1) - n(m-1)$ "free" parameters
  $\Rightarrow$ At most $f = 2 + n - m$ phases can coexist!

  Exceptions are possible if certain symmetries ensure the validities of some of the equations.

- ⋆ Classification of phase transitions

  A phase transition is always associated with a singularity in the thermodynamic potentials (as a function of intensive variables). This motivates schemes to classify phase transitions.

  Ehrenfest classification

  First order phase transition: First derivative of the thermodynamic potential with respect to an intensive variable (e.g., temperature or an applied field) is discontinuous, makes a finite jump.
  NB: Jump in the derivative with respect to temperature indicates production or consumption of latent heat at the transition.

  nth order phase transition: nth derivative is discontinuous, makes a finite jump

  Definition turns out to be problematic, because the second derivatives at "second order transitions" often diverge instead of simply jumping.
  $\rightsquigarrow$ The singularity is not characterized sufficiently !
  Possible way out: Fractional derivatives

  Most common approach in the literature
  No "classification", but just distinction between **first order transitions** and **discontinuous transitions**

  Later (Chapter 6), we will learn that it is possible to classify phase transitions in terms of so-called **universality classes**.

1.2 Statistical physics

Thermodynamics:

Macroscopic state variables and relations between them
Axiomatic (laws of thermodynamics)

Statistical physics:

Starting point: $N \sim 10^{23}$ microscopic particles, $6N$ degrees of freedom, Hamiltonian $\mathscr{H}(p_i, q_i)$

Different types of coupling to the environment

- isolated (microcanonical ensemble)
- energy exchange is possible (canonical ensemble)
- energy and particle exchange is possible (grand canonical ensemble)

Ansatz: A microscopic description of the full system is neither possible nor sensible.
(e.g., would require $3N$ initial conditions)
→ Restriction to statistical statements

1.2.1 Basic assumptions

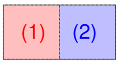
- Ergodic hypothesis: In the limit $t \to \infty$, the system comes arbitrarily close to every allowed configuration for almost all initial conditions.
  Mathematically: Time average = Ensemble average

- Principle of maximal ignorance (Jayne's principle)
  Define **information entropy** of probability distribution $p(\Gamma)$ for configurations Γ

  $I = -\sum_\Gamma p(\Gamma) \ln(p(\Gamma)) = -\langle \ln p \rangle$

  $\Rightarrow \; I \overset{!}{=} \max$

- Additivity: Subdivide system into two subsystems



$\to \; I = I^{(1)} + I^{(2)} \;\Leftrightarrow$ Partitioning possible: $p^{\text{total}} = p^{(1)} p^{(2)}$
$\Rightarrow$ Particles are indistinguishable!

1.2.2 Consequence: Distributions $p(\Gamma)$

(a) Microcanonical ensemble

Energy is in the interval $[E, E + \mathrm{d}E]$
→ Number of possible states: $\mathscr{N}(E)$
→ $p(\Gamma) = 1/\mathscr{N}(E)$; $\qquad I_{\text{max}} = \ln \mathscr{N}(E)$

(b) Canonical ensemble

I is maximal with boundary condition $\langle E\rangle = \hat{E}$ (and $\sum_\Gamma p = 1$)

$\rightarrow$ Lagrange parameters β, λ

$\Rightarrow \delta\Big(\sum p\ln p + \beta(\sum pE - \hat{E}) + \lambda(\sum p - 1)\Big) = 0$

$\Rightarrow \ln p + 1 + \beta E + \lambda = 0 \quad \Rightarrow \quad p \propto \mathrm{e}^{-\beta E}$

$\Rightarrow$ Boltzmann distribution: $p(E) = \frac{1}{\mathscr{Z}_c}\mathrm{e}^{-\beta E}$

with $\mathscr{Z}_c = \sum \mathrm{e}^{-\beta E}$: Canonical Partition function

$I_{\text{max}} = -\sum p\ln p = \beta\langle E\rangle + \ln\mathscr{Z}_c$

(c) Grand canonical ensemble

I maximal with boundary conditions $\langle E\rangle = \hat{E}$, $\langle N\rangle = \hat{N}$, $\sum_\Gamma p = 1$

$\rightarrow$ additional Lagrange parameter $(-\mu\beta)$

$\rightsquigarrow p = \frac{1}{\mathscr{Z}_{gc}}\mathrm{e}^{-\beta(E-\mu N)}$

with $\mathscr{Z}_{gc} = \sum \mathrm{e}^{-\beta(E-\mu N)}$: Grand canonical partition function

$I_{\text{max}} = \beta(\langle E\rangle - \mu\langle N\rangle) + \ln\mathscr{Z}_{gc}$

1.2.3 Relation to thermodynamics

(a) Initial remarks:

- Partition the system into two "weakly coupled" subsystems
  $\Rightarrow E_{\text{total}} = E^{(1)} + E^{(2)}$ for all partitionings
  with $p(E) \propto \mathrm{e}^{-\beta E}$
  and $p(E) = p(E^{(1)})p(E^{(2)}) \propto \mathrm{e}^{-\beta^{(1)}E^{(1)}}\mathrm{e}^{-\beta^{(2)}E^{(2)}}$
  $\Rightarrow \beta^{(1)} = \beta^{(2)} = \beta$ is an intensive quantity.
- $\langle E\rangle$ is extensive and $\langle E\rangle = -\frac{\partial\ln\mathscr{Z}}{\partial\beta} \;\Rightarrow\; \ln\mathscr{Z}$ is extensive
  $-\frac{\partial\langle E\rangle}{\partial\beta} = (\langle E^2\rangle - \langle E\rangle^2) \;\Rightarrow\; (\Delta E)^2$ is extensive $\Rightarrow \frac{\Delta E}{E} \propto \sqrt{\frac{1}{\langle N\rangle}}$
  $\rightsquigarrow$ In the limit $\langle N\rangle \rightarrow \infty$, the relative energy is arbitrarily sharp!
- Analogeously: μ is an intensive quantity, $\langle N\rangle \rightarrow \infty \;\Rightarrow\; \frac{\Delta N}{\langle N\rangle} \rightarrow 0$

(b) Thermodynamic potentials

– Grand canonical ensemble:

Define $\Omega = -\frac{1}{\beta}\ln\mathscr{Z}_{gc} = \Omega(\beta, \mu)$

$$\begin{aligned}\Rightarrow \mathrm{d}\Omega &= \mathrm{d}\beta\Big\{\tfrac{1}{\beta^2}\ln\mathscr{Z}_{gc} - \tfrac{1}{\beta}\tfrac{1}{\mathscr{Z}_{gc}}\tfrac{\partial\mathscr{Z}_{gc}}{\partial\beta}\Big\} - \tfrac{1}{\beta}\tfrac{1}{\mathscr{Z}_{gc}}\tfrac{\partial\mathscr{Z}_{gc}}{\partial\mu}\mathrm{d}\mu \\ &= \tfrac{\mathrm{d}\beta}{\beta^2}\Big\{\ln\mathscr{Z}_{gc} + \beta(\langle E\rangle - \mu\langle N\rangle)\Big\} - \tfrac{1}{\beta}\beta\langle N\rangle\mathrm{d}\mu \\ &= \tfrac{\mathrm{d}\beta}{\beta^2}I_{\text{max}} - \langle N\rangle\mathrm{d}\mu\end{aligned}$$

Identify:
$$\begin{aligned}\mu &\equiv \text{chemical potential} \\ \beta &\equiv 1/k_BT \\ I_{\text{max}} &\equiv S/k_BT\end{aligned}$$

$\Rightarrow \mathrm{d}\Omega = -S\mathrm{d}T - N\mathrm{d}\mu$

$\Rightarrow \Omega$ corresponds to grand canonical potential in thermodynamics

– Canonical ensemble

Define $F(\beta, N) = -\frac{1}{\beta} \ln \mathscr{Z}_c(\beta, N)$

Grand canonical potential: $\Omega = -\frac{1}{\beta} \ln \mathscr{Z}_{gc} = -\frac{1}{\beta} \ln \big(\sum_N \mathrm{e}^{\beta\mu N} \mathscr{Z}_c(N) \big)$

$\frac{\langle N \rangle \to \infty}{\Delta N/N \to 0} \approx -\frac{1}{\beta} \ln \big(\mathrm{e}^{\beta\mu\langle N \rangle} \mathscr{Z}_c(\langle N \rangle) \big) = F - \mu N$

F corresponds to canonical potential in thermodynamics

– Microcanonical ensemble with fixed energy E

Start from canonical potential:

$$F = -\frac{1}{\beta} \ln \mathscr{Z}_c = -\frac{1}{\beta} \ln \sum_E \mathrm{e}^{-\beta E} \overset{\langle N \rangle \to \infty, \frac{\Delta E}{E} \to 0}{\approx} -\frac{1}{\beta} \ln \mathscr{N}(E) \mathrm{e}^{-\beta E}$$
$$= E - \frac{1}{\beta} \ln \mathscr{N}(E) = E - T\, I^{\text{microc.}}_{\text{max}} / k_B \equiv E - TS \quad \checkmark$$

(c) Thermodynamic limit

To map different ensembles onto each other, we have used that a system can be partitioned into "weakly coupled" subsystems.

⇒ Energy exchange must be possible (otherwise, thermodynamic equilibrium cannot be reached), but $E = \sum_i E^{(i)} + \delta E$ with $\delta E / E \to \infty$

⇔ The energy E must be extensive (likewise, $F, \Omega, \cdots$ must be extensive)

This is the central assumption of the **thermodynamic limit**!

Beware: The thermodynamic limit does not always exist!

Example: Consider a system of particles with pair interactions that decay according to a power law: $U(r) \propto A/r^\sigma$

Calculate the energy of a sphere with radius R (volume V_R) and homogeneous density ρ in d dimensions:

$$\Rightarrow \; E(R) = A\frac{\rho^2}{2} \int_{V_R} \mathrm{d}^d r \, \mathrm{d}^d r' \, \frac{1}{|\vec{r} - \vec{r}'|^\sigma}$$
$$\overset{\substack{\vec{r} = R\vec{x} \\ \vec{r}' = R\vec{y}}}{=} A\frac{\rho^2}{2} \int_{\text{unit sphere} V_1} R^{2d} \mathrm{d}^d x \, \mathrm{d}^d y \, \frac{1}{|\vec{x} - \vec{y}|^\sigma R^\sigma}$$
$$= \frac{\rho^2}{2} R^{2d-\sigma} \text{const.} \quad (\text{with const.} = A \int_{V_1} \mathrm{d}^d x \mathrm{d}^d y \frac{1}{|\vec{x} - \vec{y}|^\sigma})$$

⇒ With $V(R) \propto R^d$, one gets $E(R)/V(R) \propto R^{d-\sigma}$

⇒ The thermodynamic limit exists only for $\sigma > d$ (at $\sigma = d$ it turns out that $E(R)/V(R) \propto \ln R$)

Consequence: In three dimensions ($d = 3$), the thermodynamic limit does not exist for $\sigma = 1$, e.g., systems of particles with Coulomb interactions or gravitational interactions!
Can often be fixed for overall neutral systems of charged particles (electrostatic screening), but not for gravitational interactions!

Why the thermodynamic limit is important

- Necessary for equivalence of ensembles (see above)
- In the canonical and grand canonical ensemble, phase transitions are only possible in the thermodynamic limit.
  ⇝ See next chapter!

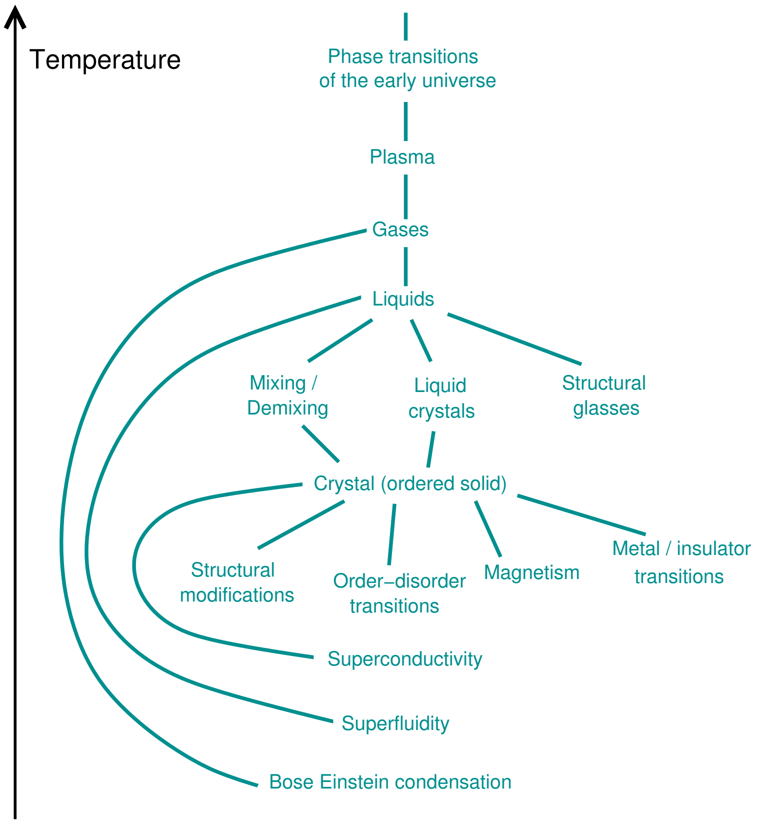
Part I

Phase Transitions and Critical Phenomena

Chapter 2

Introduction: Phase Transitions

2.1 Spectrum of possible phase transitions



2.1.1 "Classic" phase transitions

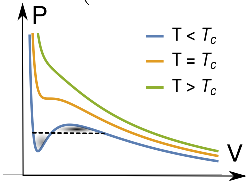
(a) Liquid-gas transition

- Phenomenological description via van der Waals equation:

  $$\boxed{(P + a/V^2)(V - b) = RT}\text{, with}$$

  b: Reduction of accessible volume due to own volume of particles
  a/V^2: "Internal pressure" due to interaction between particles

  → Two classes of isotherms (lines with temperature T = const.)



- Small T: $P(V)$ exhibits "van der Waals loop" → unphysical!
  mechanical equilibrium: Pressure must decay monotoneously
  → phase separation, horizontal isotherm in two-phase region
  chemical equilibrium: Chemical potential identical in both phases
  → Maxwell area rule (proof: exercise)

- Large T: Pressure $P(V)$ decays monotoneously, no phase transition

- Transition T_c: Critical point with $\frac{\partial P}{\partial V}\Big|_{V_c,T_c} = \frac{\partial^2 P}{\partial V^2}\Big|_{V_c,T_c} = 0$

  To analyze transition point: Rewrite van der Waals equation as

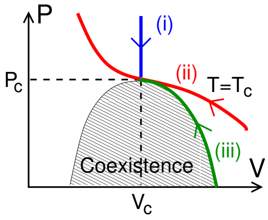
  $$\Phi(V,T,P) := V^3 - V^2\,(b + RT/P) + V\,a/P - ab/P \equiv 0$$

  $$\Big((\tfrac{\partial P}{\partial V})_T = -(\tfrac{\partial \Phi}{\partial V})_{P,T} \Big/ (\tfrac{\partial \Phi}{\partial P})_{V,T},\ (\tfrac{\partial^2 P}{\partial V^2})_T = -(\tfrac{\partial^2 \Phi}{\partial V^2})_{P,T} \Big/ (\tfrac{\partial \Phi}{\partial P})_{V,T},\ +(\tfrac{\partial \Phi}{\partial V})_{P,T}(\tfrac{\partial^2 \Phi}{\partial V \partial V})_T \Big/ (\tfrac{\partial \Phi}{\partial P})^2_{V,T}$$
  $$\Rightarrow (\tfrac{\partial P}{\partial V})_T = (\tfrac{\partial^2 P}{\partial V^2})_T = 0 \text{ with } \Phi \equiv 0 \text{ implies } (\tfrac{\partial \Phi}{\partial V})_{P,T} = (\tfrac{\partial^2 \Phi}{\partial V^2})_{P,T} = 0 \Big)$$

  - Location of critical point:
    via $\Phi(V_c, T_c, P_c) = (V - V_c)^3$ (three zeroes collapse)
    Insert and compare coefficients ⇒ $\boxed{V_c P_c / R T_c = 3/8}$
    (Experimental values: ^{4}He: 0.308; H_2: 0.304;
    O_2: 0.292; H_2O: 0.230)

  - Behavior in the vicinity of the critical point

    Compare different paths:
    (i) $V \equiv V_c$: $\kappa_T = -\frac{1}{V_c}\frac{\partial V}{\partial P}\Big|_T \propto |T - T_c|^{-\gamma}$
    with $\gamma = 1$
    (ii) $T \equiv T_c$: $P - P_c \propto |V - V_c|^{\delta}$
    with $\delta = 3$
    (iii) Coexistence: $V_{\text{gas}} - V_{\text{liquid}} \propto (T_c - T)^{\beta}$
    with $\beta = 1/2$



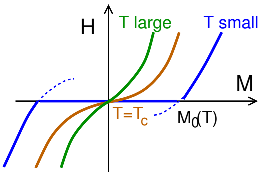
  → Algebraic behavior
  Critical exponents γ, δ, β (exp.: $\gamma = 1.24, \delta = 4.8, \beta = 0.33$)

- Conclusions:
  Phenomenological description, surprisingly successful
  Universal properties at the critical point
  (power laws, critical exponents independent of material)

(b) Magnetism

- Phase diagram

  Magnetization of a ferromagnet
  $M_0(T)$: Spontaneous magnetization

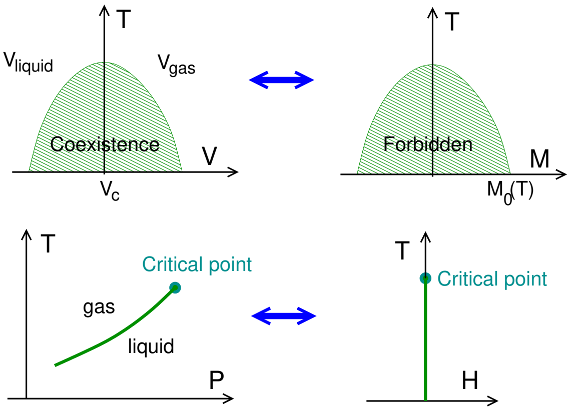


- Description by phenomenological theory

  Ideal paramagnet: Curie law $M = \frac{C}{T} H$
  Ferromagnet: Curie-law + molecular field: $H_{\text{mol}} = \lambda M$
  ($H_{\text{mol}} \propto M$: interaction with magnetized environment)
  $\Rightarrow$ $M = \frac{C}{T}(H + \lambda M)$ (Curie-Weiss law)
  $\Rightarrow$ High temperature: $\chi_T = \frac{\partial M}{\partial H}\Big|_T \propto \frac{1}{T - \lambda C} \propto \frac{1}{|T - T_c|}$
  Low temperature ($T < T_c$): Description breaks down
  Curie law must be replaced by more accurate law:
  $M \propto \tanh(\frac{CH}{T}) \rightarrow$ spontaneous magnetization etc.

- Comparison with liquid-gas transition

  Phase diagrams:



  Critical exponents:

  – Order parameter: $M_0(T); (V_{\text{gas}} - V_{\text{liquid}}) \propto |T - T_c|^\beta$
  – Susceptibility, compressibility: $\frac{\partial(\text{order parameter})}{\partial(\text{conjugated field})} \propto |T - T_c|^{-\gamma}$
  – Order parameter ↔ conjugated field: $\left\{ \begin{array}{c} H \propto M^\delta \\ (P - P_c) \propto (V - V_c)^\delta \end{array} \right\}$
  – Specific heat: $C_H; C_V \propto |T - T_c|^\alpha$

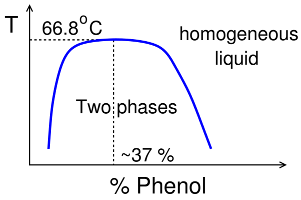
  Values of critical exponents:

  Same for both systems within phenomenological theories:
  $\alpha = 0$ (corresponds to a jump)
  $\beta = 1/2$ (corresponds to a jump)
  $\gamma = 1$ (corresponds to a jump)
  $\delta = 3$ (corresponds to a jump)
  (experimentally: not exactly the same, but similar)

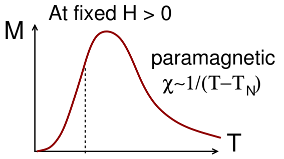
2.1.2 Other Examples of phase transitions

(c) Demixing of fluids

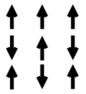
Example: Phenol and water



(d) Antiferromagnet



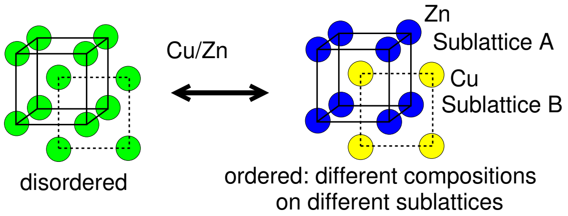
Picture: ferromagnetically ordered sublattices



Order parameter:
"sublattice magnetization"

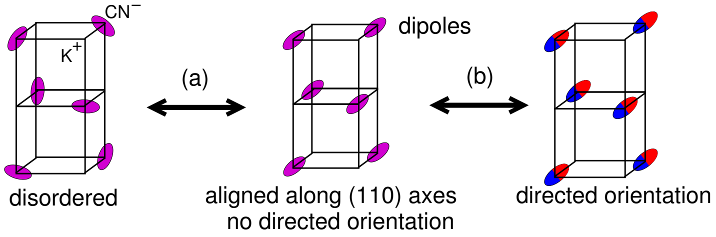
(e) Order-disorder phase transformations

- Example: Brass (CuZn alloy)



$\rightsquigarrow$ Positional order

- Example: KCn



$\rightsquigarrow$ Orientational order

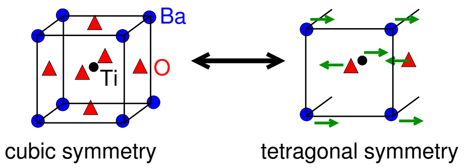
Order parameter:

(a) Orientational order tensor

(b) Mean orientation : $\sum \sigma_j$ with $\sigma_j = \pm 1$ for ◐, ◑

(f) Structural phase transitions

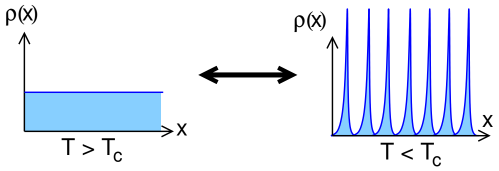
Example: Ba Ti O_3



Description: "Condensation" of a specific optical phonon with $\mathbf{q} = 0 \rightarrow$ "soft mode"

When approaching the phase transition from the "disordered" state, this phonon becomes arbitrarily "soft".
Amplitude ϕ of this phonon → "Order parameter" $\langle \phi \rangle$

(g) Melting and freezing



"Freezing
of density fluctuations"

– Phase transition is always discontinuous

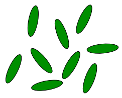
– Possible description: $\rho(\vec{r}) = \sum_{\vec{G}} \hat{\rho}_{\vec{G}} \mathrm{e}^{i\vec{G}\vec{r}}$; with order parameter $\{\hat{\rho}_{\vec{G}}\}$

(h) Liquid crystals

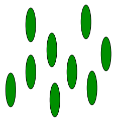
Liquids of strongly anisotropic molecules or building blocks

Possible phases:

– Disordered:

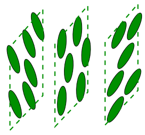


– Nematic:



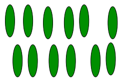
No positional order,
but orientational order
Order parameter: Orientation tensor

– Cholesteric:



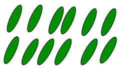
Nematic within (xy) planes
Twisted in z direction

– Smectic A:



Nematic order
Positional order in one direction (layers)
Liquid within layers

– Smectic B:



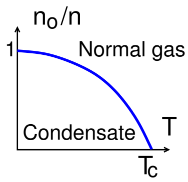
Same as smectic A,
but tilted orientation

Application: Liquid crystal displays (LCDs)
– exploit optical anisotropy in nematic or smectic phases

(i) Macroscopic quantum states

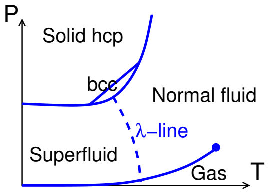
- Bose condensation: Consider a gas of non-interacting bosons

  At low temperatures, high densities:
  Macroscopic fraction of particles
  occupies ground state.
  Order parameter: $\psi = \sqrt{n}e^{i\phi}$
  with $n(r)$: density of condensate



- Superfluidity: (He^3, He^4)

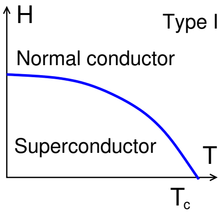
  Superfluid state: Similar to Bose condensate,
  but "liquid", not "gas"
  (particles interact strongly)
  Consequences: e.g., dissipation free flow
  through tubes and capillaries



- Superconductivity:

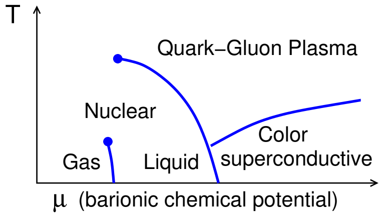
  Superconductive state: Bose condensate of electron pairs (Cooper pairs)

  Consequences: No resistance (⇝ dissipation free current)
  Meissner effect (magnetic fields are expelled), etc.



(j) Phase diagrams of quantum chromodynamics

(schematic, conjectured)



(k) Electroweak phase transition

Depends on the mass of the Higgs boson

- Large → Spontaneous symmetry breaking
- Small → Symmetric

2.2 Description of phase transitions: Important concepts

(1) Order parameter

A quantity, that distinguishes between phases, e.g., magnetization
(ideally zero in one of the two phases)

Continuous phase transitions
→ Order parameter vanishes continuously at a critical point T_c

"First order" phase transition
→ Finite jump at the transition point

⇒ Order parameter should be extensive !
If it were intensive, the second scenario would not be possible!

(2) Fluctuations

In the vicinity of phase transitions, one often observes strong fluctuations
– in particular, close to continuous phase transitions

Examples:

- Liquid/Gas critical point: Strong density fluctuations (critical opalescence)
- Soft mode at structural phase transitions

Fluctuations are generally related to susceptibilities
(e.g. density fluctuations ↔ compressibility)
⇝ Susceptibilities often diverge in the vicinity of phase transitions

Consequences:

- Energy fluctuations: Peak in the specific heat
  ⇝ Calorimetric measurements are often the first method of choice when looking for possible phase transitions
- Large correlation lengths / cluster sizes
  ⇝ experimentally measurable effects (e.g., critical opalescence)
- Large clusters → longer relaxation times "Critical slowing down"
  (Ordering processes are slower close to phase transitions)

(3) Symmetry and Symmetry breaking

Phase transitions often come with changes of the symmetry of a system
(e.g., magnetism, order-disorder transitions, electroweak transition)

In such cases, the order parameter characterizes the symmetry breaking.

(4) Critical behavior

At the critical point of a continuous phase transition, one often observes
- Power laws
- Critical exponents
- Universality

e.g., Liquid/Gas: Compressibility $\kappa_T \propto |T - T_c|^{-\gamma}$
Pressure ↔ Volume at T_c: $|P - P_c| \propto |V - V_c|^{\delta}$
Coexistence curve: $V_{\text{gas}} - V_{\text{liquid}} \propto (T_c - T)^{\beta}$
Magnetism: Susceptibility $\chi = (\frac{\partial M}{\partial H})_T \propto |T - T_c|^{-\gamma}$
Field ↔ Magnetization at T_c: $|H| \propto |M|^{\delta}$
Magnetization: $M \propto (T_c - T)^{\beta}$
in both cases: Specific heat: $c \propto |T - T_c|^{\alpha}$

Specifically: Categorization in universality classes
according to:
- Spatial dimension
- Symmetry of the order parameter
- Range of interactions

(will be explained in more detail later)

(5) Thermodynamic limit

From the above, one concludes:
Phase transitions are always associated with singularities
First order phase transition: Order parameter jumps
Continuous phase transition: Power laws or essential singularity

$\leadsto$ Phase transitions can only exist in the thermodynamic limit!

Reason: Consider canonical or grand canonical ensemble
In finite systems: $F = -\frac{1}{\beta} \ln \mathscr{Z} = -\frac{1}{\beta} \ln \sum_{\Gamma} \mathrm{e}^{-\beta E(\Gamma)}$
→ Finite sum of analytical functions
→ Analytical function, no singularity

Singularities can only emerge if the sum is infinite.

Exception: In the microcanonical ensemble,
singularities may be possible even in finite systems.

Second (related) aspect: In the thermodynamic limit, it is possible to effectively break ergodicity in macroscopic times.

Assume that a system is ergodic: Almost every configuration can be reached after sufficiently long time.

In finite systems: "Sufficiently long time" means finite time.

In infinite systems: "Sufficiently long time" may mean infinite time
$\leadsto$ System is effectively trapped in one phase
$\leadsto$ Ergodicity breaking
(one possible signature of a phase transition)

Chapter 3

The Ising Model

3.1 Introduction

3.1.1 Definition of the Ising model

Given some regular lattice in d dimensions (d=1,2,3,...)
(e.g., in 3 dimensions, cubic, fcc, bcc, ...)

Ingredients:

(i) Each lattice site carries a "Spin" $S_i = \pm 1$, i.e., a variable that can take one out of two values (not a quantum mechanical spin)

(ii) Cooperativity: The value of one spin influences the neighbor spins

(iii) Possibly an external "field" H that favors a certain value of S_i

No kinetic degrees of freedom (momentum etc.)

⇒ Energy function
("Hamiltonian")

$$\boxed{\mathscr{H}[\{S_i\}] = -J \sum_{\substack{\langle ij \rangle \\ \text{nearest neighbors}}} S_i S_j - H \sum_i S_i}$$

Cooperativity (ii) Field (iii)

The most common choice is $\boxed{J > 0}$ ("ferromagnetic"),
but $J < 0$ is also possible ("antiferromagnetic").

Based on the energy function, one calculates

– The partition function $\mathscr{Z} = \sum_{\{S_i = \pm 1\}} \mathrm{e}^{-\beta \mathscr{H}[\{S_i\}]}$

– The free energy $F = -k_B T \ln \mathscr{Z}$

etc.

Extensions and generalizations are possible and have been studied,

e.g., additional interactions between spins that are further apart,
anisotropic or spatially varying interactions J_{ij} or fields H_i,
Ising models on irregular lattices or other graphs, etc.

3.1.2 Motivation

- Original motivation: Designed as simple model for magnetism, therefore "magnetic" language (spins, field, etc.)
  However, the Ising model is actually not a good model for a magnetic system, since magnetic moments ("Spins") are quantum objects and three dimensional vectors ($\vec{S}$)

- Can be a good model for certain binary alloys in the context of order-disorder transitions (a "spin" $S = \pm 1$ then indicates the occupation of a lattice site with an atom of type A or B).

- The Ising model at $H = 0$ is one of the simplest model systems that exhibits a phase transition
  $\rightsquigarrow$ used to study fundamental properties of phase transitions

- Universality: Many practically important phase transitions are in the so-called "Ising universality class", e.g., the liquid-gas transition, binary mixtures, ... (→ see sections 4 and 6)

(• Historically: Has been studied extensively. Many techniques and arguments that were developed in this context are simply fun!
First case, where a non-trivial phase transition has been calculated exactly from first principles, i.e., starting from the partition function of a microscopic model)

3.1.3 History

1925: Introduction by Ising (in his PhD thesis, supervised by Lenz)
Model for magnetism
Exact solution in one dimension, unfortunately no phase transition :-(
(Ising believed/argued, that there would be no phase transition in higher dimensions either)

1934, 35: Bragg, Williams, Bethe
Took interest in Ising model as model for binary mixtures
→ Developed approximate solution methods ("mean-field approximations") that gave a phase transition

1936: Peierls
Argument, why there should be a phase transition in 2 dimensions
(not entirely accurate, later completed in 1964 by Griffiths)

1941: Kramers, Wannier
Symmetry considerations → exact expression for T_c in two dimensions

1944: Onsager
Exact solution in two dimensions for the case $H = 0$
(Solutions for $H \neq 0$ also became available later.)

3.1.4 Remark: Identifying phase transitions in the Ising model

Problem: For symmetry reasons, one always has $M = \langle \sum_i S_i \rangle = 0$ at $H = 0$.

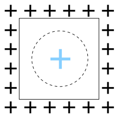
→ How can one identify a phase transition then?

Possible approaches:

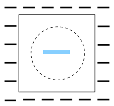
(i) Calculate free energy F and search for singularities

(ii) Introduce a symmetry breaking <u>infinitesimal field</u> $H \to 0^\pm$
Symmetry breaking phase transition: $\lim_{H \to 0^+} M(T,H) \neq \lim_{H \to 0^-} M(T,H)$

(iii) Symmetry breaking <u>boundary conditions</u>

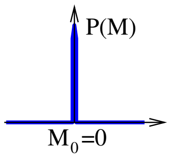


$\to M_0(T)$

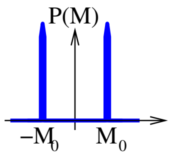


$\to -M_0(T)$

(iv) Analyze <u>histogram</u> of M



(disordered)



(ordered)

3.2 One-Dimensional Ising Model

We first consider the one dimensional Ising chain:

$$\underset{1}{+}\ -\ -\ +\ -\ +\ +\ -\ \underset{N}{-} \qquad \mathscr{H} = -J \sum_{i=1}^{N-1} S_i S_{i+1}$$

3.2.1 Why there cannot be a phase transition

- ”Ground state” (State with lowest energy)

  All Spins have the same sign, e.g., + + + + + + +
  Energy: $E = -J(N-1) =: E_0$

- Lowest excitation:

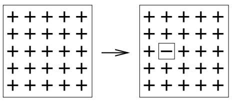
  One ”kink”: + + + +|- - -
  Energy: $E = -J(N-2) + J = E_0 + 2J$
  $\rightsquigarrow$ Energy costs compared to ground state: $\Delta E = 2J$
  $\rightsquigarrow$ Boltzmann probability of such a kink
  $P_{\text{kink}} \propto \mathrm{e}^{-\beta \Delta E} = \mathrm{e}^{-2\beta J}$: Finite number ($0 < P_{\text{kink}} < 1$).

  But: Every kink destroys the order
  Probability, that no kink is present (i.e., order persists):

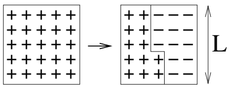
  $$P_{\text{no kink}} \propto (1 - P_{\text{kink}})^{\underset{\substack{\downarrow \\ \text{possible positions of kinks}}}{N-1}} \xrightarrow{N\to\infty} 0$$

$\Rightarrow$ Ising chain is always disordered !

NB: Argument does not work in two dimensions, since lowest excitation (one flipped spin) does not yet destroy global order



Global order is destroyed by an excitation of the form



(boundary line between domains)

However, the energy costs of this excitation are: $\Delta E \geqslant 2JL$
$\Rightarrow \quad P \propto \mathrm{e}^{-2\beta LJ} \to 0$ for $L \to \infty$

3.2.2 Solution of the one-dimensional Ising model

Consider one dimensional Ising chain $\mathscr{H} = -J \sum_{i=1}^{N} S_i S_{i+1} - H \sum_i S_i$
with periodic boundary conditions: $S_{N+1} := S_1$

- Free energy: Exact calculation *via* transfer matrix method

  Starting point: Partition function $\mathscr{Z} = \sum_{\{S_i\}} \mathrm{e}^{-\beta \mathscr{H}[\{S_i\}]}$

  Notation (motivated by quantum mechanical bras and kets):

  $S \mathrel{\widehat{=}} |S\rangle$ with $S = +1 \mathrel{\widehat{=}} \binom{1}{0}$, $\quad S = -1 \mathrel{\widehat{=}} \binom{0}{1}$

  $$\Rightarrow \ \mathrm{e}^{-\beta\mathscr{H}} = \underbrace{\mathrm{e}^{\beta J S_1 S_2 + \beta \frac{H}{2}(S_1+S_2)}}\ \underbrace{\mathrm{e}^{\beta J S_2 S_3 + \beta \frac{H}{2}(S_2+S_3)}} \cdots$$
  $$\mathrel{\widehat{=}} \quad \langle S_1 | V | S_2 \rangle \qquad \langle S_2 | V | S_3 \rangle \cdots$$

  $$\text{with } V = \begin{pmatrix} \mathrm{e}^{\beta J + \beta H} & \mathrm{e}^{-\beta J} \\ \mathrm{e}^{-\beta J} & \mathrm{e}^{\beta J - \beta H} \end{pmatrix} \quad \text{(check by inserting!)}$$

  $$\Rightarrow \mathscr{Z} = \sum_{S_1 \cdot\cdot S_N} \langle S_1 | V | S_2 \rangle \cdot\cdot \langle S_N | V | S_1 \rangle = \sum_{S_1} \langle S_1 | V^N | S_1 \rangle = \mathrm{Tr}(V^N)$$
  $$= \underbrace{(\lambda_1^N + \lambda_2^N)}_{\text{Eigenvalues, } \lambda_1 > \lambda_2} = \lambda_1^N (1 + (\lambda_2/\lambda_1)^N) \xrightarrow{N \to \infty} \lambda_1^N$$

  $$\Rightarrow F = -k_B T \ln \mathscr{Z} = -k_B T N \ln \lambda_1$$

  Specifically: Eigenvalues of V are given by

  $$\lambda_{1,2} = \mathrm{e}^{\beta J} \cosh(\beta H) \pm \sqrt{\mathrm{e}^{2\beta J} \sinh^2(\beta H) + \mathrm{e}^{-2\beta J}}$$

  (at $H = 0$: $\lambda_{1,2} = \mathrm{e}^{\beta J} \pm \mathrm{e}^{-\beta J}$)

  $$\Rightarrow \quad F = -k_B T \ N \ \ln \Big[\mathrm{e}^{\beta J} \cosh(\beta H) + \sqrt{\mathrm{e}^{2\beta J} \sinh^2(\beta H) + \mathrm{e}^{-2\beta J}} \Big]$$

  In particular, at $H = 0$: $F = -k_B T \ N \ \ln \big[2 \cosh(\beta J) \big]$

  Analytical function for all temperatures ⇝ No phase transition!

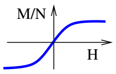
- "Magnetization" : $M = \langle \sum_i S_i \rangle = -\frac{\partial F}{\partial H}$

  (Since: $F = -k_B T \ln \sum \mathrm{e}^{-\beta \mathscr{H}} = -k_B T \ln (\sum \mathrm{e}^{\beta J \sum S_i S_j + \beta H \sum S_i}$

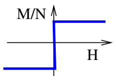
  $\Rightarrow \ \frac{\partial F}{\partial H} = -\cancel{k_B T} \sum \mathrm{e}^{-\beta \mathscr{H}} \cancel{\beta} \sum S_i \Big/ \sum \mathrm{e}^{-\beta\mathscr{H}} = -\langle \sum S_i \rangle$ ✓)

  $$\Rightarrow \ M = \cdots = N \sinh(\beta H) \Big/ \sqrt{\cosh^2(\beta H) - 1 + \mathrm{e}^{-2\beta J}}$$

  $$\beta J \to 0 \quad : \quad M/N \approx \tanh(\beta H)$$



  $$\beta J \to \infty \quad : \quad M/N \approx \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H)}} = \mathrm{sign}(\beta J)$$



  step function

  ⇝ "Phase transition" at $T = 0$?

- Correlations: $G_{ij} = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle$

  Specifically $H = 0$ ⇝ $\langle S_i \rangle = \langle S_j \rangle = 0$

  Longer calculation (homework) ⇒ $\boxed{G_{ij} \propto \mathrm{e}^{-|i-j|/\xi}}$

  with $\xi(H = 0, T) = \frac{1}{-\ln(\tanh(\beta J))} \sim \mathrm{e}^{2\beta J} \to \infty$ for $\beta \to \infty$

  ⇝ Correlation length ξ diverges at $T \to 0$

  ⇝ Characteristic feature of critical behavior

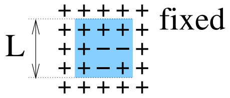
3.3 Two-Dimensional Ising Model: Exact Results

Now we discuss the two dimension Ising model at $H = 0$,
$\mathscr{H} = -J \sum_{\langle ij \rangle} S_i S_j$ (with $\langle ij \rangle$: nearest neighbors)
In this section we will restrict ourselves to the square lattice. (Generalizations of the arguments below to other lattices are sometimes possible, but not always.)

3.3.1 Peierl's argument for the existence of a phase transition

(Peierls 1936, Griffiths 1964, Dobrushin 1965)

Idea of the argument:

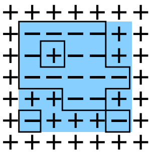


- Consider Ising system $\widehat{\Omega}$
  with fixed boundary condition:
  Surrounded by spins $S = +1$.
- Show, that for sufficiently low temperatures, there exists an $\alpha > 0$ such that, at $H = 0$, the magnetization per spin $M_{\widehat{\Omega}}/N = \frac{1}{N}\langle \sum_i S_i \rangle$ is always larger than α, $M_{\widehat{\Omega}}/N \geqslant \alpha$, independent of system size (i.e., this system has positive magnetization).
- At these temperatures, $\lim_{N\to\infty, H\to 0^+} M/N \geqslant \alpha$ holds generally, independent of the boundary condition. ($H \to 0^+$ is introduced to break the $S = \pm 1$ symmetry in the absence of the boundary condition.)

  (Reason: Free energy $F(T, H)$
  Magnetization at $H \to 0^+$: $M = -\left(\frac{\partial F}{\partial H}\right)_{H\to 0^+}$
  But: F is extensive (additive) at $L \to \infty$
  $\rightsquigarrow$ Boundary only contributes with surface term to F, $F_{\text{surf}} \propto L \propto \sqrt{N}$
  $\rightsquigarrow$ $F_{\text{general}} = F_{\widehat{\Omega}} + \mathscr{O}(N^{1/2}) \Rightarrow \lim_{H\to 0^+} M_{\widehat{\Omega}} = \lim_{H\to 0^+} M_{\text{general}} + \mathscr{O}(N^{1/2})$)

Goal therefore: Search for lower bound for $\frac{M_{\widehat{\Omega}}}{N} = 1 - 2\frac{\langle N_- \rangle}{N}$ in the system $\widehat{\Omega}$
where N_-: Number of sites with $S_i = -1$

⋆ Consider some (arbitrary) configuration $\mathscr{C}$



Draw domain wall lines between spins of different sign
$\rightsquigarrow$ Lines form closed polygons
$\rightsquigarrow$ Every spin $S = -1$ lies inside at least one polygon
Label all possible polygons ($\to$ label p)

Define variables $X_p = \begin{cases} 1 & : \text{ polygon } p \text{ appears in configuration } \mathscr{C} \\ 0 & : \text{ otherwise} \end{cases}$

$l_p :=$ contour length of polygon p

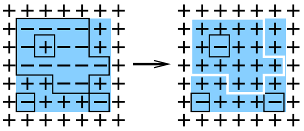
Polygon p contains at most $(l_p/4)^2$ spins

$\Rightarrow$ Estimate: $N_- \leqslant \sum_p X_p \left(\frac{l_p}{4}\right)^2$

⋆ Also holds in the thermal average $\Rightarrow \langle N_- \rangle \leqslant \sum_p \langle X_p \rangle \left(\frac{l_p}{4}\right)^2$

$$\text{with } \langle X_p \rangle = \frac{\sum' \mathrm{e}^{-\beta\mathscr{H}}}{\sum \mathrm{e}^{-\beta\mathscr{H}}} \quad \begin{array}{l} \text{configurations } \mathscr{C} \text{ that contain polygon } p \\ \text{all configurations} \end{array}$$

- ⋆ Upper bound for $\langle X_p \rangle$ and $\langle N_- \rangle$



Trick: For each configuration $\mathscr{C}$ (in Σ') that contains polygon p, construct a partner configuration $\mathscr{C}^*$ by inverting all spins inside the polygon.

$\rightsquigarrow$ Energy difference: $\mathscr{H}(\mathscr{C}^*) = \mathscr{H}(\mathscr{C}) - 2 l_p J$

$$\Rightarrow \text{Estimate}: \sum_{\text{all confs}} \mathrm{e}^{-\beta \mathscr{H}} \geqslant \sum_{\mathscr{C}^*} \mathrm{e}^{-\beta \mathscr{H}} = \mathrm{e}^{2 l_p \beta J} \sum{}' \mathrm{e}^{-\beta \mathscr{H}}$$

$$\Rightarrow \langle X_p \rangle = \frac{\sum' \mathrm{e}^{-\beta \mathscr{H}}}{\sum \mathrm{e}^{-\beta \mathscr{H}}} \leqslant \mathrm{e}^{-2 l_p \beta J}$$

$$\Rightarrow \langle N_- \rangle \leqslant \sum_p \mathrm{e}^{-2 l_p \beta J} \left(\tfrac{l_p}{4}\right)^2 = \sum_l \mathrm{e}^{-2 l \beta J} \left(\tfrac{l}{4}\right)^2 \overbrace{n(l)}^{\text{number of polygons of length } l}$$

- ⋆ Upper bound for $n(l)$ (number of polygons of length l)

Construction of a polygon:

$$\left.\begin{array}{l}\text{First line: } 2N \text{ possibilities } (+ \text{ border}) \\ \text{Second line: At most 3 possibilities}\end{array}\right\} \Rightarrow n(l) \leqslant 2N\, 3^{l-1}$$

- ⋆ Combine everything:

$$\langle N_- \rangle \leqslant \sum_l \mathrm{e}^{-2 l \beta J} \left(\tfrac{l}{4}\right)^2 2N 3^{l-1} = \tfrac{N}{24} \sum_{l=0}^{\infty} \left(3\mathrm{e}^{-2\beta J}\right)^l l^2 = \tfrac{N}{24} f(3\mathrm{e}^{-2\beta J})$$

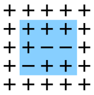
with $f(x) = \frac{x(1+x)}{(1-x)^3}$ (since: $\sum_l x^l l^2 = \frac{\mathrm{d}^2}{\mathrm{d}\alpha^2} \sum_l (x \mathrm{e}^{\alpha})^l \big|_{\alpha=0} = \cdots = \frac{x(1+x)}{(1-x)^3}$)

$f(x)$ becomes arbitrarily small at $x \to 0$:

For example, choose β large enough $f(3\mathrm{e}^{-2\beta J}) \leqslant \frac{1}{2} \Rightarrow \langle N_- \rangle \leqslant \frac{N}{48}$

$\Rightarrow \frac{M_{\hat{\Omega}}}{N} = 1 - \frac{2\langle N_- \rangle}{N} \geqslant 1 - \frac{1}{24}$ independent of system size ✓

3.3.2 Kramers-Wannier method to determine T_c



Consider Ising model, square lattice, $H = 0$:

Number of sites: N

Number of edges ("bonds"): K

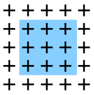
This subsection: Exact method to determine T_c (under certain assumptions) based on a comparison of different series expansions of the partition function

$\rightsquigarrow$ Smart approach (fun), will also teach us about series expansions

(a) **Series Expansions** of the partition function: Two approaches

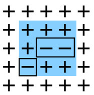
(i) Low temperature expansion

- ⋆ $T = 0$:



$$\mathscr{Z}_N = \sum_{\{S_i\}} \mathrm{e}^{\beta J \sum_{\langle ij \rangle} S_i S_j} = \mathrm{e}^{\beta J K}$$

- ⋆ T finite:

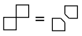


$\rightsquigarrow$ Polygons P with total contour length l

Costs: $\Delta \mathscr{H} = 2Jl$

$$\mathscr{Z}_N = \sum_{\{S_i\}} \mathrm{e}^{\beta J \sum_{\langle ij \rangle} S_i S_j} = \mathrm{e}^{\beta J K} \underbrace{\sum_{P}}_{\substack{\text{all polygon}\\ \text{configurations}}} \mathrm{e}^{-2\beta J\, l(P)}$$

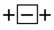
summed over all polygons

(NB: Uniqueness: Polygons do not cross each other: )

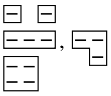
- ⋆ At low temperatures, the dominant contributions correspond to polygons with short contour lengths.

$\Rightarrow$ "Low temperature expansion": Expansion in powers of $\boxed{\mathrm{e}^{-2\beta J}}$

⋆ Construction of the coefficients (lowest order terms)

$l = 4$:  → N possibilities

$l = 6$:  → $\frac{1}{2}N \cdot 4$ possibilities

$l = 8$: 

$$\left.\begin{array}{l} \frac{1}{2}N(N-5) \\ +6N \\ +N \end{array}\right\} = \frac{1}{2}N(N+9) \text{ possibilities}$$

$$\rightsquigarrow \ \mathscr{Z}_N = \mathrm{e}^{\beta JK}(1 + N\mathrm{e}^{-2\beta J \cdot 4} + 2N\mathrm{e}^{-2\beta J \cdot 6} + \tfrac{1}{2}N(N+9)\mathrm{e}^{-2\beta J \cdot 8} + \cdots)$$

⇒ General result: $\boxed{\mathscr{Z}_N = \mathrm{e}^{\beta JK} \sum_l \sum_{\{P\}_l} \mathrm{e}^{-2\beta J l}}$

Possible polygon configurations made of boundary lines with total contour length l (all polygons)

NB: Expansion is finite ($l \leqslant 2N$) for finite systems

Infinite series at $N \to \infty$, possibly with convergence radius

(ii) High temperature expansion

⋆ $T \to \infty$ or $\beta = 0 \Rightarrow \mathscr{Z}_N = \sum_{\{S_i\}} 1 = 2^N =: \mathscr{Z}_{N,0}$

⋆ T finite: $\mathscr{Z}_N = \sum\limits_{\{S_i\}} \mathrm{e}^{\beta J \sum_{\langle ij \rangle} S_i S_j} = \mathscr{Z}_{N,0} \dfrac{\sum_{\{S_i\}} \mathrm{e}^{\beta J \sum_{\langle ij \rangle} S_i S_j}}{\sum_{\{S_i\}} 1}$

$$= \mathscr{Z}_{N,0} \left\langle \mathrm{e}^{\beta J \sum_{\langle ij \rangle} S_i S_j} \right\rangle_{0\text{–average at } \beta = 0}$$

$$\mathrm{e}^{\beta J S_i S_j} = \cosh(\beta J) + S_i S_j \sinh(\beta J)$$

$$= \mathscr{Z}_{N,0} \, (\cosh(\beta J))^K \left\langle \prod_{\langle ij \rangle} (1 + v \, S_i S_j) \right\rangle_0$$

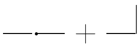
with $v = \tanh(\beta J)$

⋆ At high temperatures, the dominant contributions correspond to terms of low order in $\boxed{v = \tanh(\beta J)}$.

⇒ "High temperature expansion": Expansion in powers of v

⋆ Construction of the coefficients: Graphical approach

Every term "$v S_i S_j$" corresponds to a line $_i$—$_j$ along the edge $\langle ij \rangle$.

⇝ First Order: — ; Second order:  etc.

◇ For unequal indices i, j, one has $\langle S_i^{n_1} S_j^{n_2} \rangle_0 = \langle S_i^{n_1} \rangle_0 \langle S_j^{n_2} \rangle_0$

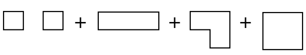
For odd powers n, one has $\langle S_i^n \rangle_0 = 0$

⇝ Graphs with free line ends or graphs, where an odd number of lines meet at one vertex, do not contribute (e.g., first order terms: - $\hat{=} \langle S_i S_j \rangle_0 = \langle S_i \rangle_0 \langle S_j \rangle_0 = 0$).

⇝ Only graphs consisting of closed polygons contribute.

◇ Lowest nonvanishing order: v^4 (□)

Next orders: v^6 (▭)

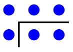
v^8 ()

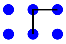
⇒ General result: $\boxed{\mathscr{Z}_N = 2^N (\cosh(\beta J))^K \sum_l \sum_{\{P\}_l} (\tanh(\beta J))^l}$

Possible polygon configurations made of edges with total length l (all polygons)

(b) Duality

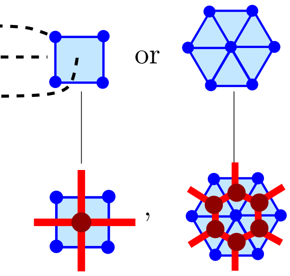
Compare (i) and (ii): Very similar expressions
$\mathscr{Z}$ $\widehat{=}$ in both cases a sum over polygon configurations,
however, different alignment with the underlying lattice

(i) Low temperature expansion
 Polygon lines perpendicular to bonds between lattice sites

(ii) High temperature expansion
 Polygon lines lie on to bonds between lattice sites

Formal relation: Dual lattice

Original lattice: N_0 lattice sites (vertices)
N_1 edges (bonds)
N_2 faces (plaquettes)



Dual lattice:
Plaquette centers → vertices ($N_0^* = N_2$)
Bonds → transverse bonds ($N_1^* = N_1$)
Vertices → plaquettes ($N_2^* = N_0$)

Euler relation: $N_0 - N_1 + N_2 = N_0^* - N_1^* + N_2^* = 2$
(NB: The outside of the graph counts as one face.)

Consequence for partition function

High temperature expansion: Polygon expansion on original lattice:
$\mathscr{Z}_{N_0,\mathrm{HT}}(\beta)/2^{N_0}(\cosh(\beta J))^{N_1} = \sum\limits_l \sum\limits_{\{P\}_l} (\tanh(\beta J))^l$

Low temperature expansion: Polygon expansion on dual lattice:
$\mathscr{Z}_{N_2^*,\mathrm{LT}}(\beta)/\mathrm{e}^{2\beta J N_1^*} = \sum\limits_l \sum\limits_{\{P\}_l} (\mathrm{e}^{-2\beta J})^l$

⇝ Consider now an Ising model on the dual lattice with partition function $\mathscr{Z}^*_{N_0^*}$. Then the expansions of $\mathscr{Z}$, $\mathscr{Z}^*$ can be mapped onto each other: $\mathscr{Z}^*_{N_0^*,\mathrm{HT}}(\beta^*) \propto \mathscr{Z}_{N_2^*,\mathrm{LT}}(\beta)$
with $\tanh(\beta^* J) = \mathrm{e}^{-2\beta J} \Leftrightarrow \boxed{\sinh(2\beta J)\sinh(2\beta^* J) = 1}$

⇝ Duality relation: High temperatures map onto low temperatures
Specifically, the square lattice is self dual: $\mathscr{Z}^*(\beta^*) = \mathscr{Z}(\beta^*)$

Consequence for phase transition

Phase transition ↔ Singularity of $F = -k_B T \ln \mathscr{Z}$ at $N \to \infty$
Here: $F(\beta) = -k_B T \ln\big(\sum\limits_l \sum\limits_{\{P\}_l} (\mathrm{e}^{-2\beta J})^l\big) + N\cdot$ analytic terms
$F^*(\beta^*) = -k_B T \ln\big(\sum\limits_l \sum\limits_{\{P\}_l} (\tanh(\beta^* J)^l\big) + N\cdot$ analytic terms
⇒ If $F(\beta)$ is nonalytic at β_c, then $F^*(\beta^*)$ is nonalytic at β_c^*

Self dual lattice: $F^*(\beta^*) = F(\beta^*)$
⇒ $F(\beta)$ is also nonanalytic at β_c^*, singularities come in pairs

Assume only one singularity ⇒ $\beta_c = \beta_c^*$ ⇒ $(\sinh(2\beta_c J))^2 = 1$

$$\Rightarrow \quad \boxed{\beta_c J = \frac{1}{2}\mathrm{arsinh}(1) = \frac{1}{2}\ln(1+\sqrt{2}) = 0.4407}$$

Summary and Conclusions

- We have used symmetry considerations to determine T_c without actually "solving" the Ising model (i.e., calculating the partition function)
- On this occasion, we also introduced the method of series expansions for $\beta \to 0$ and $\beta \to \infty$. They generally play an important role independent of this argument here.

Remarks

- Duality trick does not work in three dimensions, since the lattice and the dual lattice are too different
- The trick can also be used for the triangular lattice / honeycomb lattice $\leadsto$ "star-triangle transformation"

  Result: $(\tanh(\beta_c J))^{-1} = \begin{cases} 2+\sqrt{3} & : \text{ triangular lattice} \\ \sqrt{3} & : \text{ honeycomb lattice} \end{cases}$

3.3.3 Exact solution of the Ising model on the square lattice

In his original solution of the 2D Ising model, Onsager (1944) used the transfer matrix method (see Sec. 3.2.2).

Here, we present an alternative approach due to Samuel (1980), which is based on the high temperature expansion (Sec. 3.3.2) and the mathematical framework of "Grassmann variables".

For a more detailed discussion see also the book by F. Wegner:
"Supermathematics and its Applications to Statistical Physics"

We consider an Ising model with $N = L_x \times L_y$ spins on a square lattice

(1) General properties of Grassmann variables

- Symbols ξ with $\xi_i \xi_j = -\xi_j \xi_i \quad (\Rightarrow \ \xi_i^2 = 0)$

  Application example: $\exp(\xi_i) = 1 + \xi_i$
- Generate so-called "Grassmann algebra"

  with elements $A = a + \sum_i a_i \xi_i + \sum_{i,j} a_{ij} \xi_i \xi_j + \cdots$
- Formally define "Integration" *via* $\int \mathrm{d}\xi_N \mathrm{d}\xi_{N-1} \cdots \mathrm{d}\xi_1 \, \xi_1 \xi_1 \cdots \xi_N = 1$, where integral becomes zero, if one of the ξ_i is missing.

  $\Rightarrow \int \mathrm{d}\bar{\xi} \mathrm{d}\xi \exp(\xi a \bar{\xi}) = \int \mathrm{d}\bar{\xi} \mathrm{d}\xi (1 + \xi a \bar{\xi}) = a$

  $\int \mathrm{d}[\bar{\xi}] \mathrm{d}[\xi] \exp(\sum_{ij} \xi_i A_{ij} \bar{\xi}_j) = \det(A)$

  with $\int \mathrm{d}[\bar{\xi}] \mathrm{d}[\xi] := \int \mathrm{d}\bar{\xi}_N \mathrm{d}\xi_N \mathrm{d}\bar{\xi}_{N-1} \mathrm{d}\xi_{N-1} \cdots \mathrm{d}\bar{\xi}_1 \mathrm{d}\xi_1$
- Change of variables: Given a Grassmann integral $\int \mathrm{d}[\xi] f[\xi]$

  Linear substitution $\xi_i \to \theta_j = \sum_k J_{jk} \xi_k$

  Then, one has (no proof): $\int \mathrm{d}[\xi] f[\xi] = \int \mathrm{d}[\theta] f[\xi[\theta]] \frac{1}{\det(J)}$

  NB: For nonlinear substitution rules, the transformation rule may be more complicated, but we will not need that here!

(2) Strategy for solving the two dimensional Ising model (Samuel, 1980)

⋆ Starting point: High temperature expansion (Sec. 3.3.2)

$\mathscr{Z}_N = 2^N (\cosh(\beta J))^{2N} \widehat{\mathscr{Z}_N}$ with $\widehat{\mathscr{Z}_N} = \sum_{\mathscr{C}_P} v^{l_P}$, $v = \tanh(\beta J)$

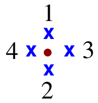
with $\sum_{\mathscr{C}_P}$: Sum over all configurations of closed polygons

l_P: Total length of polygons

Idea: Generate sum over all polygon configurations *via* Grassmann integral

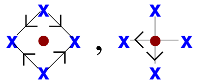
⋆ Procedure

- Assign four Grassmann variables $\xi_{nm}^{(i)}$ $(i = 1 \cdot\cdot 4)$ to each lattice site (n, m)



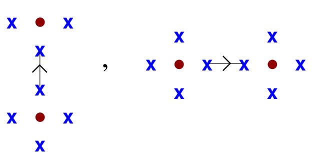
- Define linker $\hat{l}$: Pairs of Grassmann variables

Local: $\hat{e}_{nm}^{(ij)} = \xi_{nm}^{(i)} \xi_{nm}^{(j)}$ for $i < j$ $\quad\hat{=}$



Bond: $\hat{b}_{nm}^{(x)} = \xi_{nm}^{(3)} \, \xi_{(n+1)m}^{(4)}$

$\hat{b}_{nm}^{(y)} = \xi_{nm}^{(1)} \xi_{n(m+1)}^{(2)}$



- Define "action" (quadratic in ξ)

$$S[\xi] = \sum_{nm} \left[v \, (a_x \hat{b}_{nm}^{(x)} + a_y \hat{b}_{nm}^{(y)}) + \sum_{i<j} a_{ij} \hat{e}_{nm}^{(ij)} \right] \equiv \sum c_\alpha \hat{l}_\alpha$$

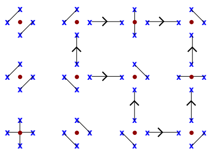
with $a_x, a_y, a_{ij} = \pm 1$ (sign to be determined below).

- Consider Grassmann integral $I = \int \mathrm{d}[\xi] \exp(S[\xi])$

(Order: $\int \mathrm{d}[\xi] = \int \mathrm{d}\xi_{L_x,L_y}^{(4)} \cdot\cdot \, \mathrm{d}\xi_{L_x,L_y}^{(1)} \mathrm{d}\xi_{L_x-1,L_y}^{(4)} \cdot\cdot \, \mathrm{d}\xi_{1,L_y}^{(1)} \mathrm{d}\xi_{L_x,L_y-1}^{(4)} \cdot\cdot \, \mathrm{d}\xi_{1,1}^{(1)}$)

$\rightsquigarrow$ I has additive contributions from all configurations, in which $2L_xL_y$ linkers $\hat{l}_\alpha$ are distributed such that every position (n, m, i) is occupied by precisely one Grassmann variable.

Example:



Configurations contribute (additively) with $\int \mathrm{d}[\xi] \prod\limits_\alpha c_\alpha \hat{l}_\alpha \propto \pm v^{l_P}$

Sign: Depends on the power of a_x, a_y, a_{ij} in I and the number of transpositions needed to sort $\prod_\alpha \hat{l}_\alpha$ by ascending $\xi_{nm}^{(i)}$

$\Rightarrow$ - I sums automatically over all configurations with closed polygons. Free ends are not possible :-)

- Contribution of each polygon configuration is $\propto v^{l_P}$:-)
- But: Prefactor could be negative :-(

$\rightsquigarrow$ Goal: Choose $a_x, a_y, a_{ij} = \pm 1$ such that every polygon configuration has the weight v^{l_P}. Then we have $\widehat{\mathscr{Z}_N} = I$, and I can be calculated following the integration rules described in (1).

(3) Determination of coefficients a_x, a_y, a_{ij}

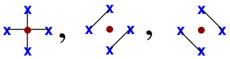
First consider configurations, in which polygons don't touch, i.e., don't share corners (For touching polygons see step (iii) below). Calculate their weight by rearranging, reorienting and reassigning linkers.

Notation: k_x, k_y: Number of bonds in x,y direction ($l_P = k_x + k_y$)
N_p: Number of polygons

NB: Linkers commute, since they are pairs of Grassmann variables.
k_x and k_y are even, since polygons are closed.

Steps:

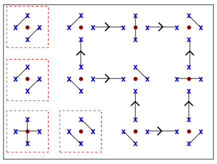
(i) Calculate contribution of isolated lattice sites

Three possibilities, 

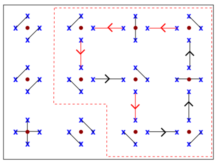
Factor: $(a_{12}a_{34} + a_{23}a_{14} - a_{13}a_{24})$ per site.

$\rightsquigarrow$ Postulate $(a_{12}a_{34} + a_{23}a_{14} - a_{13}a_{24}) \overset{!}{=} 1$

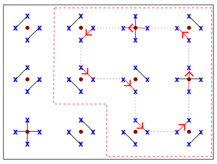
(ii) Now consider polygons. Assemble all *bonds* belonging to same polygons together in chains.



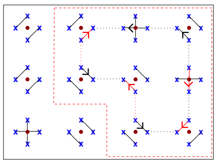
(iia) Reorient bonds in polygons such that they run counterclockwise.
Costs: Factor $(-1)^{(k_x+k_y)/2}$
(half of all bonds must be reoriented)



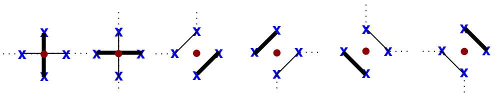
(iib) Shift linkers in polygon chains by one ξ
$\rightsquigarrow$ New linkers are all local.
n_{ij} new linkers of the form $\hat{e}^{(ij)}_{nm}$.
Costs: $(-1)^{N_p}$ (one cyclic permutation of ξ variables per polygon)



(iic) Reorient new linkers $\hat{e}^{(ij)}$ such that $i < j$
Costs: Factor $(-1)^{\sum_{i>j} n_{ij}}$.



(iid) Determine weight of polygon elements:
- Bonds: $v^{l_p}\, a_x^{k_x}\, a_y^{k_y} = v^{l_p}$ (k_x, k_y even)
- Joints between bonds:



$(\bar{n}_{ij} = n_{ij} + n_{ji})$

$a_{12}^{\bar{n}_{34}}$ $a_{34}^{\bar{n}_{12}}$ $a_{23}^{\bar{n}_{14}}$ $a_{14}^{\bar{n}_{23}}$ $(-a_{13})^{\bar{n}_{24}}$ $(-a_{24})^{\bar{n}_{13}}$

(Sign: $\int d\xi^{(4)} d\xi^{(3)} d\xi^{(2)} d\xi^{(1)} \hat{e}^{(ij)} \hat{e}^{(kl)}$ for site with linkers $\hat{e}^{(ij)} \hat{e}^{(kl)}$)

(iie) Summarize: Polygon configuration has weight $W v^{l_P}$ with

$$W = a_{12}^{\bar{n}_{34}} a_{34}^{\bar{n}_{12}} a_{23}^{\bar{n}_{14}} a_{14}^{\bar{n}_{23}} a_{13}^{\bar{n}_{24}} a_{24}^{\bar{n}_{13}} (-1)^{N_p + \frac{1}{2}(k_x+k_y) + \sum_{i>j} n_{ij} + \bar{n}_{24} + \bar{n}_{13}}$$

Exploit relations between $k_{x,y}$ and n_{ij}:

- Every straight polygon line has corners at both ends
  $\Rightarrow$ Lines up: $k_y/2 - n_{21} = n_{24} + n_{23} = n_{41} + n_{31}$
  Lines down: $k_y/2 - n_{12} = n_{42} + n_{32} = n_{14} + n_{13}$
  Lines right: $k_x/2 - n_{43} = n_{41} + n_{42} = n_{13} + n_{23}$
  Lines left: $k_x/2 - n_{34} = n_{14} + n_{24} = n_{31} + n_{32}$
- If one runs through a polygon in a counterclockwise way, one has four more left corners than right corners.
  $\Rightarrow$ $n_{24} + n_{32} + n_{13} + n_{41} = 4N_p + n_{42} + n_{14} + n_{31} + n_{23}$
- Collect all this:
  $n_{24} = N_p + n_{31},\ n_{13} = N_p + n_{42},\ n_{32} = N_p + n_{14}.\ n_{41} = N_p + n_{23}$
  $\bar{n}_{14} = \bar{n}_{23},\ \bar{n}_{13} = \bar{n}_{24},\ k_y - \bar{n}_{12} = k_x - \bar{n}_{34} = \bar{n}_{13} + \bar{n}_{14}$

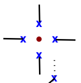
$$\Rightarrow W = (a_{13}a_{24})^{\bar{n}_{13}}\, (-a_{14}a_{23})^{\bar{n}_{14}}\, (a_{12}a_{34})^{-\bar{n}_{13}-\bar{n}_{14}}$$

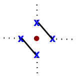
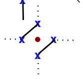
(iii) Possible choices for a_x, a_y, a_{ij}

- ⋆ Recall $|a_x| = |a_y| = |a_{ij}| = 1$
- ⋆ Further conditions from (i) and (ii)
  - (i) $a_{12}a_{34} + a_{23}a_{14} - a_{13}a_{24} \overset{!}{=} 1$
  - (ii) $W = (a_{13}a_{24})^{\bar{n}_{13}} (-a_{14}a_{23})^{\bar{n}_{14}} (a_{12}a_{34})^{-\bar{n}_{13}-\bar{n}_{14}} \overset{!}{=} 1 \; \forall \, \bar{n}_{12}, \bar{n}_{14}$

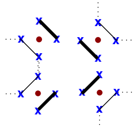
$$\Rightarrow \quad \boxed{a_{12}a_{34} = -1, \quad a_{13}a_{24} = -1, \quad a_{14}a_{23} = 1, \quad a_{x.y} = \pm 1}$$

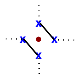
Consistency check: What happens, if polygons touch each other?

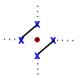
Corresponds to bond constellation  ("cross")

Steps in (ii) turn this into  or  (equivalent)

$\rightsquigarrow$ In W (iii), two "corners" are replaced by one "cross"



$\widehat{=} \; (-a_{13})(-a_{24}) = -1 \; \rightarrow$  $= -1$ ✓

$\widehat{=} \; (a_{14})(a_{23}) = 1 \; \rightarrow$  $= 1$ ✓

Conclusion: Conditions (iii) make sure that I corresponds to a sum over all polygon configurations with weight v^{l_P}.
$\Rightarrow I = \widehat{\mathscr{Z}} = \sum_{\mathscr{C}_P} v^{l_P}$, hence I can be used to calculate $\widehat{\mathscr{Z}}$.
In practice, we still have some freedom and choose

$$\boxed{a_x = -1, \; a_y = 1, \; a_{12} = a_{24} = -1, \; a_{13} = a_{14} = a_{23} = a_{34} = 1}$$

(4) Calculation of the partition function

- ⋆ Remaining task: Calculate $\widehat{\mathscr{Z}_N} = \int \mathrm{d}[\xi] \, \exp S[\xi]$
  with $S[\xi] = \sum_{nm} \left[v(a_x \hat{b}^{(x)}_{nm} + a_y \hat{b}^{(y)}_{nm}) + \sum_{i<j} a_{ij} \hat{e}^{(ij)}_{nm} \right] \quad (v = \tanh(\beta J))$
  and coefficients $a_{x,y}, a_{ij}$ from (3)
  $(\hat{e}^{(ij)}_{nm} = \xi^{(i)}_{nm}\xi^{(j)}_{nm}, \; \hat{b}^{(x)}_{nm} = \xi^{(3)}_{nm}\,\xi^{(4)}_{(n+1)m}, \; \hat{b}^{(y)}_{nm} = \xi^{(1)}_{nm}\xi^{(2)}_{n(m+1)})$
- ⋆ Fourier transform: Assume periodic boundary conditions (as in 3.2.2).
  Then, configurations exist where domain interfaces span the whole system, i.e., they do not form closed polygons. However, the statistical weight of such configurations decreases exponentially with increasing system size, and we will thus neglect them.

Define $p_k = \frac{2\pi k}{L_x}, \; q_l = \frac{2\pi l}{L_y}$ with $k \in [-\frac{L_x}{2}, \frac{L_x}{2}], \; l \in [-\frac{L_y}{2}, \frac{L_y}{2}]$
and $\zeta^{(i)}_{kl} = \frac{1}{\sqrt{L_x L_y}} \sum_{mn} \mathrm{e}^{-i(p_k n + q_l m)} \xi^{(i)}_{nm} \qquad (\Rightarrow \; \xi^{(i)}_{-k,-l} = \xi^{(i)*}_{kl})$

$$\begin{aligned}
\Rightarrow \; \xi^{(i)}_{nm} &= \sqrt{L_x L_y}^{-1} \sum_{kl} \mathrm{e}^{i(p_k n + q_l m)} \zeta^{(i)}_{kl} \\
\sum_{nm} \hat{e}^{(ij)}_{nm} &= \sum_{kl} \zeta^{(i)}_{kl} \zeta^{(j)}_{-k,-l} = \tfrac{1}{2} \sum_{kl} \left(\zeta^{(i)}_{kl} \zeta^{(j)}_{-k,-l} - \zeta^{(j)}_{kl} \zeta^{(i)}_{-k,-l} \right) \\
\sum_{nm} \hat{b}^{(x)}_{nm} &= \sum_{kl} \zeta^{(1)}_{kl} \zeta^{(3)}_{-k,-l} \mathrm{e}^{-iq_l} = \tfrac{1}{2} \sum_{kl} \left(\zeta^{(1)}_{kl} \zeta^{(3)}_{-k,-l} \mathrm{e}^{-iq_l} - \zeta^{(3)}_{kl} \zeta^{(1)}_{-k,-l} \mathrm{e}^{iq_l} \right) \\
\sum_{nm} \hat{b}^{(y)}_{nm} &= \sum_{kl} \zeta^{(2)}_{kl} \zeta^{(4)}_{-k,-l} \mathrm{e}^{-ip_k} = \tfrac{1}{2} \sum_{kl} \left(\zeta^{(2)}_{kl} \zeta^{(4)}_{-k,-l} \mathrm{e}^{-ip_k} - \zeta^{(4)}_{kl} \zeta^{(2)}_{-k,-l} \mathrm{e}^{ip_k} \right)
\end{aligned}$$

$$\Rightarrow \; S = \tfrac{1}{2} \sum_{kl} \sum_{ij} \zeta^{(i)}_{kl} A^{(kl)}_{ij} \zeta^{(j)}_{-k,-l} = \sum\nolimits'_{kl} \left(\sum_{ij} \zeta^{(i)}_{kl} \; A^{(kl)}_{ij} \; \zeta^{(j)*}_{kl} \right) =: S[\zeta, \zeta^*],$$

where $\sum'_{kl}$ sums only over half of the (kl),
such that (kl) and $(-k,-l)$ are both fully covered

$$\text{and } A^{(kl)} = \begin{pmatrix} 0 & -1 - v\mathrm{e}^{-iq_l} & 1 & 1 \\ 1 + v\mathrm{e}^{iq_l} & 0 & 1 & -1 \\ -1 & -1 & 0 & 1 + v\mathrm{e}^{-ip_k} \\ -1 & 1 & -1 - v\mathrm{e}^{ip_k} & 0 \end{pmatrix}$$

$$\big(\text{NB: } A_{ij}^{(kl)} = -A_{ji}^{(-k,-l)} = -A_{ji}^{(kl)*}\big)$$

$\Rightarrow$ Partition function (using equations from (1))

$$\widehat{\mathscr{Z}_N} = \textstyle\int \mathrm{d}[\xi]\ \exp S[\xi]$$

(Jacobi determinant is one)

$$= \textstyle\int \mathrm{d}[\zeta^*]\mathrm{d}[\zeta] \exp S[\zeta, \zeta^*] = \int \mathrm{d}[\zeta^*]\mathrm{d}[\zeta] \exp \Big(\sum'_{kl} \big(\sum_{ij} \zeta_{kl}^{(i)} A_{ij}^{(kl)} \zeta_{kl}^{(j)*} \big) \Big)$$

$$= \textstyle\prod'_{kl} \det A^{(kl)} = \prod_{\binom{kl}{\text{all}}} \sqrt{\det A^{(kl)}}$$

$$= \textstyle\prod_{kl} \sqrt{(1+v^2)^2 - 2v(1-v^2)(\cos p_k + \cos q_k))}$$

(5) Conclusion: Exact solution of the Ising model

Free energy: (From $\mathscr{Z}_N = 2^N (\cosh(\beta J))^{2N} \widehat{\mathscr{Z}_N}$)

$$F = -k_B T \ln \mathscr{Z}$$

$$= -N k_B T \Big\{ \ln(2\cosh^2 \beta J) + \tfrac{1}{2N} \textstyle\sum_{kl} \ln \big[(1+v^2)^2 - 2v(1-v^2)(\cos p_k + \cos q_l)\big] \Big\}$$

$v = \tanh \beta J$

$$= -N k_B T \tfrac{1}{2N} \textstyle\sum_{kl} \ln \Big[4\cosh^2(2\beta J) - 4\sinh(2\beta J)(\cos p_k + \cos q_l) \Big]$$

Thermodynamic limit: $\sum_{kl} \ \to \ \frac{1}{(2\pi)^2} \iint_{-\pi}^{\pi} \mathrm{d}p_x\, \mathrm{d}p_y$

$$\Rightarrow \boxed{F = -N k_B T \frac{1}{8\pi^2} \iint_{-\pi}^{\pi} \mathrm{d}p_x\, \mathrm{d}p_y\ \ln \Big[4\cosh^2(2\beta J) - 4\sinh(2\beta J)(\cos p_x + \cos p_y) \Big]}$$

Corresponds to the result of Onsager!

Analysis:

A phase transition is expected, if the argument of $\ln[\cdots]$ is zero.

$\rightsquigarrow$ $\cosh^2(2\beta J) = \sinh(2\beta J)(\cos p_x + \cos p_y)$ for one (p_x, p_y)

$\rightsquigarrow$ Possible for $(\cos p_x + \cos p_y) = 2$, i.e., $(p_x, p_y) = (0, 0)$

Then, one has: $\cosh^2 2\beta_c J = 1 + \sinh^2 2\beta_c J \overset{!}{=} 2 \sinh 2\beta_c J$

$\Rightarrow$ $(1 - \sinh^2 2\beta_c J) = 0$

$\Rightarrow$ $\beta_c J = \frac{1}{2}\mathrm{arsinh} 1 = \frac{1}{2}\ln(1 + \sqrt{2})$

$\rightsquigarrow$ Same result as in Sec. 3.3.2!

But: from the exact solution, one can also calculate other quantities, such as, e.g., the specific heat → Exercise
(One obtains $c \sim \ln(T - T_c)$: Logarithmic divergence)

3.4 Series Expansions: General Remarks

Last subsection (3.3.2): Introduction of the concept of series expansions – an important technique when studying phase transitions analytically

In particular, the high temperature expansion turns out to be a powerful and highly versatile tool in statistical physics.

Basic idea (in quantum mechanics notation)

- For arbitrary statistical averages (canonical ensemble), we have $$\langle A\rangle_\beta = \frac{\mathrm{Tr}(A\mathrm{e}^{-\beta H})}{\mathrm{Tr}(\mathrm{e}^{-\beta H})}$$ (Classically, ”Tr” refers to the suitable phase space integral or sum, e.g. in the Ising model, ”$\sum_{\{S_i\}}\cdots$”, and $H \mathrel{\widehat{=}} \mathscr{H}$ to the Hamiltonian.)
- Define $\mathscr{Z}_0 = \mathrm{Tr}(1)$ and rewrite:
  Numerator of $\langle A\rangle_\beta$: $\mathrm{Tr}(A\mathrm{e}^{-\beta H}) = \frac{1}{\mathscr{Z}_0}\langle A\mathrm{e}^{-\beta H}\rangle_0$
  Denominator of $\langle A\rangle_\beta$: $\mathrm{Tr}(\mathrm{e}^{-\beta H}) = \frac{1}{\mathscr{Z}_0}\langle \mathrm{e}^{-\beta H}\rangle_0$,
  where $\langle\cdots\rangle_0$: Statistical average at $\beta = 0$ ($T \to \infty$)
- Then expand $\langle A\rangle_\beta = \frac{\langle A\mathrm{e}^{-\beta H}\rangle_0}{\langle \mathrm{e}^{-\beta H}\rangle_0}$ in powers of β
  ($\mathrm{e}^{-\beta H} = 1 - \beta H + \frac{1}{2}\beta^2 H^2 + \cdots$)
  Leading terms:
  $$\begin{aligned}\langle A\rangle_\beta &= \frac{\langle A\rangle_0 - \beta\langle AH\rangle_0 + \frac{1}{2}\beta^2\langle AH^2\rangle_0 + \cdots}{1 - \beta\langle H\rangle_0 + \frac{1}{2}\beta^2\langle H^2\rangle_0 + \cdots}\\ &= \langle A\rangle_0 - \beta\big(\langle AH\rangle_0 - \langle A\rangle_0\langle H\rangle_0\big)\\ &\quad + \tfrac{1}{2}\beta^2\Big(\langle AH^2\rangle_0 - 2\langle AH\rangle_0\langle H\rangle_0 - \langle A\rangle_0\langle H^2\rangle_0 + 2\langle A\rangle_0\langle H\rangle_0^2\Big)\\ &\quad + \mathscr{O}(\beta^3)\end{aligned}$$

Free energy ($\beta F = -\ln(\mathrm{Tr}(\mathrm{e}^{-\beta H}))$) can be expanded analogeously.

Very general approach

Low temperature expansions are also possible (see, e.g., Sec. 3.3.2), but the design principles are less generic (Setting up such an expansion requires the knowledge of the elementary excitations in the system).

General remarks on series expansions

- In general, graphical methods are useful for the construction, see, e.g., the graphical expansions in Sec. 3.3.2 in polygon configurations (The ”diagrams” of the expansion are the polygon configurations.)
- Simplifications can often be identified beforehand based on general considerations (e.g., symmetry considerations).
- Important example: **Linked Cluster Theorem**: Only connected diagrams (configurations with connected polygons) contribute to $F \propto \ln\mathscr{Z}$, diagrams with unconnected components cancel out.

  (Heuristic ”proof”: Every unconnected component comes with a combinatorial factor $\propto N$. However, F is extensive, therefore, they must all cancel each other!)

Analysis of series expansions

Starting point: Series $f(z) = \sum_n a_n z^n$
Only a finite number of coefficients are known.

Question: Assume that $f(z)$ has a singularity, $f(z) \sim (z - z_c)^{-\gamma}$
What can we learn from the series about the singularity?

Example: Consider simple function $f(z) = (1 - z/z_c)^{-\gamma}$ (with $\gamma > 1$)

$\Rightarrow$ Expansion $f(z) = \sum_n \binom{-\gamma}{n}(\frac{-1}{z_c})^n z^n$

$\Rightarrow$ $a_n = (\frac{1}{z_c})^n(-1)^n\binom{-\gamma}{n} = (\frac{1}{z_c})^n \frac{\gamma(\gamma+1)\cdots(\gamma+n-1)}{n!}$

$\Rightarrow$ $\frac{a_n}{a_{n-1}} = \frac{1}{z_c}\frac{\gamma+n-1}{n} = \frac{1}{z_c}(1 + \frac{\gamma-1}{n})$

$\Rightarrow$ Possible strategies for determining z_c:

- Simply plot $r_n = \frac{a_n}{a_{n-1}}$ versus $\frac{1}{n}$ ⇝ Axis intercept gives $1/z_c$!
  (Generally, $\lim_{n\to\infty}\frac{a_{n-1}}{a_n}$ gives the radius of convergence of the series. Therefore, this method works, if the convergence radius is determined by the singularity at z_c)
- More efficient method: Eliminate term $\frac{\gamma-1}{n}$ in our example by choosing $r_n = n\frac{a_n}{a_{n-1}} - (n-1)\frac{a_{n-1}}{a_{n-2}}$
  (Gives $r_n \equiv \frac{1}{z_c}$ in our example.
  In general, corrections apply.)
- There exist numerous other, much more sophisticated approaches, e.g., Padé approximants.
  Analyzing series expansions is an art in itself

If z_c is known, similar techniques can be applied to determine γ.
For example, a simple estimator is $S_n = 1 + n(\frac{a_n}{a_{n-1}} z_c - 1)$

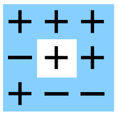
3.5 Mean-Field Approximation

Often less involved than series expansions, more general approach, not restricted to regions without singularities. "Sufficient" for many purposes.

But: Uncontrolled approximation

3.5.1 Simplest approach: Spins in mean fields

3.5.1.1 Approach *via* effective field (intuitive approach)



$$\mathscr{H} = -J \underbrace{\sum_{\langle ij \rangle}}_{\text{nearest neighbors}} S_i S_j - H \sum_i S_i$$

Interactions ↔ Effective field $H^i_{\text{eff}} = -\frac{\partial \mathscr{H}}{\partial S_i} = H + J \sum_j S_j$

Mean-field approximation: Replace S_j by $\langle S \rangle = m$.

$H_{\text{eff}} = H + Jqm$, with q: coordination number (cubic lattice: $2 \cdot D$)

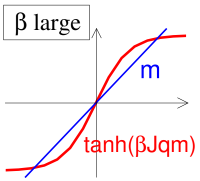
Consider single spin in the external field H_{eff} : $\mathscr{H}^{(i)}_{\text{eff}} = -H_{\text{eff}}\, S$

$\rightsquigarrow$ Partition function $\mathscr{Z} = \mathrm{e}^{\beta H_{\text{eff}}} + \mathrm{e}^{-\beta H_{\text{eff}}}$

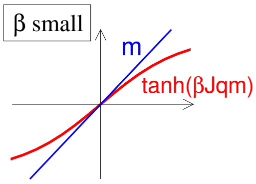
Magnetization: $m = \frac{\mathrm{e}^{\beta H_{\text{eff}}} - \mathrm{e}^{-\beta H_{\text{eff}}}}{\mathrm{e}^{\beta H_{\text{eff}}} + \mathrm{e}^{-\beta H_{\text{eff}}}} = \tanh(\beta H_{\text{eff}})$

⇒ Implicit, self consistent equation for m: $\boxed{m = \tanh\big(\beta(Jqm + H)\big)}$

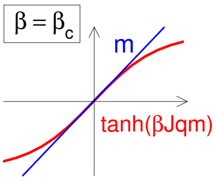
At $H = 0$, the equation can be solved graphically:



Three crossings



Only one crossing



Tangent crossing

At the critical point $\beta = \beta_c$

⇒ Only one crossing point, but slopes are equal

$$\Rightarrow \frac{\mathrm{d}}{\mathrm{d}m} \tanh(\beta_c Jqm)\Big|_{m=0} = \frac{\mathrm{d}}{\mathrm{d}m}\Big|_{m=0} m = 1$$

$$\Rightarrow \quad \boxed{\beta_c Jq = 1}$$

Close to the critical point, $\tanh(\cdots)$ can be expanded in powers of m.

$$\Rightarrow m = \tanh(\beta qJm) \approx \beta qJm - \tfrac{1}{3}(\beta qJ)^3 m^3 + \cdots$$

$$\Rightarrow m(T) \approx \sqrt{3(\beta qJ - 1)/(\beta qJ)^3} = \sqrt{3}\frac{T}{T_c}\sqrt{1 - \frac{T}{T_c}} \propto (T_c - T)^{1/2}$$

⇒ Critical exponent β: $\beta = 1/2$

Within this approach, one can calculate the spontaneous magnetization and the susceptibility, but not the entropy or the free energy.

3.5.1.2 Approach *via* free energy (Bragg-Williams approximation)

Starting point: Free energy $F = U - T\mathscr{S}$

"Mean-field" approximation: Spins are not correlated:
$\rightsquigarrow$ Joint probability function factorizes: $P(S_1, S_2, \cdots, S_N) \approx \prod_{j=1}^{N} p^{(1)}(S_j)$
with $p^{(1)}(S)$: probability distribution for single spin

(a) Energy: $\frac{1}{N}U = \frac{1}{N}\big\langle \mathscr{H} \big\rangle = \frac{1}{N}\Big\langle -J\sum\limits_{\langle ij \rangle} S_i S_j - H\sum\limits_i S_i \Big\rangle$

$$\approx \frac{1}{N}\Big(-J \sum_{\langle ij \rangle} \big\langle S_i \big\rangle \big\langle S_j \big\rangle - H\sum_i \big\langle S_i \big\rangle \Big) = -\tfrac{1}{2} Jq\, m^2 - H\, m$$

(b) Entropy: $\mathscr{S} = -k_B \sum_{\{S_1, \cdots, S_N\}} P(S_1, \cdots, S_N)\, \ln(P(S_1, \cdots, S_N))$

$$\approx -k_B \textstyle\sum_{S_1} p^{(1)}(S_1) \cdots \sum_{S_N} p^{(1)}(S_N) \Big[\sum_j \ln p^{(1)}(S_j) \Big]$$

$$= -k_B \sum_j \underbrace{\sum_{S_j} p^{(1)}(S_j) \ln p^{(1)}(S_j)}_{\text{independent of } j} \prod_{i \neq j} \underbrace{\Big(\sum_{S_i} p^{(1)}(S_i) \Big)}_{1}$$

$$= -k_B N \textstyle\sum_S p^{(1)}(S) \ln p^{(1)}(S)$$

Given magnetization m, uncorrelated spins S_j
$\rightsquigarrow$ Construct probability function $p^{(1)}(S)$ such that $\langle S \rangle = m$
Notation: $p_+^{(1)} := p^{(1)}(+1), \quad p_-^{(1)} := p^{(1)}(-1)$
$\Rightarrow \big\langle S \big\rangle = p_+^{(1)} - p_-^{(1)} = m$ and $p_+^{(1)} + p_-^{(1)} = 1$
$\Rightarrow p_+^{(1)} = (1+m)/2, \quad p_-^{(1)} = (1-m)/2$

$$\Rightarrow \tfrac{1}{N}\mathscr{S} = -k_B \big(p_+^{(1)} \ln p_+^{(1)} + p_-^{(1)} \ln p_-^{(1)} \big)$$
$$= k_B \big[-\tfrac{1+m}{2} \ln \tfrac{1+m}{2} - \tfrac{1-m}{2} \ln \tfrac{1-m}{2} \big]$$

$\Rightarrow$ Free energy: $\dfrac{F}{N} = -\frac{1}{2}Jqm^2 - Hm + k_B T\big[\frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \big]$

Minimization: $\frac{\partial F}{\partial m} = -qJm - H + k_B T \frac{1}{2} \ln\big(\frac{1+m}{1-m} \big) \overset{!}{=} 0$

$$\Rightarrow \boxed{\ln\Big(\frac{1+m}{1-m} \Big) = 2\beta(qJm + H)} \Rightarrow \boxed{m = \tanh \beta(qJm + H)}$$

$\rightsquigarrow$ Approximation equivalent to the approximation of 3.5.1

3.5.1.3 Problems with this mean-field aproximation

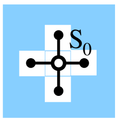
– Geometry enters only *via* coordination number q
$\rightsquigarrow$ no dependence on dimension, local structure etc.

– Predicts a phase transition for the one dimensional Ising model (wrong !)

– Wrong critical point T_c, wrong critical exponents
Example: Two dimensional Ising model on the square lattice:
Mean-field → $\beta_c J = \frac{1}{q}$, Critical exponent $\beta = 1/2$
Exact → $\beta_c J = \frac{1}{q}\, 2\ln(1+\sqrt{2}) = \frac{1}{q} \cdot 1.76$
Critical exponent $\beta = 1/8$

3.5.2 Improved theory: Clusters in mean fields

3.5.2.1 Approach *via* effective field (Bethe approximation)



Cluster with central particle ”0”

$\Rightarrow \mathscr{H}_{\text{Cluster}} = -J\, S_0 \sum_{j=1}^{q} S_j - H_{\text{eff}} \sum_{j=1}^{q} S_j$

(Effective field H_{eff} acts on outer spins only
Central spin is treated exactly)

$$\begin{aligned} \Rightarrow \mathscr{Z}_{\text{Cluster}} &= \left(e^{\beta(J+H_{\text{eff}})} + e^{-\beta(J+H_{\text{eff}})}\right)^{q} \quad &&: \text{Contribution of } S_0 = +1 \\ &+ \left(e^{\beta(-J+H_{\text{eff}})} + e^{-\beta(-J+H_{\text{eff}})}\right)^{q} \quad &&: \text{Contribution of } S_0 = -1 \end{aligned}$$

$$\langle S_0 \rangle = \frac{1}{\mathscr{Z}_{\text{Cluster}}} \left[\left(e^{\beta(J+H_{\text{eff}})} + e^{-\beta(J+H_{\text{eff}})}\right)^{q} - \left(e^{\beta(-J+H_{\text{eff}})} + e^{-\beta(-J+H_{\text{eff}})}\right)^{q} \right]$$

$$\begin{aligned} \langle S_j \rangle = \frac{1}{\mathscr{Z}_{\text{Cluster}}} \Big[&\left(e^{\beta(J+H_{\text{eff}})} + e^{-\beta(J+H_{\text{eff}})}\right)^{q-1} \cdot \left(e^{\beta(J+H_{\text{eff}})} - e^{-\beta(J+H_{\text{eff}})}\right) \\ &+ \left(e^{\beta(-J+H_{\text{eff}})} + e^{-\beta(-J+H_{\text{eff}})}\right)^{q-1} \cdot \left(e^{\beta(-J+H_{\text{eff}})} - e^{-\beta(-J+H_{\text{eff}})}\right) \Big] \end{aligned}$$

$\rightsquigarrow$ Condition for H_{eff}: $\langle S_0 \rangle \overset{!}{=} \langle S_j \rangle \ (= m)$

$$\Rightarrow \quad \boxed{\frac{\cosh \beta(J + H_{\text{eff}})}{\cosh \beta(-J + H_{\text{eff}})} = e^{2\beta H_{\text{eff}}/(q-1)}}$$

<u>Solutions</u>:

(i) $H_{\text{eff}} = 0$: Disordered state

(ii) $H_{\text{eff}} \neq 0$ (if β is not too small): Ordered state

<u>Transition point</u>: Expand about small H_{eff}

$$\rightsquigarrow \left[\frac{\cosh \beta(J+H_{\text{eff}})}{\cosh \beta(-J+H_{\text{eff}})} \approx 1 + 2\beta H_{\text{eff}} \tanh \beta J \right] \overset{!}{=} \left[e^{2\beta H_{\text{eff}}/(q-1)} \approx 1 + 2\beta \frac{H_{\text{eff}}}{(q-1)} \right]$$

$$\Rightarrow \quad \boxed{\coth(\beta_c J) = q - 1} \quad \Rightarrow \quad \boxed{2\beta_c J = \ln\left(\frac{q}{q-2}\right)}$$

<u>Remarks</u>:

- In one dimensions, one has $q = 2$ $\rightsquigarrow$ no phase transition ✓
- Two dimensional Ising model on the square lattice:
  Exact: $\beta_c J = 0.44$
  Bragg-Williams: $\beta_c J = 1/4 = 0.25$
  Bethe: $\beta_c J = \ln(2) = 0.35$: Significant improvement!
- Higher coordination numbers:
  Bragg-Williams: $2\beta_c J = 2/q$
  Bethe: $2\beta_c J = \ln \frac{q}{q-2} = -\ln(1 - 2/q) = 2/q + \cdots$
  $\rightsquigarrow$ Bragg-Williams and Bethe approximation agree at lowest order of $1/q$. Results are never identical!
- Critical exponents in Bethe and Bragg-Williams approximation are the same: No improvement in this respect.

3.5.2.2 Approach *via* free energy (Guggenheim approximation)

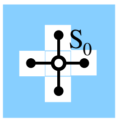
Main approximation in Bragg-Williams theory: Independent spins

Guggenheim approximation: Independent clusters, neglect cluster correlations

$\rightsquigarrow$ Improved treatment of pairs of neighbor spins

- Probability for one single cluster:
  $p_{\text{cluster}}(S_0;\{S_j\}) = p^{(1)}(S_0)\,\prod_{j=1}^{q} P(S_0S_j|S_0)$

  conditional probability for (S_0S_j) given S_0

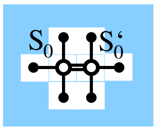


$$P(S_0S_j|S_0) = p^{(2)}(S_0S_j)/p^{(1)}(S_0)$$

with $p^{(2)}(S_0S_j)$: Pair probability

$$= p^{(1)}(S_0)\prod_{j=1}^{q}\frac{p^{(2)}(S_0S_j)}{p^{(1)}(S_0)}$$

- Two neighbor clusters: Must correct for double counting of bonds
  $\rightsquigarrow\ p_{\text{cluster}}\big(S_0;\{S_j\}\big)\ P_{\text{cluster}}\big(S_0';\{S_j\}|(S_0S_0')\big)$
  $= p_{\text{cluster}}\big(S_0;\{S_j\}\big)p_{\text{cluster}}\big(S_0';\{S_j\}\big)\Big/p^{(2)}(S_0S_0')$



$\rightsquigarrow$ Whole system: $\boxed{P(S_1,\cdots,S_N) \approx \prod_{\langle ij\rangle} p^{(2)}(S_iS_j)\Big/\prod_{i} p^{(1)}(S_i)^{q-1}}$

Construct probability functions such that $\langle S\rangle = m$

Notation: $p_{\pm}^{(1)} := p^{(1)}(\pm1)$, $\quad p_{\pm\pm}^{(2)} := p^{(2)}(\pm1,\pm1), p_{+-}^{(2)} = p_{-+}^{(2)} =: a$
$\Rightarrow p_{+}^{(1)} = p_{++}^{(2)} + p_{+-}^{(2)} = \frac{1+m}{2}, \quad p_{-}^{(1)} = p_{+-}^{(2)} + p_{--}^{(2)} = \frac{1-m}{2}$
$\Rightarrow p_{++}^{(2)} = \frac{1+m}{2} - a, \quad p_{--}^{(2)} = \frac{1-m}{2} - a$

$\Rightarrow$ Entropy: $\mathscr{S} = \sum_{\{S_1,\cdots,S_N\}} P(S_1,\cdots,S_N)\ \ln P(S_1,\cdots,S_N)$

$$\Rightarrow \frac{1}{N}\mathscr{S} \approx -k_B\Big(\frac{q}{2}\sum_{SS'} p^{(2)}(SS')\ln p^{(2)}(SS') - (q-1)\sum_{S} p^{(1)}(S)\ln p^{(1)}(S)\Big)$$

$$= -k_B\Big\{\frac{q}{2}\big[(\tfrac{1+m}{2}-a)\ln(\tfrac{1+m}{2}-a) + (\tfrac{1-m}{2}-a)\ln(\tfrac{1-m}{2}-a) + 2a\ln a\big] - (q-1)\big[(\tfrac{1+m}{2})\ln(\tfrac{1+m}{2}) + \tfrac{1-m}{2})\ln(\tfrac{1-m}{2})\big]\Big\}$$

Energy: $\frac{1}{N}U = \frac{1}{N}\langle\mathscr{H}\rangle = -J\frac{q}{2}\big[(p_{++}^{(2)}+p_{--}^{(2)}) - (p_{+-}^{(2)}+p_{-+}^{(2)})\big] = J\frac{q}{2}\,(4a-1)$

Free energy: $F = U - \frac{1}{\beta}\mathscr{S}$

Minimize free energy: $\frac{\partial F}{\partial a} \overset{!}{=} 0, \quad \frac{\partial F}{\partial m} \overset{!}{=} 0$

- $\frac{1}{N}\frac{\partial F}{\partial a} = 2qJ + \frac{1}{\beta}\frac{q}{2}\Big[2\ln(2a) - \ln\big((1+m-2a)(1-m-2a)\big)\Big] \overset{!}{=} 0$

$$\Rightarrow \boxed{4\beta J = \ln\Big(\frac{(1+m-2a)(1+m+2a)}{(2a)^2}\Big)} \qquad \text{(i)}$$

- $\frac{1}{N}\frac{\partial F}{\partial m} = \frac{1}{\beta}\Big[\frac{q}{4}\ln\frac{1+m-2a}{1-m-2a} - \frac{q-1}{2}\ln\frac{1+m}{1-m}\Big] \overset{!}{=} 0$

$$\Rightarrow \quad \boxed{\frac{q}{2}\ln\Big(\frac{1+m-2a}{1-m-2a}\Big) = (q-1)\ln\Big(\frac{1+m}{1-m}\Big)} \qquad \text{(ii)}$$

Critical point: $m \to 0$

$$\text{(ii)} \Rightarrow \Big[\ \frac{q}{2}\ln\big(1+\frac{2m}{1-2a}\big) \approx \frac{q}{2}\frac{2m}{1-2a}\ \Big] \overset{!}{=} \Big[\ (q-1)\ln(1+2m) \approx (q-1)2m\ \Big]$$

$$\Rightarrow\ 2a = \frac{q-2}{2(q-1)}, \quad 1-2a = \frac{q}{2(q-1)}$$

$$\text{(i):} \Rightarrow\ 4\beta_c J = 2\ln\frac{1-2a}{2a} = 2\ln\frac{q}{q-2} \quad \Rightarrow \quad \boxed{2\beta_c J = \ln\big(\frac{q}{q-2}\big)}$$

Remarks:

- Same result as in Bethe approximation ✓
- Systematic generalization to larger clusters is possible
  ⇝ Cluster variation method
  Popular method in the context of order/disorder phase transitions
  For large clusters: Very good phase diagrams
  But still: wrong critical behavior (see next chapter)

3.5.3 Critical behavior in mean-field theory

As already mentioned earlier, one often observes critical behavior at continuous transitions: Many properties exhibit singularities when plotted against intensive variables such as temperature and magnetic field, which are often characterized by power laws.

At a qualitative level, the same behavior can already be seen in mean-field approximation. This will be shown in the present section.

Preview: Defining $t = (T - T_c)/T_c$ and d: Spatial dimension

Quantity	Exponent	Power law	Value		
			Mean-field	Ising exact	
				2D	3D
Magnetization m	β	$m \sim (-t)^{\beta}$	$\beta = 1/2$	1/8	0.33
	δ	$m^{\delta} \sim H$ at $t = 0$	$\delta = 3$	15	4.8
Susceptibility $\chi = \frac{\partial m}{\partial H}$	γ	$\chi \sim \lvert t\rvert^{-\gamma}$	$\gamma = 1$	7/4	1.24
Specific heat $c_H = T(\frac{\partial S}{\partial T})_H = (\frac{\partial E}{\partial T})_H$	α	$c_H \sim \lvert t\rvert^{-\alpha}$	$\alpha = 0$	0(log)	0.1
Correlations $G_{ij} = \langle S_i S_j\rangle - \langle S_i\rangle\langle S_j\rangle =: G(\vec{r}_i - \vec{r}_j)$	η	$G(\vec{r}) \sim r^{2-d-\eta}$ at $t = 0$	$\eta = 0$	1/4	0.04
Correlation length $G(\vec{r}) \sim \mathrm{e}^{-r/\xi}$	ν	$\xi \sim \lvert t\rvert^{-\nu}$	$\nu = 1/2$	1	0.63

Calculation: In Bragg-Williams approximation

Bethe-Guggenheim calculation shall not be shown here, but the results are the same. In the next section we will see, why.

Define $\boxed{h = \beta H}$ and $\boxed{t = (T - T_c)/T_c = \beta_c/\beta - 1}$

with $\beta_c = 1/qJ$ (q: Coordination number)

3.5.3.1 Magnetization

Starting point: (see Sec. 3.5.1.2): $m = \tanh\beta(qJm + H) = \tanh(\frac{\beta}{\beta_c}m + h)$

At $|t|, |h| \ll 1$, one has $|m| \ll 1$ and hence $m \approx \frac{\beta}{\beta_c}m + h - \frac{1}{3}(\frac{\beta}{\beta_c}m + h)^3$

Consider limit $t \to 0^-,\ h = 0$

$$\Rightarrow\ m \approx \frac{\beta}{\beta_c}m - \frac{1}{3}(\frac{\beta}{\beta_c}m)^3$$

$$\Rightarrow\ \frac{\beta}{\beta_c}m = \sqrt{3}\,(-t)^{1/2} \quad \Rightarrow \quad m \sim (-t)^{1/2} \quad \Rightarrow \quad \boxed{\beta = 1/2}$$

Consider limit $t = 0,\ h \to 0$ (i.e., $\beta/\beta_c = 1$)

$$\Rightarrow\ m \approx m + h - \frac{1}{3}(m + h)^3$$

$$\Rightarrow\ h \approx \frac{1}{3}m^3 + \mathscr{O}(m^2 h, m h^2) \quad \Rightarrow \quad h \sim m^3 \quad \Rightarrow \quad \boxed{\delta = 3}$$

3.5.3.2 Susceptibility

Starting point: Same as before in Section 3.5.3.1

Consider limit $t \to 0,\ h \to 0$

Define $g(m,h) := \tanh(\frac{\beta}{\beta_c}m + h) - m \approx m(\frac{\beta}{\beta_c} - 1) + h - \frac{1}{3}(\frac{\beta}{\beta_c}m)^3$

$$\Rightarrow\ g(m,h) \equiv 0 \quad \Rightarrow \quad \frac{\partial m}{\partial h}\Big|_t = -\frac{\partial g}{\partial h}\Big/\frac{\partial g}{\partial m}$$

with $\frac{\partial g}{\partial h} = 1$, $\quad \frac{\partial g}{\partial m} = (\frac{\beta}{\beta_c} - 1) - \frac{\beta}{\beta_c}(\frac{\beta}{\beta_c}m)^2 = -\frac{\beta}{\beta_c}(t + (\frac{\beta}{\beta_c}m)^2)$

$$\Rightarrow\ \frac{\partial m}{\partial h}\Big|_t = \frac{\frac{\beta_c}{\beta}}{t + (\frac{\beta}{\beta_c}m)^2} = \frac{\beta_c}{\beta}\begin{cases} t^{-1} & : t > 0\ (m = 0) \\ (-2t)^{-1} & : t < 0\ ((\frac{\beta}{\beta_c}m)^2 = -3t) \end{cases}$$

$$\Rightarrow \quad \boxed{\gamma = 1}$$

3.5.3.3 Specific heat

Starting point: $U = \langle \mathscr{H} \rangle = -J\sum_{\langle ij \rangle}\langle S_i \rangle \langle S_j \rangle = -NJ\frac{q}{2}\,m^2 = -N\frac{1}{2\beta_c}\,m^2$

$$\text{with } m^2 = \begin{cases} 0 & : T > T_c \\ (-t)3\frac{\beta_c}{\beta} = \frac{(T - T_c)}{T_c}\,(\frac{T}{T_c})^2 & : T < T_c \end{cases}$$

$$\Rightarrow\ c_H = \frac{\partial U}{\partial T}\Big|_H = \begin{cases} 0 & : T > T_c \\ -\frac{N}{2}k_B & : T \lesssim T_c \end{cases} \quad \text{with } (T \to T_c^-)$$

Consider limit $t \to 0$: Finite jump $\Rightarrow \boxed{\alpha = 0}$

3.5.3.4 Correlation functions

Less straightforward, since correlations are ignored in mean-field theory.

Starting point: Consider Ising model at $H = 0$, regular lattice with simple unit cell and lattice vectors $\vec{r}_i$, d dimensions, periodic boundary conditions. The interaction range is characterized by a set of neighbor vectors $\{\vec{\tau}\}$, i.e., spins S_i, S_j interact if $\vec{r}_{ij} := (\vec{r}_j - \vec{r}_i) \in \{\vec{\tau}\})$. NB: If τ is a neighbor vector, then (- τ) is a neighbor vector as well.

Goal: Calculate $G(\vec{r}_{ij}) = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle$

Trick: Use general relation between <u>fluctuations</u> and <u>susceptibilities</u>

Consider generally an energy function of the form B: $\mathscr{H} = \mathscr{H}_0 - H_B B$

Then we have the <u>general</u> relation $\langle AB \rangle - \langle A \rangle \langle B \rangle = \frac{1}{\beta} \frac{\partial \langle A \rangle}{\partial H_B}$

(Proof: $\langle A \rangle = \frac{1}{\mathscr{Z}} \sum\limits_{\text{Configurations}} \mathrm{e}^{-\beta \mathscr{H}} A = \frac{\sum \mathrm{e}^{-\beta \mathscr{H}_0 + \beta H_B B} A}{\sum \mathrm{e}^{-\beta \mathscr{H}_0 + \beta H_B B}}$

$\Rightarrow \frac{\partial \langle A \rangle}{\partial H_B} = \frac{\mathscr{Z} \sum \mathrm{e}^{-\beta \mathscr{H}_0 + \beta H_B B} \beta B A - (\sum \mathrm{e}^{-\beta \mathscr{H}_0 + \beta H_B B} \beta B)(\sum \mathrm{e}^{-\beta \mathscr{H}_0 + \beta H_B B} A)}{\mathscr{Z}^2}$

$= \beta \langle AB \rangle - \beta \langle A \rangle \langle B \rangle \quad \checkmark$)

Of course also valid in the case $H_B = 0$

Here: Consider $\mathscr{H} = -J \sum_{\langle ij \rangle} S_i S_j - \sum_i H_i S_i$

$\rightsquigarrow$ Inhomogeneous system with $\langle S_i \rangle = m_i$ different for all i

Solution as before: $m_i = \tanh\big(\beta(J \sum_{\text{neighbors } j \text{ of } i} m_j + H_i)\big)$

Can be evaluated $\Rightarrow$ $G_{\vec{r}_{ij}} = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle = \frac{1}{\beta} \frac{\partial m_i}{\partial H_j}\Big|_{h_k = 0 \forall k}$

Solution for $T \geqslant T_c$:

$$\boxed{G(\vec{r}) = \frac{1}{(2\pi)^d} \int\limits_{\substack{\text{1st Brillouin}\\ \text{zone}}} \mathrm{d}^d k \; \frac{1}{1 - \beta J \sum_{\vec{\tau}} \cos(\vec{k} \cdot \vec{\tau}))} \, \mathrm{e}^{i\vec{k} \cdot \vec{r}}}$$

(Calculation:

First linearize: $m_i = \tanh\big(\beta(J \sum\limits_{\text{neighbors}} m_j + H_i)\big) \approx \beta(J \sum\limits_{\text{neighbors}} m_j + H_j)$

$\Rightarrow \sum_j B_{ij} m_j = H_j$ with $B_{ij} = \frac{1}{\beta} \delta_{ij} - \begin{cases} J & : \vec{r}_{ij} \in \{\vec{\tau}\} \\ 0 & : \text{otherwise} \end{cases}$

$\Rightarrow m_i = \sum_j (B^{-1})_{ij} H_j \quad \Rightarrow G(\vec{r}_{ij}) = \frac{1}{\beta} \frac{\partial m_i}{\partial H_j} = \frac{1}{\beta} (B^{-1})_{ij}$

Then diagonalize and invert B by Fourier transform. Define $B_{ij} =: B(\vec{r}_{ij})$

$\Rightarrow \tilde{B}(\vec{k}) = \sum\limits_{\substack{\text{lattice}\\ \text{vectors } \vec{r}}} \mathrm{e}^{-i\vec{k} \cdot \vec{r}} B(\vec{r}) = \frac{1}{\beta} - J \sum\limits_{\vec{\tau}} \cos(\vec{k} \cdot \vec{\tau})$

$\Rightarrow \frac{1}{\beta} (B^{-1})_{ij} = \frac{1}{(2\pi)^d} \int d^d k \, (\beta \tilde{B}(\vec{k}))^{-1} \, \mathrm{e}^{i(\vec{r}_i - \vec{r}_j) \cdot \vec{k}} \qquad \checkmark$)

Simplification for $t \to 0+$:

$$\boxed{G(\vec{r}) = \frac{1}{(2\pi)^d} \int_\infty \mathrm{d}^d k \; \frac{\beta_c / \beta}{t + k^2 v(\vec{e}_{\vec{k}})} \, \mathrm{e}^{i\vec{k} \cdot \vec{r}}}$$

with $\vec{e}_{\vec{k}} = \frac{\vec{k}}{k}$ and $v(\vec{e}) = \frac{1}{2q} \sum_{\vec{\tau}} (\vec{e} \cdot \vec{\tau})^2$

(Calculation:

Rewrite $B(\vec{k}) = \frac{1}{\beta_c} \big(t - \frac{1}{q} \sum_{\vec{\tau}} (1 + \cos(\vec{k} \cdot \vec{\tau})\big)$

$t \to 0$: Main contribution to integral stems from small $\vec{k}$!

$\Rightarrow$ Expand $\big[t + \frac{1}{q} \sum_{\vec{\tau}} (1 - \cos(\vec{k} \cdot \vec{\tau}))\big] \approx \big[t + k^2 \, v(\vec{e}_{\vec{k}})\big] \qquad \checkmark$)

Consider $t = 0$ $(\vec{e}_{\vec{r}} = \vec{r}/r)$

$$\Rightarrow G(\vec{r}) = \tfrac{1}{(2\pi)^d}\tfrac{\beta_c}{\beta}\int_\infty \mathrm{d}^d k \, \tfrac{1}{k^2 v(\vec{e}_{\vec{k}})} \, \mathrm{e}^{i\vec{k}\cdot\vec{r}} \overset{\tilde{k}=\vec{k}r}{=} \underbrace{\tfrac{1}{(2\pi)^d}\tfrac{\beta_c}{\beta}\int_\infty \mathrm{d}^d\tilde{k} \, \tfrac{1}{\tilde{k}^2 v(\vec{e}_{\vec{k}})}\mathrm{e}^{i\tilde{k}\cdot\vec{e}_{\vec{r}}}}_{\text{independent of } r} \, r^{2-d}$$

$$\Rightarrow \boxed{G(\vec{r}) \sim r^{2-d}} \qquad \Rightarrow \boxed{\eta = 0}$$

Now consider case $t \to 0$

$$\Rightarrow G(\vec{r}) = \tfrac{1}{(2\pi)^d}\tfrac{\beta_c}{\beta}\int_\infty \mathrm{d}^d k \, \tfrac{1}{t+k^2 v(\vec{e}_{\vec{k}})} \, \mathrm{e}^{i\vec{k}\cdot\vec{r}} \overset{\tilde{k}=\vec{k}r}{=} \tfrac{1}{(2\pi)^d}\tfrac{\beta_c}{\beta}\int_\infty \mathrm{d}^d\tilde{k} \, \tfrac{1}{r^2 t+\tilde{k}^2 v(\vec{e}_{\vec{k}})}\mathrm{e}^{i\tilde{k}\cdot\vec{e}_{\vec{r}}} \, r^{2-d}$$

- $r^2 t \ll 1 \Rightarrow r^2 t \approx 0 \Rightarrow G(\vec{r}) \sim r^{2-d}$ as before
- $r^2 t \gg 1$: Choose x direction in direction of $\vec{r}$. Other directions: $\vec{k}_\perp$

  $$\Rightarrow G(\vec{r}) = \tfrac{1}{2\pi}\int_{-\pi}^{\pi} \mathrm{d}k_x \, \mathrm{e}^{irk_x} \underbrace{\tfrac{\beta}{\beta_c}\tfrac{1}{(2\pi)^{d-1}}\int \mathrm{d}^{d-1}k_\parallel \tfrac{1}{t+(k_x^2+k_\perp^2)v(\vec{e}_{\vec{k}})}}_{=:g(k_x)}$$

  Use theorem of residues, search for poles p_j of $g(k_x)$ in the upper complex plane.

  $$\Rightarrow \tfrac{1}{2\pi}\int_\infty^\infty \mathrm{d}k_x \mathrm{e}^{irk_x} g(k_x) = i\sum_j \lim_{z\to p_j}\left[(z-\bar{k}_j)f(z)\,\mathrm{e}^{irz}\right] \xrightarrow{r\to\infty} \text{const } \mathrm{e}^{ir\bar{p}}$$

  where $\bar{p}$ is the pole that is closest to the real axis.

  Main contribution to the integral stems from $k_\perp \approx 0$

  $$\Rightarrow \text{ Pole at } t = -\bar{k}_x^2 v(\vec{e}_x) \;\Rightarrow \bar{k}_x = i\sqrt{t/v(\vec{e}_x)} =: i/\xi(\vec{e}_x)$$

  $$\Rightarrow \boxed{G(\vec{r}) \sim \mathrm{e}^{-r/\xi(\vec{e}_{\vec{r}})}} \quad \text{with} \quad \boxed{\xi \sim 1/\sqrt{t}} \qquad \Rightarrow \boxed{\nu = 1/2}$$

3.5.4 Validity of mean-field theory, Ginzburg criterion

3.5.4.1 Compare two methods for determining specific heat

Consider specifically the case $t > 0, \quad t \to 0^+$

Recall Sec. 3.5.3.3: $c_H = \text{const} = 0$
Calculated from $U = -J\sum_{\langle ij\rangle}\langle S_i\rangle\langle S_j\rangle$

Now: Alternative calculation from $U = -J\sum_{\langle ij\rangle}\langle S_i S_j\rangle = -J\sum_{\langle ij\rangle} G_{ij}$
using the results from Sec. 3.5.3.4

$$U = -N\frac{1}{(2\pi)^d}\int_{\substack{\text{1st Brillouin}\\ \text{zone}}} \mathrm{d}^d k \, \frac{1}{1-\beta J\sum_{\vec{\tau}}\cos(\vec{k}\cdot\vec{\tau}))} \, \frac{J}{2}\sum_{\vec{\tau}} \mathrm{e}^{i\vec{k}\cdot\vec{\tau}}$$

Expansion about $k = 0$

$$\approx -\frac{Nk_BT}{2}\frac{1}{(2\pi)^d}\int_\infty \mathrm{d}^d k \, \frac{1-k^2 v(\vec{e}_{\vec{k}})}{t+k^2 v(\vec{e}_{\vec{k}})}$$

$\tilde{k} = \vec{k}/\sqrt{t}, \quad t \to 0^+$

$$\approx -\frac{Nk_BT}{2}\,t^{d/2-1}\,\frac{1}{(2\pi)^d}\int_\infty \mathrm{d}^d\tilde{k}\,\frac{1}{1+v(\vec{e}_{\tilde{k}})} \qquad \propto T\,t^{d/2-1}$$

$$\Rightarrow c_H = \frac{1}{N}\frac{\partial U}{\partial T} \propto T_c\,t^{d/2-2} + T\,t^{d/2-1} \propto t^{d/2-2} \qquad \text{at } t \to 0^+$$

$$\Rightarrow c_H \sim \begin{cases} \text{finite} & \text{for } d > 4 \quad : \text{consistent with Sec. 3.5.3.3} \\ \text{divergent} & \text{for } d < 4 \quad : \underline{\text{not}} \text{ consistent with Sec. 3.5.3.3} \end{cases}$$

⇒ Apparently, mean-field approximation breaks down for dimensions $d < 4$.

⇝ ”Upper critical dimension”

3.5.4.2 Alternative argument: Ginzburg criterion

Mean-field theory neglects correlations.

$\rightsquigarrow$ should be oK, if the fluctuations within the correlation length ξ are small compared to the magnetization!

Consider $V(\xi)$: Volume with diameter ξ

$$\Rightarrow \underbrace{\sum_{V(\xi)}\sum_{V(\xi)}\Big[\langle S_i S_j\rangle - \langle S_i\rangle\langle S_j\rangle\Big]}_{\sum_{i\in V(\xi)}\sum_j G_{ij}\,\sim\,\xi^d\chi} \quad\ll\quad \underbrace{\sum_{V(\xi)}\sum_{V(\xi)}\langle S_i\rangle\langle S_j\rangle}_{\big(\sum_{i\in V(\xi)}\langle S_i\rangle\big)^2\,\sim\,(\xi^d\, m)^2}$$

Note: Here we have used $\sum_{\text{all}j} G_{ij} \approx \sum_{j\in V(\xi)} G_{ij}$ for $G_{ij} = \langle S_i S_j\rangle - \langle S_i\rangle\langle S_j\rangle$
and $\chi = \frac{1}{N\beta^2}\big(\langle(\sum_i S_i)^2\rangle - \langle\sum_i S_i\rangle^2\big) = \frac{1}{\beta^2}\big(\frac{1}{N}\sum_i\big)\sum_j G_{ij}$,
which follows from $\chi = \frac{\partial m}{\partial H} = \frac{1}{N}\frac{\partial}{\partial H}\langle\sum_i S_i\rangle = \frac{1}{N\beta^2}\frac{\partial^2}{\partial H^2}\ln\mathscr{Z}_H$
(example of the relation between fluctations and response functions probably shown in the theory 4 class; else prove it as an exercise).

$$\Rightarrow \frac{\chi}{\xi^d m^2} \ll 1 \qquad \text{with } \xi\sim|t|^{-\nu},\ m\sim|t|^{\beta},\ \gamma\sim|t|^{-\gamma}$$

$$\Rightarrow R\,|t|^{-\gamma+d\nu-2\beta} \ll 1$$

R : System dependent factor (range of interactions etc.)

At the critical point $t\to 0$

$\Rightarrow$ Condition $d\nu-2\beta-\gamma>0$ with $\gamma=1,\ \beta=\nu=1/2$
$\Rightarrow$ Fulfilled for $\frac{d}{2}-2>0 \quad\Rightarrow\quad \boxed{d>4}$

$\rightsquigarrow$ Mean-field approximation captures correct critical behavior at $d>4$.
However: Fails for $t\to 0^+$ at $d\leqslant 4$

3.6 The Monte Carlo method

Problem: Calculate partition functions, statistical expectation values, phase transitions in the Ising model or other "microscopic" models

Looking back: Approaches we have discussed so far

3.3: Exact techniques
$\rightsquigarrow$ Exact solutions for special cases (1D, 2D Ising)

3.4: Series expansions
$\rightsquigarrow$ Also exact, but limited applicability (convergence radius)

3.5: Mean-field approximation
$\rightsquigarrow$ More generally applicable, but uncontrolled approximation

Question: How can one obtain an "exact" solution in the general case?

Answer: Up to now - Only numerically
"Sledgehammer approach":
Calculate $\langle A\rangle = \frac{\sum e^{-\beta\mathscr{H}} A}{\sum e^{-\beta\mathscr{H}}}$ directly for finite systems
But: Use "smart" sledgehammer $\rightsquigarrow$ Monte Carlo Simulations

Very general method
Broad applications in all areas of statistical physics and beyond. Also heavily used in Mainz. Shall therefore be briefly illustrated here at the example of the Ising model. (For more details see class "Computer simulations in statistical physics").

3.6.1 Main idea of Monte Carlo integration

Task: Calculate statistical expectation values $\langle A\rangle = \frac{\sum e^{-\beta\mathscr{H}} A}{\sum e^{-\beta\mathscr{H}}}$

Solution strategies

(a) Exact enumeration : Full Sum over all configurations

Pros: Exact

Cons: very time consuming, only possible for tiny systems
Inefficient at small temperatures, since most configurations don't contribute much to the sum

Way out: Monte Carlo Integration
Sum only over a random sample of configurations, not all!

(b) Simple sampling Entirely random sample (every configuration has equal probability)
(e.g.: Sample $j \leftrightarrow N$ random numbers $r_i^{(j)} \in [0:1]$,

$$S_i^{(j)} = \begin{cases} +1 & : r_i^{(j)} > 1/2 \\ -1 & : r_i^{(j)} < 1/2 \end{cases}$$

Analysis: $\langle A\rangle = \lim_{n\to\infty} \frac{\sum_{j=1}^n A[\{S_i^{(j)}\}] e^{-\beta\mathscr{H}[\{S_i^{(j)}\}]}}{\sum_{j=1}^n A[\{S_i\}] e^{-\beta\mathscr{H}[\{S_i^{(j)}\}]}}$

Pro: Results can already be obtained with small samples
Can be improved systematically by increasing sample size
$\rightsquigarrow$ One is less restricted with respect to system size
Cons: – No longer exact
(however, accuracy can be controlled via sample size)
– Still inefficient at low temperatures

(c) Importance sampling Draw sample according to the distribution $P\{S_i\} \propto \mathrm{e}^{-\beta\mathscr{H}[\{S_i\}]}$

Analysis: $\langle A \rangle = \lim_{n\to\infty} \sum_{j=1}^{n} A[\{S_i^{(j)}]$
Pros: – First results can already be obtained with small samples
Can be improved systematically by increasing sample size (as in (b))
– Efficient: Configurations that contribute to the sum with higher weight are drawn more often
(Cons: Not fully exact, but that's life!)

$\Rightarrow$ Importance sampling seems to be the method of choice, but ...

Question: How generate a sample with a prescribed probability distribution?

Solution: Generate a Markov Chain

- ⋆ Stochastic process without memory defined by
  - – State space (Here: Configuration space $\Gamma = \{S_i\}$
  - – Transition probability $W_{\Gamma\to\Gamma'}$
    $\rightsquigarrow$ generates chain of states $\Gamma_0 \overset{W}{\Longrightarrow} \Gamma_2 \overset{W}{\Longrightarrow} \Gamma_2 \cdots$
    or, respectively, chain of probabilities $P_n(\Gamma)$

  Master equation: $P_{n+1}(\Gamma) = P_n(\Gamma) + \sum_{\Gamma'} \{ \underbrace{W_{\Gamma'\to\Gamma} P_n(\Gamma')}_{\text{flow in}} - \underbrace{W_{\Gamma\to\Gamma'} P_n(\Gamma)}_{\text{flow out}} \}$
- ⋆ For Markov chains with finite state space, one has a central limit theorem (stated without proof)
  If the Markov chain is irreducible, i.e., every state can be reached from every other states (possibly by more than one step), then there exists a unique stationary limit distribution $\bar{P}(\Gamma)$ with $\lim_{n\to\infty} P_n(\Gamma) = \bar{P}(\Gamma)$, independent of the initial distribution $P_0(\Gamma)$
- ⋆ The stationary limit distribution fulfills $\boxed{\sum_{\Gamma'} W_{\Gamma'\to\Gamma} \bar{P}(\Gamma') = \sum_{\Gamma'} W_{\Gamma\to\Gamma'} \bar{P}(\Gamma)}$
- ⋆ $\Rightarrow$ Trick: (Metropolis, Rosenbluth, Teller)
  Construct the transition function $W_{\Gamma\to\Gamma'}$ such that the limit distribution is just the target distribution function. This can be achieved with the following sufficient (but not necessary) conditions:
  (i) irreducible (every state can be reached from every other state)
  (ii) detailed balance $\boxed{\dfrac{W_{\Gamma\to\Gamma'}}{W_{\Gamma'\to\Gamma}} = \dfrac{\bar{P}(\Gamma')}{\bar{P}(\Gamma)}}$

One example of a popular implementation is the Metropolis algorithm

$$W_{\Gamma\to\Gamma'} = N_{\Gamma\Gamma'}\min(1,\frac{\bar{P}(\Gamma)}{\bar{P}(\Gamma')}) \quad \text{with } N_{\Gamma\Gamma'} = N_{\Gamma'\Gamma}$$

⋆ In particular, to obtain the Boltzmann distribution, one requires

$$\frac{W_{\Gamma\to\Gamma'}}{W_{\Gamma'\to\Gamma}} = \mathrm{e}^{-\beta(\mathscr{H}(\Gamma)-\mathscr{H}(\Gamma'))} = \mathrm{e}^{-\beta\Delta E}$$

which in the Metropolis algorithm results in

$$W_{\Gamma\to\Gamma'} = N_{\Gamma\Gamma'}\min(1,\mathrm{e}^{-\beta\Delta E}) \quad \text{with } N_{\Gamma\Gamma'} = N_{\Gamma'\Gamma}$$

Remarks:

- The Metropolis algorithm is the most popular algorithm, but every other algorithm works too, as long as it fulfills the conditions (i) and (ii) or, instead of (ii), at least the condition of "global balance" $\sum_{\Gamma'} W_{\Gamma'\to\Gamma}\bar{P}(\Gamma') = \sum_{\Gamma} W_{\Gamma\to\Gamma'}\bar{P}(\Gamma)$
- It is not strictly necessary to target the Boltzmann distribution in the Markov chain (i.e., choose $\bar{P}(\Gamma) \sim \mathrm{e}^{-\beta\mathscr{H}}$. In some cases, it may be more convenient to choose another target distributions and then "reweight" the data when calculating the expectation values.
  (⇝ "Reweighting" methods such as "multicanonical" sampling, "Wang/Landau" sampling, "Metadynamics" etc.)

3.6.2 Examples of Monte Carlo algorithms

3.6.2.1 Simple "Single Flip" Metropolis algorithm

Algorithm

(0) Initial configuration $\Gamma = \{S_i\}$

↓

(i) Choose randomly a spin site j

↓

(ii) Calculate energy difference ΔE between configuration Γ and a configuration Γ^* where $S_j \to -S_j$
(2D cubic: $\Delta E = 0, \pm 2J, \pm 4J$)

↓

(iii) Pick a random number $r \in [0:1]$

↓

(iv) Adopt $\Gamma' = \Gamma^*$ if $r < \mathrm{e}^{-\beta\Delta E}$, otherwise keep $\Gamma' = \Gamma$

↓

(v) New configuration Γ'

↑

Remarks:

– Similar algorithms can be designed easily also for other systems.

– Close to the critical point, spin clusters become very large
⇝ Dynamics become very slow (critical slowing down)
⇝ Sampling becomes inefficient!

3.6.2.2 Ising model: Cluster algorithm (Wolff algorithm)

Algorithm

(0) Initial configuration Γ

$\downarrow$

(i) Choose randomly a spin site j

$\downarrow$

(ii) Identify neighbors k of j with same spin direction $S_k = S_j$
and bonds (jk) that connect them

$\downarrow$

(iii) Assign bond variables u_{jk} to these bonds,
choosing $u_{ij} = -1$ with probability $\mathrm{e}^{-2\beta J}$.
Spins connected by bonds with $u_{ij} = 1$ form a "cluster"

$\downarrow$

(iv) Identify neighbors of cluster with the same spin value.
Assign bond variables to unoccupied connecting bonds.
Extend cluster accordingly.

$\downarrow$

(v) Continue until cluster can no longer grow.

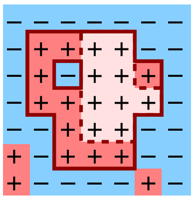
$\downarrow$

(vi) Change sign of <u>all</u> spins in the cluster ($S_k \to -S_k$)

$\downarrow$

(vi) New configuration Γ'

Proof that this algorithm fulfills detailed balance



Γ, Γ': Configurations, in which light pink cluster
contains spins $+1$ or -1, respectively
Cluster is bounded by the countour $L = l^+ + l^-$
with l^+: Boundary to spins $+1$ (dashed line)
l^-: Boundary to spins -1 (solid line)

Transition $\Gamma \to \Gamma'$: Energy difference $\Delta E = 2J(l^+ - l^-)$

$$W_{\Gamma\to\Gamma'} = \underbrace{W_{\text{inside}}}_{\substack{\text{Probability of having}\\ \text{selected pink cluster}}} \cdot \underbrace{\mathrm{e}^{-2\beta J l^+}}_{\substack{\text{Probability that cluster}\\ \text{does not grow further}}}$$

$$W_{\Gamma'\to\Gamma} = \overbrace{W_{\text{inside}}} \cdot \overbrace{\mathrm{e}^{-2\beta J l^-}}$$

$$\Rightarrow\ W_{\Gamma\to\Gamma'} \Big/ W_{\Gamma'\to\Gamma} = \mathrm{e}^{-2\beta J(l^+ - l^-)} = \mathrm{e}^{-2\beta\Delta E} \quad \checkmark$$

Remark: Global dynamics, totally 'unrealistic',
but correlations break up much faster. $\rightsquigarrow$ more efficient sampling!

3.6.3 ”Problems” with the Monte Carlo method

If one could invest an infinite amount of computing time, the Monte Carlo method would be exact, on principle. Nevertheless, one has to apply caution when analyzing the data.

- ⋆ In fact, the computing time is never infinite
  $\rightsquigarrow$ Statistical error
- ⋆ The systems have finite sie
  $\rightsquigarrow$ Systematic error

  Causes problems in particular in the vicinity of critical points, where the corrrelation length diverges.

  Way out: Finite size scaling (Chapter 5)
- ⋆ When using importance sampling, the entropy and free energy cannot be calculated directly. (NB: Similar to experiments: Only observables can be calculated!)

  $\rightsquigarrow$ Special methods must be developed, e.g., ”thermodynamic integration”, determination of free energy differences from histograms etc.
  (See textbooks on simulation methods)

Chapter 4

The Ginzburg-Landau Theory

Recall Chapter 3:

- Extensive discussion of the Ising model as one of the simplest "microscopic" models with a phase transition
- Introduction of several methods than can also be applied to other systems (e.g., transfer matrix method, series expansions, mean-field approximation, Monte Carlo simulations, others like renormalization will follow).
- Still, the Ising model is rather very special. It is not clear, to which extent our findings can be generalized to phase transitions in general.

In this chapter: General approach, based on symmetry considerations, which highlights the relation between phase transitions "of same type". The derivation is based on a mean-field point of view, but this can be relieved later on.

Ginzburg-Landau theories are popular starting point for developing field theories in statistical physics.

4.1 Landau expansion for scalar order parameter

4.1.1 Ising symmetry

Recall: Bragg-Williams approximation for Ising model

Close to $T = T_c$, $m = M/N$ is small $\Rightarrow$ expand in powers of m.

$$\Rightarrow \frac{F}{N} = -\frac{1}{\beta_c} m^2 + \frac{1}{\beta}\Big[\tfrac{1+m}{2}\ln(\tfrac{1+m}{2}) + \tfrac{1-m}{2}\ln(\tfrac{1-m}{2})\Big]$$
$$\approx -\frac{1}{\beta}\ln 2 + \frac{1}{2\beta_c}\big[\tfrac{\beta_c}{\beta} - 1\big]\, m^2 + \frac{1}{12\beta} m^4 + \cdots$$

The same form can already be inferred from general symmetry considerations

Requirement: $\frac{F}{N} = f(m)$ symmetric with respect to $m \leftrightarrow (-m)$.

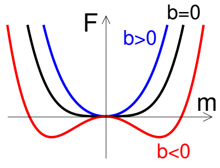
$$\Rightarrow \quad \boxed{\frac{F}{N} = a(T) + \frac{1}{2} b(T)\, m^2 + \frac{1}{4} c(T)\, m^4 + \frac{1}{6} d(T)\, m^6 + \cdots}$$

$\rightsquigarrow$ Landau expansion: Generally valid for systems with this symmetry!

Remark and Caveat: Strictly speaking, the expansion in powers of m is only allowed if F/N is analytic as a function of m. At phase transition points, this is not valid in the thermodynamic limit. Therefore, the Landau Ansatz represents an approximation and cannot be exact.

(Way out: Corresponding expansion for small subsystems
$\rightsquigarrow$ Ginzburg-Landau theory)

4.1.1.1 Case $c(T) > 0$



In that case, neglect $d(T)$

$\rightsquigarrow$ Graphical representation (vary b at fixed $c > 0$):

$\rightsquigarrow$ Continuous phase transition at $\boxed{b = 0}$

In the vicinity of T_c, one approximates $\boxed{b(T) = b_0\,(T - T_c)}$

Order parameter: $\frac{\partial F}{\partial m} = bm + cm^3 \overset{!}{=} 0$

$$\Rightarrow\ m = \pm\sqrt{b_0/c}\,\sqrt{T_c - T} \quad (T < T_c)$$

$\Rightarrow\ m \sim (T_c - T)^{\beta}$ with critical exponent $\boxed{\beta = 1/2}$ as in Section 3.5

Specific heat c_H:

$$\frac{S}{N} = -\frac{1}{N}\frac{\partial F}{\partial T} = -a'(T) - \tfrac{1}{2}b'(T)\,m^2 - \tfrac{1}{4}c'(T)\,m^4 - \tfrac{1}{2}b(T)(m^2)' - \tfrac{1}{4}c(T)(m^4)'$$

$$c_H = \frac{T}{N}\frac{\partial S}{\partial T}$$

For $T \to T_c:\ b = 0,\ b' = b_0,\ m^2 = \frac{b_0}{c}(T_c - T) \to 0$ or $m^2 \equiv 0$

$(m^2)' = -\frac{b_0}{c}$ or 0, $(m^4)' = 0$, $(m^4)'' = 2(\frac{b_0}{c})^2$ or 0

$$\Rightarrow c_H = -Ta'' - Tb'\,(m^2)' - T\tfrac{c}{4}\,(m^4)'' = \begin{cases} -Ta'' + T\frac{b_0^2}{2c} & : T < T_c \\ -Ta'' & : T > T_c \end{cases}$$

$\rightsquigarrow$ Finite jump!

$\Rightarrow$ "$c_H \sim |T - T_c|^{\alpha}$" with Critical exponent $\boxed{\alpha = 0}$ as in Section 3.5

Other exponents also the same as in Section 3.5

Reason: Results from the analytic expansion of F/N in powers of m. $\Rightarrow$ characteristic for mean-field exponents!

4.1.1.2 Case $c(T) < 0$

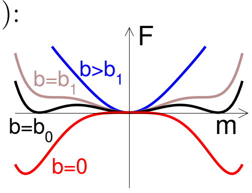
If $c(T) < 0$, $d(T)$ cannot be neglected. Assume $d(T) > 0$

$\rightsquigarrow$ Graphical representation (vary b at fixed $c < 0, d > 0$):

$b_1 = \frac{c^2}{4d}$: External minima form

$b_0 = \frac{3c^2}{16d}$: First order phase transition
(with $m_0^2 = 3|c|/4d$)

$b = 0$: Middle minimum at $m = 0$ disappears



Spinodals:

At $b \in [0 : b_0]$: metastable disordered states, "undercooling" is possible.

$b \in [b_0 : b_1]$: metastable ordered states, "overheating" is possible.

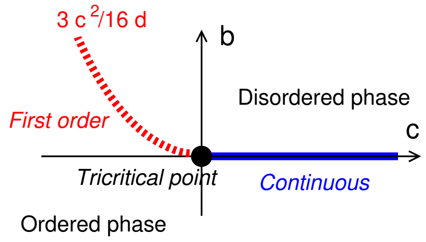
The spinodals $b = b_0$, $b = b_1$ mark the points where metastable states become unstable.

Example: M_nO, antiferromagnet
Before b changes sign, one already has a first order phase transition

4.1.1.3 Special case $b = c = 0$

$\rightsquigarrow$ Tricritical point

”Phase diagram” in the vicinity



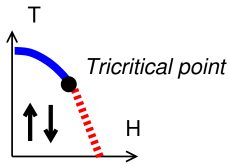
Practical relevance

If one has two intensive quantities that do not directly couple to the order parameter, a tricritical point may occur.

Example: Uniaxial antiferromagnet in a magnetic field

$b = b(T, H)$, $c = c(T, H)$

Possible phase diagram:



4.1.2 No Ising symmetry

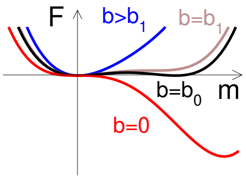
Example: Liquid-gas transition, liquid crystals,

Consider cases, where free energy F does not have to be symmetric with respect to an exchange $m \leftrightarrow -m$

Known: $\frac{F}{N} \to \infty$ for large $|m|$ $\Rightarrow$ At least one turning point $\bar{m}$ in between. Choose m axis such that $\bar{m} = 0$, hence $F'(\bar{m}) = 0$.

$$\rightsquigarrow \quad \boxed{\frac{F}{N} = a(T) + \frac{1}{2}b(T)\, m^2 - \frac{1}{3}c(T)\, m^3 + \frac{1}{4}d(T)\, m^4 + \cdots}$$

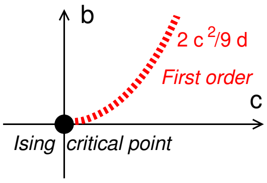
$b = b_1 = \frac{c^2}{4d}$: Second minimum forms
$b = b_0 = \frac{2c^2}{9d}$: First order phase transition
(with $m_0 = 2c/3d$)
$b = 0$: First minimum disappears



$\rightsquigarrow$ Similar scenario as in Ising symmetric case 4.1.1.2
– First order phase transition,
– Spinodals at $b = 0$ and $b = b_1$,
– Metastable states in between

Conclusion: If Landau expansion contains a third order cubic term due to lack of symmetry, then the transition is first order!

NB: Consider as an example the liquid-gas transition.
Generically first order → consistent with argument!
Special point: $b = c = 0$: If one has two control parameters $(T,\ P)$, a point (P_c, T_c) with $c(T_c, P_c) = b(T_c, P_c) = 0$ may exist. Here, the transition is continuous and Ising like!



4.2 Landau theory in systems with multicomponent order parameter

In this section, some examples are given how to construct Landau expansions from symmetry arguments for more complex systems with multicomponent order parameter.

4.2.1 Heisenberg model

System: Three dimensional spins on a lattice,
Interact with "Hamiltonian" $\mathscr{H} = -J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j$

→ Invariant under simultaneous rotation of all spins $\vec{S}_i$

→ Invariants: $\vec{m}^2,\ (\vec{m}^2)^2,\ \cdots$
where $\vec{m} = \langle \vec{S} \rangle$: Order parameter per site

⇒ Landau expansion: $\frac{F}{N} = a + \frac{1}{2} b\, \vec{m}^2 + \frac{1}{4} c (\vec{m}^2)^2$

4.2.2 Heisenberg model with cubic anisotropy

Example: A real magnetic system on a cubic lattice.
Spins preferably orient along the main lattice directions.

Symmetry: $m_\alpha \leftrightarrow -m_\beta$ for all pairs (α, β)

→ Invariants: $\vec{m}^2,\ (\vec{m}^2)^2,\ (m_x^4 + m_y^4 + m_z^4)$

⇒ Landau expansion: $\frac{F}{N} = a + \frac{1}{2} b\, \vec{m}^2 + \frac{1}{4} c (\vec{m}^2)^2 + \frac{1}{4} d\, (m_x^4 + m_y^4 + m_z^4)$

4.2.3 Three component order parameter with uniaxial anisotropy

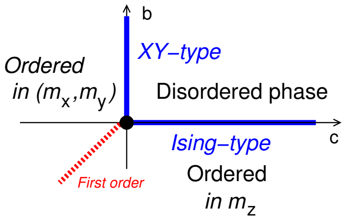
Symmetries: $m_z \leftrightarrow -m_z$ (m_x, m_y) invariant under (2D) rotation

→ Invariants: $m_z^2,\ m_x^2 + m_y^2,\ m_z^4,\ (m_x^2 + m_y^2)^2,\ m_z^2(m_x^2 + m_y^2)$

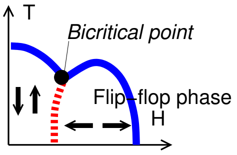
$$\Rightarrow \frac{F}{N} = a + \frac{1}{2} b\, m_z^2 + \frac{1}{2} c\, (m_x^2 + m_y^2) + \frac{1}{4} d\, m_z^4 + \frac{1}{4} e\, (m_x^2 + m_y^2)^2 + \frac{1}{4} f\, m_z^2 (m_x^2 + m_y^2)$$

Discussion:

$b = 0,\ c > 0$: Ising-type transition
$c = 0,\ b > 0$: "XY"-symmetry
(m_x, m_y) order
$b = c = 0$: Ising- and XY-lines meet:
Bicritical point
$b < c < 0$: Different types of order compete
⇝ First order phase transition

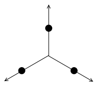


Example: Antiferromagnet with weak uniaxial anisotropy in a homogeneous external magnetic field H



4.2.4 Two component order parameter with trigonal symmetry

Symmetry: Invariance under a rotation of $2\pi/3$



Examples: Some adsorbate systems

Three-state Potts model:

$\mathscr{H} = -J\sum_{\langle ij\rangle}\delta_{q_i,q_j}$ with $q_i = 1, 2, 3$.

Possible way to determine invariants:

Rotation by $2\pi/3 \;\widehat{=}\;$ rotation matrix $\mathscr{D} = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$

For any $f(\vec{m})$, the function $g(\vec{m}) = f(\vec{m}) + f(\mathscr{D}\vec{m}) + f(\mathscr{D}^2\vec{m})$ is invariant.

Apply this to polynomials $f(\vec{m})$ to get invariants of ...

$$\begin{array}{lll} \text{2nd order:} & f(\vec{m}) = m_x^2,\ m_y^2 & \rightarrow\ g(\vec{m}) \propto m_x^2 + m_y^2 \\ & f(\vec{m}) = m_x\, m_y & \rightarrow\ g(\vec{m}) = 0 \text{ (trivial)} \\[1em] \text{3d order:} & f(\vec{m}) = m_x^3,\ m_x\, m_y^2 & \rightarrow\ g(\vec{m}) \propto m_y(3m_x^2 - m_y^2) \\ & f(\vec{m}) = m_y^3,\ m_y\, m_x^2 & \rightarrow\ g(\vec{m}) \propto m_x(3m_y^2 - m_x^2) \\[1em] \text{4th order:} & f(\vec{m}) = m_x^4,\ m_y^4,\ m_x^2\, m_y^2 & \rightarrow\ g(\vec{m}) \propto (m_x^2 + m_y^2)^2 \\ & f(\vec{m}) = m_x\, m_y^2,\ m_y\, m_x^2 & \rightarrow\ g(\vec{m}) = 0 \end{array}$$

$$\Rightarrow \frac{F}{N} = a + \frac{1}{2}b(m_x^2 + m_y^2) + \frac{1}{3}cm_x(m_x^2 - 3m_y^2) + \frac{1}{3}dm_y(m_y^2 - 3m_x^2) + \frac{1}{4}e(m_x^2 + m_y^2)^2$$

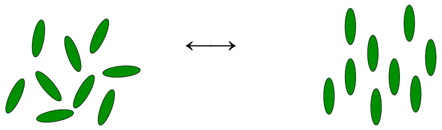
Remarks:

- Cubic term ⇝ phase transition is first order!
- Six-fold symmetry: Trigonal symmetry and mirror symmetry ⇝ Cubic term disappears, phase transition may be continuous
- Exception: 3-State Potts model in two dimensions: Trigonal symmetry, but nevertheless continuous transition due to fluctuations !

  (So this may occasionally happen, but as a rule, phase transitions in systems with trigonal symmetry should be first order! For example, the phase transition in the 3-state Potts model in higher dimensions is first order)

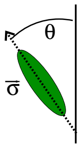
4.2.5 Liquid crystals

Example of a more complex order parameter
Orientational order, but no positional order



Isotropic phase ⟷ Nematic phase

Order parameter:



- Assume, there exists one preferred orientation
  $\rightsquigarrow$ Suitable order parameter is $S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$:
  Disordered fluid: $\langle \cos^2\theta\rangle = 1/3 \quad \rightarrow \quad S = 0$
  Ordered fluid: $\langle \cos^2\theta\rangle = 1 \quad \rightarrow \quad S = 1$
- No preferred orientation $\rightsquigarrow$ Natural generalization
  Tensor: $Q_{\alpha\beta} = \frac{1}{2}\langle \sigma_\alpha\sigma_\beta - \delta_{\alpha\beta}\rangle$
  where $\vec{\sigma}_i$ points along the main axis of molecule i
  Note: Q is symmetric with $\mathrm{Tr}(Q) = 0$.

Landau expansion

- With preferred orientation: "Maier-Saupé model"
  $\frac{F}{N} = a + \frac{1}{2}bS^2 + \frac{1}{3}cS^3 + \frac{1}{4}dS^4 + \cdots$
  Due to the cubic term, the phase transition is first order.
- Without preferred orientation:
  Invariants under rotation: $\mathrm{Tr}(Q^2),\ \mathrm{Tr}(Q^3),\ \mathrm{Tr}(Q^4) = \frac{1}{2}(\mathrm{Tr}(Q^2))^2$.
  (Last identity holds because Q is symmetric and traceless)
  $\Rightarrow \quad \frac{F}{N} = a + \frac{1}{2}b\ \mathrm{Tr}(Q^2) + \frac{1}{3}c\ \mathrm{Tr}(Q^3) + \frac{1}{4}d\ \mathrm{Tr}(Q^4)$
  $\rightsquigarrow$ Again first order transition due to cubic term!

4.3 Ginzburg-Landau theory

Extension of Landau theory for inhomogeneous systems
Here: Discuss only systems with one-component order parameter

4.3.1 Ansatz

Homogeneous system $\rightsquigarrow$ Landau expansion
Different from previous section: Normalize with $1/V$ instead of $1/N$, i.e., $m = M/V$, $f := F/V$ etc. Expansion still has the same form.
$\Rightarrow \quad F/V = a + \frac{1}{2}b\,m^2 + \frac{1}{4}c\,m^4 - h\,m$

Inhomogeneous system $\rightsquigarrow$ Search for generalization

Naïve Ansatz: $F = \int \mathrm{d}^d r\, f(m(\vec{r}))$ with $f(m) = a + \frac{1}{2}b\,m^2 + \frac{1}{4}c\,m^4 - h\,m$
Problematic, since the order parameter profile has no "stiffness", i.e., it adjusts instantaneously to $h(\vec{r})$
$\rightsquigarrow$ Spatial variations of $m(\vec{r})$ should be penalized

New Ansatz: $$\boxed{\mathscr{F}[m(\vec{r})] = \int \mathrm{d}^d r\, \left(f(m) + \frac{1}{2}g\,(\nabla m)^2\right)}$$

Corresponds to lowest order expansion in m and ∇m, taking into account the symmetry $m \leftrightarrow (-m)$ and cubic symmetry in space!

4.3.2 Interpretation

Question: What is the meaning of $\mathscr{F}[m(\vec{r})]$? What does it describe?

(a) Not the free energy

- Not necessarily convex
- The free energy is a thermodynamic potential. It cannot depend on a microscopic order parameter field $m(\vec{r})$: Microscopic degrees of freedom must be integrated out!

Instead: A functional (a function from function space to $\mathbb{R}$), where the partition function has been partially evaluated (but not fully)!

(b) "Derivation" of the Ginzburg-Landau functional

(Not a rigorous derivation, rather a description of the object that $\mathscr{F}[m(\vec{r})]$ is supposed to represent)

Starting point, e.g., Ising model

Discrete spins S_i

"Coarse-graining": Averaging over blocks of size l_0, where l_0 has roughly the size of the correlation length far from T_c (but: chosen fixed, independent of T, not singular)

Slowly varying order parameter $m(\vec{r})$

No longer fluctuates on the scale of the lattice constant.
Fourier components with $k > 1/l_0$ have been integrated out.

Important: Block size l_0 must be chosen with care

Too large ⇝ uncorrelated blocks, can be equilibrated independent of each other, nothing gained!

Too small ⇝ correlations too strong and nonlocal, defining a "local" quantity $m(\vec{r})$ does not make sense!

Formal description: partial trace

Define $m(\vec{r})$: Average over block $v_{\vec{r}}$: $\quad m(\vec{r}) = \frac{1}{v_{\vec{r}}} \sum_{\vec{r}} S_i$

Now assume that $m(\vec{r})$ be given, then we have

$$\exp\Big(- \beta \mathscr{F}[m(\vec{r})]\Big) \overset{!}{=} \sum_{\{S_i\}} \mathrm{e}^{-\beta \mathscr{H}\{S_i\}} \prod_{\vec{r}} \delta\Big(\frac{1}{v_{\vec{r}}} \sum_{v_{\vec{r}}} S_i - m(\vec{r})\Big)$$

⇝ Calculate trace over all configurations which would yield the order parameter landscape $m(\vec{r})$ upon coarse-graining.

$\Rightarrow \quad \mathscr{F}[m(\vec{r})]$ has both energetic and entropic contributions!

Full Partition function:

$$\mathscr{Z} = \int \mathscr{D}[m(\vec{r})]\, \mathrm{e}^{-\beta \mathscr{F}[m(\vec{r})]} = \mathrm{e}^{-\beta F}$$

⇝ Functional integral over all smoothly varying functions!

(c) Comparison with density functional (for the experts)

Construction of density functional $\tilde F[\overline{m}(\vec r)]$

- Definition of a microscopic order parameter field $m(\vec r)$,
  e.g. as in (b): $m(\vec r) = \frac{1}{v_{\vec r}} \sum_{\vec r} S_i$
- Introduction of a conjugate field $h(\vec r)$ that couples to $m(\vec r)$
  $\Rightarrow$ Modified "Hamiltonian" $\tilde{\mathscr{H}}[h] = \mathscr{H} - \int \mathrm{d}^d r\, m(\vec r)\, h(\vec r)$
  $\rightsquigarrow$ Thermodynamic potential: $\tilde G[h(\vec r)] = -k_B T \ln\Big(\sum_{\{S_i\}} \mathrm{e}^{-\beta \tilde{\mathscr{H}}[h]}\Big)$
  $\overline{m}(\vec r) := \langle m(\vec r)\rangle = \frac{1}{\beta}\frac{\delta \tilde{\mathscr{G}}}{\delta h(\vec r)}$ is almost always a unique function of $h(\vec r)$
- Legendre transform: $\tilde F[\overline{m}(\vec r)] = \tilde G[h(\vec r)] - \int \mathrm{d}^d r\, \overline{m}(\vec r)\, h(\vec r)$

Then we have (exactly): $F|_{h\equiv 0} = \min_{\{\overline{m}(\vec r)\}} \tilde F[\overline{m}(\vec r)]$ (since $\frac{\partial \tilde F}{\partial \overline{m}} = h = 0$)

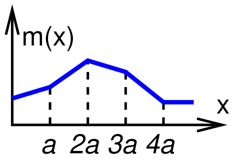
But: $\tilde F[\overline{m}(\vec r)]$ and $\mathscr{F}[m(\vec r)]$ are not the same functional!
In particular, $\tilde F[\overline{m}(\vec r)]$ is generally nonlocal!
Moreover, $\overline{m}(\vec r)$ (average local order parameter) does not refer to the same field as $m(\vec r)$ (actual microscopic local order parameter)!

4.3.3 Brief digression: Dealing with functionals

I) Functional integral

$$\int \mathscr{D}[m(\vec r)]\cdots = \lim_{\substack{a\to 0\\ \text{lattice constant}}} \Big[\prod_{\vec r}\int_{-\infty}^{\infty} \mathrm{d}m_{\vec r}\Big]\cdots$$

e.g., in one dimension:
$\int \mathscr{D}[m(x)]\cdots = \int \mathrm{d}m_0\, \mathrm{d}m_a\, \mathrm{d}m_{2a}\cdots$
$\rightarrow$ Path integral



II) Functional derivatives

Definition:
$$\frac{\delta \mathscr{F}[m(\vec r)]}{\delta m(\vec r\,')} = \lim_{\epsilon\to 0^+}\frac{1}{\epsilon}\Big[\mathscr{F}[m(\vec r) + \epsilon\,\delta(\vec r - \vec r\,')] - \mathscr{F}[m(\vec r)]\Big]$$

Examples:

- $\mathscr{F}[m(x)] = \int \mathrm{d}x\, f(m(x))$

$$\Rightarrow \frac{\delta\mathscr{F}}{\delta m(y)} = \lim_{\epsilon\to 0}\frac{1}{\epsilon}\Big[\int \mathrm{d}x\,\big(f(m(x)+\epsilon\,\delta(x-y)) - f(m(x))\big)\Big]$$
$$\overset{\text{Taylor}}{=} \lim_{\epsilon\to 0}\frac{1}{\epsilon}\Big[\int \mathrm{d}x\,\big(f(m(x)) + \epsilon\,\delta(x-y)\, f'(m(x)) - f(m(x))\big)\Big]$$
$$= \int \mathrm{d}x\, \delta(x-y)\, f'(m(x)) = f'(m(y))$$

- $\mathscr{F}[m(x)] = \int \mathrm{d}x\, \big(\frac{\mathrm{d}}{\mathrm{d}x} m(x)\big)^2$

$$\Rightarrow \frac{\delta\mathscr{F}}{\delta m(y)} = \lim_{\epsilon\to 0}\frac{1}{\epsilon}\Big[\int \mathrm{d}x\Big(\Big(\tfrac{\mathrm{d}}{\mathrm{d}x}\big(m(x)+\epsilon\delta(x-y)\big)\Big)^2 - \big(\tfrac{\mathrm{d}}{\mathrm{d}x}m(x)\big)^2\Big)\Big]$$
$$= 2\int \mathrm{d}x\big(\tfrac{\mathrm{d}}{\mathrm{d}x}m(x)\big)\big(\tfrac{\mathrm{d}}{\mathrm{d}x}\delta(x-y)\big)$$
$$\overset{\substack{\text{partial}\\ \text{integration}}}{=} -2\int \mathrm{d}x\,\delta(x-y)\,\tfrac{\mathrm{d}^2}{\mathrm{d}x^2}m(x) = -2\tfrac{\mathrm{d}^2}{\mathrm{d}x^2}m(x)\Big|_{x=y}$$

Rules: $\dfrac{\delta}{\delta m(\vec{r}')} \displaystyle\int \mathrm{d}^d r \, m(\vec{r}) = 1$

$\dfrac{\delta}{\delta m(\vec{r}')} \, m(\vec{r}) = \delta(\vec{r} - \vec{r}')$

$\dfrac{\delta}{\delta m(\vec{r}')} \, \dfrac{1}{2} \displaystyle\int \mathrm{d}^d r \, (\nabla \, m(\vec{r}))^2 = -\Delta m$

Product rule, chain rule, etc.

III) Functional derivatives in the Ginzburg-Landau theory

Construct "Generating functional"

$$\boxed{\mathscr{Z}[h(\vec{r})] = \int \mathscr{D}[m(\vec{r})] \, \mathrm{e}^{-\beta\left[\mathscr{F}_0[m(\vec{r}] - \int \mathrm{d}^d r \, h(\vec{r}) \, m(\vec{r}) \, \right]} =: \mathrm{e}^{-\beta F[h(\vec{r})]}}$$

$\Rightarrow$ Order parameter: $\langle m(\vec{r}) \rangle = \big(- \frac{\delta F}{\delta h(\vec{r})} \big)_{h(\vec{r}) \to 0^+}$

"Local" susceptibility: (meaning will become clear later)

$$\chi(\vec{r}, \vec{r}') = \big[\tfrac{\delta \langle m(\vec{r}) \rangle}{\delta h(\vec{r}')}\big]_{h \to 0^+} = - \frac{\delta^2 F}{\delta h(\vec{r}) \delta h(\vec{r}')}\Big|_{h \to 0^+}$$
$$= \cdots = \beta \, \big(\langle m(\vec{r}) m(\vec{r}') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}') \rangle \big)_{h \to 0^+}$$

Same in Fourier space with $m(\vec{k}) = \int \mathrm{d}^d r \, \mathrm{e}^{i\vec{k}\cdot\vec{r}} m(\vec{r})$

$$\mathscr{Z}[h(\vec{k})] = \int \mathscr{D}[m(\vec{k})] \, \mathrm{e}^{-\beta\left[\mathscr{F}_0[m(\vec{k}] - \frac{1}{(2\pi)^d} \int \mathrm{d}^d k \, h(-\vec{k}) \, m(\vec{k}) \, \right]} \equiv \mathrm{e}^{-\beta F[h(\vec{k})]}$$

$\Rightarrow$ Order parameter: $\langle m(\vec{k}) \rangle = - \frac{1}{(2\pi)^d} \frac{\delta F}{\delta h(-\vec{k})}\Big|_{h \to 0^+}$

Susceptibility:

$$\chi(\vec{k}, \vec{k}') = \big[\tfrac{\delta \langle m(\vec{k}) \rangle}{\delta h(\vec{k}')}\big]_{h \to 0^+}$$
$$= \frac{\beta}{(2\pi)^d} \, \big(\langle m(\vec{k}) m(-\vec{k}') \rangle - \langle m(\vec{k}) \rangle \langle m(-\vec{k}') \rangle \big)_{h \to 0^+}$$
$$= \frac{1}{(2\pi)^d} \int \mathrm{d}^d r \, \mathrm{d}^d r' \, \mathrm{e}^{i\vec{k}\cdot\vec{r} - \vec{k}'\cdot\vec{r}'} \chi(\vec{r}, \vec{r}')$$

Specifically, if $\chi(\vec{r}, \vec{r}') = \tilde{\chi}(\vec{r} - \vec{r}')$ (homogeneous system):

$\Rightarrow \; \chi(\vec{k}, \vec{k}') = \tilde{\chi}(\vec{k}) \, \delta(\vec{k} - \vec{k}') \frac{(2\pi)^d}{V}$ (NB: $\delta(0) = \frac{V}{(2\pi)^d}$)

with $\tilde{\chi}(\vec{k}) = \chi(\vec{k}, \vec{k}) = \frac{V}{(2\pi)^d} \int \mathrm{d}^d r \mathrm{e}^{i\vec{k}\cdot\vec{r}} \tilde{\chi}(\vec{r})$

NB: Relation to global susceptibility $\chi = \frac{\partial \bar{m}}{\partial H}$:

Choose $h(\vec{r}) \equiv H = \text{const.}$, $\bar{m} = \frac{1}{V} \int \mathrm{d}^d r \, m(\vec{r})$

$$\Rightarrow \; \chi = \frac{1}{V} \int \mathrm{d}^d r \int \mathrm{d}^d r' \, \underbrace{\frac{\delta m(\vec{r})}{\delta h(\vec{r}')}}_{\chi(\vec{r},\vec{r}')} \, \underbrace{\frac{\partial h(\vec{r}')}{\partial H}}_{1} = \int \mathrm{d}^d r \, \tilde{\chi}(\vec{r}) = \tilde{\chi}(\vec{k} = 0) \, \frac{(2\pi)^d}{V}$$
$$= \cdots = \frac{\beta}{V} \big(\langle M^2 \rangle - \langle M \rangle^2 \big) \quad \text{with} \quad M = \int \mathrm{d}^d r \, m(\vec{r}).$$

4.3.4 Mean-field approximation and transition to the Landau theory

Preliminary remark: If the functional $\mathscr{F}[m(\vec{r})]$ were known, the expression for the partition function would be exact: $\mathscr{Z} = \int \mathscr{D}[m(\vec{r})] \mathrm{e}^{-\beta \mathscr{F}[m(\vec{r})]}$

(a) Mean-field approximation

Ansatz: Main contribution to the integral $\mathscr{Z} = \int \mathscr{D}[m(\vec{r})] \mathrm{e}^{-\beta \mathscr{F}[m]} =: \mathrm{e}^{-\beta F}$
comes from the minimum of $\mathscr{F}$ $\Rightarrow$ $F = \min\limits_{\{m(\vec{r})\}} \mathscr{F}[m(\vec{r})]$

Specifically: Consider $\mathscr{F}[m(\vec{r})] = \int \mathrm{d}^d r \left[\frac{1}{2} g (\nabla m)^2 + f(m) - h(\vec{r})\, m(\vec{r})\right]$
Minimum $\frac{\delta F}{\delta m} \equiv 0 \;\Rightarrow\; -g \Delta m + f'(m) - h = 0$
Homogeneous system in the bulk ($h(\vec{r}) \equiv 0$, free boundaries)
$\rightsquigarrow$ $m(\vec{r}) \equiv \bar{m} = \text{const.},\; f'(\bar{m}) = 0,\; F = V f(\bar{m})$
$\rightsquigarrow$ Effectively a Landau theory

(Specifically: $f(m) = \frac{1}{2} b m^2 + \frac{c}{4} m^4 \;\Rightarrow\; \bar{m} = \left\{ \begin{array}{cl} 0 & : b > 0 \\ \pm\sqrt{|b|/c} =: \pm m_0 & : b < 0 \end{array} \right.$)

But: Ginzburg-Landau theory also allows to calculate mean-field profiles $m(\vec{r})$ in inhomogeneous systems! (see Sec. 4.3.6)

(b) Next step: Gaussian approximation

"Saddle point integration":

Main contribution to the integral $\mathscr{Z} = \int \mathscr{D}[m(\vec{r})] \mathrm{e}^{-\beta \mathscr{F}[m]} = \mathrm{e}^{-\beta F}$ stems from the minimum of $\mathscr{F}$ and small fluctuations around the minimum

Given $\mathscr{F}[m(\vec{r})] = \text{min. for } m(\vec{r}) = \bar{m}(\vec{r})$
$\rightsquigarrow$ Consider $m(\vec{r}) = \bar{m}(\vec{r}) + \eta(\vec{r})$, assume η is small,
expand $\mathscr{F}[\bar{m} + \eta]$ up to second order in η

$$\Rightarrow \mathscr{F}[m(\vec{r})] = \mathscr{F}[\bar{m}(\vec{r})] + \int \mathrm{d}^d r \underbrace{\left.\frac{\delta \mathscr{F}}{\delta m(\vec{r})}\right|_{\bar{m}}}_{0:\bar{m} \text{ minimizes } \mathscr{F}} \eta(\vec{r}) + \frac{1}{2} \int \mathrm{d}^d r \mathrm{d}^d r' \left.\frac{\delta^2 \mathscr{F}}{\delta m(\vec{r}) \delta m(\vec{r}')}\right|_{\bar{m}} \eta(\vec{r}) \eta(\vec{r}')$$

$$\Rightarrow \mathscr{Z} = \mathrm{e}^{-\beta \mathscr{F}_{\min}} \underbrace{\int \mathscr{D}[\eta(\vec{r})]\, \mathrm{e}^{-\frac{\beta}{2} \int \mathrm{d}^d r\, \mathrm{d}^d r' \left.\frac{\delta^2 \mathscr{F}}{\delta m(\vec{r})\, \delta m(\vec{r}')}\right|_{\bar{m}} \eta(\vec{r})\, \eta(\vec{r}')}}_{\text{Gaussian integral}} =: \mathrm{e}^{-\beta F}$$

Gaussian integral can be solved analytically.
$\rightsquigarrow$ $(2\pi)^{\frac{V}{2}} \Big/ \sqrt{\det(\beta \frac{\delta^2 \mathscr{F}}{\delta m(\vec{r})\, \delta m(\vec{r}')}}$
Use $\frac{1}{\det A} = \prod_i \lambda_i^{-1} = \mathrm{e}^{-\sum_i \ln \lambda_i} = \mathrm{e}^{-\operatorname{Tr}(\ln A)}$ (with λ_i: Eigenvalues)

$$\Rightarrow F = \mathscr{F}_{\min} + \frac{1}{2\beta} \operatorname{Tr} \left(\ln \left.\frac{\delta^2 \mathscr{F}}{\delta m(\vec{r}) \delta m(\vec{r}')}\right|_{\bar{m}} \right) + \text{const}$$

Furthermore: $\langle \eta(\vec{r}) \rangle \propto \int \mathscr{D}[\eta(\vec{r})]\, \eta(\vec{r})\, \mathrm{e}^{-\frac{\beta}{2} \int \mathrm{d}^d r'\, \mathrm{d}^d r'' \left.\frac{\delta^2 \mathscr{F}}{\delta m(\vec{r}')\, \delta m(\vec{r}'')}\right|_{\bar{m}} \eta(\vec{r})\, \eta(\vec{r}')} \equiv 0$
$\Rightarrow \langle m(\vec{r}) \rangle = \bar{m}(\vec{r}), \quad \frac{\partial \langle m(\vec{r}) \rangle}{\partial h(\vec{r}')} = \frac{\partial \bar{m}(\vec{r})}{\partial h(\vec{r}')}$
$\rightsquigarrow$ Basically same results than in mean-field theory.
Non-mean field behavior only emerges if fluctuations are large!

(c) Application: Correlation functions in mean-field approximation

Consider homogeneous system with $\bar{m}(\vec{r}) \equiv \bar{m} = \text{const.}$

Trick: Exploit $\tilde{\chi}(\vec{k}) = \frac{\delta\langle m(\vec{k})\rangle}{\delta h(\vec{k})}\Big|_{h=0} = \frac{\beta}{(2\pi)^d}\langle m(\vec{k})m(-\vec{k})\rangle\Big|_{h=0}$

$\rightsquigarrow$ Response of the system to a periodic perturbation with amplitude $h(\vec{k})$ gives correlation functions in Fourier space

$$C(\vec{r}) = \langle m(\vec{r})m(\vec{r}')\rangle - \bar{m}^2 \;\rightarrow\; C(\vec{k}) \sim \langle m(\vec{k})m(-\vec{k})\rangle$$

Specifically: Consider again expansion $m(\vec{r}) = \bar{m} + \eta(\vec{r})$

Euler-Lagrange equation: $bm - g\Delta m = h \;\Rightarrow\; b\eta + 3c\bar{m}^2\eta - g\Delta\eta + \mathscr{O}(\eta^2) = h$

$$\left| \begin{array}{lll} T > T_c \quad (\bar{m} = 0) & : \; b\eta - g\Delta\eta & \overset{!}{=} h(\vec{r}) \\ T < T_c \quad (\bar{m} = \sqrt{\frac{-b}{c}}) & : \; -2b\eta - g\Delta\eta & \overset{!}{=} h(\vec{r}) \end{array} \right\} + \mathscr{O}(\eta^2)$$

In Fourier space

$$\left| \begin{array}{lll} T > T_c & : \; b\,\eta + g\,k^2\eta = h(\vec{k}) & \Rightarrow \; \eta(\vec{k}) = h(\vec{k})/(b + gk^2) \\ T < T_c & : \; -2b\,\eta + g\,k^2\eta = h(\vec{k}) & \Rightarrow \; \eta(\vec{k}) = h(\vec{k})/(2|b| + gk^2) \end{array} \right.$$

$\Rightarrow$ Lorentz curve: $C(\vec{k}) \sim \tilde{\chi}(\vec{k}) \sim \frac{\delta\langle m(\vec{k})\rangle}{\delta h(\vec{k})\rangle} \sim \frac{\delta\langle \eta(\vec{k})\rangle}{\delta h(\vec{k})\rangle} \;\Rightarrow\; \boxed{C(\vec{k}) \sim \frac{1}{k^2 + \xi^{-2}}}$

with $\boxed{\xi = \begin{cases} \sqrt{g/b} & : T > T_c \\ \sqrt{g/(2|b|)} & : T < T_c \end{cases}}$

Back transformation in real space (for calculation see below or 3.5.3.4)

$$\Rightarrow \quad \boxed{C(\vec{r}) \sim \int \mathrm{d}^d k \mathrm{e}^{i\vec{k}\cdot\vec{r}} C(\vec{k}) \sim \begin{cases} \mathrm{e}^{-r/\xi} & : r/\xi \gg 1 \\ r^{2-d} & : r/\xi \ll 1 \end{cases}}$$

Interpretation:

ξ is the correlation length, diverges at the critical point ($b = 0$).
At the critical point with $\xi \to \infty$, $C(\vec{r})$ decays algebraically!
Critical behavior: Exponents ν and η (Recall $b = b_0(T - T_c)$)

- Correlation length: $\boxed{\xi \sim |T - T_c|^{-\nu}}$, $\boxed{\nu = 1/2}$ ($\xi \sim 1/\sqrt{|b|}$)
- "Anomalous dimension": $\boxed{C(r) \sim r^{2-d+\eta}}$, $\boxed{\eta = 0}$ at $T = T_c$

(exact: 2D Ising: $\nu = 1$, $\eta = 1/4$ 3D Ising: $\nu = 0.63$, $\eta = 0.04$)

(Addendum: Back transformation $C(\vec{k}) \to C(\vec{r})$ (similar to Sec. 3.5.3.4)

$C(\vec{k}) = \frac{1}{k^2+\xi^{-2}}$; $C(\vec{r}) \sim \int \mathrm{d}^d k\, \mathrm{e}^{-i\vec{k}\cdot\vec{r}} \frac{1}{k^2+\xi^{-2}}$, d dimensions

Use: ($\star$) $\int_{-\infty}^{\infty} \mathrm{d}p\, \mathrm{e}^{-ipx} \frac{1}{p^2+a^2} = \frac{\pi}{a}\mathrm{e}^{-|x|/a}$ (derived, e.g., via theorem of residues)

$d = 1$: $\int \mathrm{d}k \frac{1}{k^2+\xi^{-2}} \overset{\star}{=} \pi\xi\mathrm{e}^{-|x|/\xi}$

$$d \geqslant 2: \; C(\vec{r}) \sim \mathrm{d}^d k\, \mathrm{e}^{-i\vec{k}\cdot\vec{r}} \frac{1}{k^2+\xi^{-2}} \overset{\vec{\hat{k}}=\vec{k}r}{=} r^{2-d} \int \mathrm{d}^d \hat{k} \mathrm{e}^{-i\vec{\hat{k}}\cdot\vec{e}_{\vec{r}}} \frac{1}{\hat{k}^2+(r/\xi)^2}$$

$\Big|$ Choose x axis along $\vec{e}_{\vec{r}}$, Set $\vec{\hat{k}} =: (p, \vec{q})$

$$= r^{2-d} \int_{-\infty}^{\infty} \mathrm{d}p\, \mathrm{e}^{-ip} \int \mathrm{d}^{d-1}q \frac{1}{p^2+q^2+(\frac{r}{\xi})^2}$$

$$\overset{\star}{\sim} r^{2-d} \underbrace{\int_0^{\infty} \mathrm{d}q\, q^{d-2}\, \mathrm{e}^{-\sqrt{q^2+(\frac{r}{\xi})^2}} \frac{1}{\sqrt{q^2+(\frac{r}{\xi})^2}}}_{=:I(r/\xi)}$$

Consider asymptotic behavior of $I(x)$:

$x \to \infty: \sqrt{x^2+q^2} \approx x(1+\frac{1}{2}(\frac{q}{x})^2 = x + \frac{1}{2x}q^2; \frac{1}{\sqrt{q^2+x^2} \approx \frac{1}{x}(1-\frac{q^2}{2x^2}}$

$$\Rightarrow I(x) \approx \mathrm{e}^{-x}\frac{1}{x}\underbrace{\int_0^\infty \mathrm{d}q\, q^{d-2}\mathrm{e}^{-\frac{1}{2x}q^2}}_{\Gamma(\frac{1-d}{2})x^{(d-1)/2}}(1+\mathscr{O}(\tfrac{1}{x})) \sim \mathrm{e}^{-x}x^{(d-3)/2}$$

$x \to 0$, $d > 2$: $I(x) \approx \int_0^\infty \mathrm{d}q\, q^{d-3}\mathrm{e}^{-q} = \Gamma(d-2)$.

$d = 2$: Exact solution $\int_0^\infty \mathrm{d}q\mathrm{e}^{-\sqrt{q^2+x^2}}\frac{1}{\sqrt{q^2+x^2}} = K_0(x) \overset{x\to 0}{\to} -\ln(x)$

Apply this to $C(\vec{r}) \sim r^{2-d}I(r/\xi)$

$$\Rightarrow r/\xi \gg 1: \; C(r) \sim r^{2-d+(d-3)/2}\mathrm{e}^{-r/\xi} = r^{(1-d)/2}\mathrm{e}^{-r/\xi}$$

$$r/\xi \ll 1: \; C(r) \sim \begin{cases} r^{2-d} & \text{for } d > 2 \\ -\ln(r/a) & \text{for } d = 2 \end{cases} \quad)$$

4.3.5 Validity region of the mean-field approximation

Mean-field approximation neglects fluctuations.

Question: When is this acceptable?

Estimate: Ginzburg criterion (see also Section 3.5.4.2)

Fluctuations of the order parameter in the range of the correlation length must be small compared to the order parameter!

Specifically: Compare $M = \int_{\xi^d} \mathrm{d}^d r\, m(\vec{r})$ at $t \propto (T - T_c)$

$$\text{Request: } \underset{\chi\xi^d}{\underset{||}{\langle M^2\rangle - \langle M\rangle^2}} \quad \ll \quad \underset{\langle m\rangle^2\xi^{2d}}{\underset{||}{\langle M\rangle^2}}$$

$$\Rightarrow \; \chi\xi^{-d}\langle m\rangle^{-2} \ll 1 \quad \Rightarrow \quad \boxed{R|t|^{-\gamma+\nu d-2\beta} \ll 1}$$

Specifically for $|t| \to 0$: $\quad (-\gamma + \nu d - 2\beta) > 0$

$\Rightarrow$ Mean-field approximation describes critical behavior correctly for

$$\boxed{d > d_c = \frac{2\beta_{MF} + \gamma_{MF}}{\nu_{MF}}}$$

d_c : "Upper critical dimension"
($\beta_{MF}, \gamma_{MF}, \nu_{MF}$: Mean-field exponents)

For $d < d_c$: Fluctuations dominate, mean-field approximation fails
For $d = d_c$: Logarithmic corrections
For $d > d_c$: Mean-field approximation captures critical behavior

Ising-type transitions: $\gamma_{MF} = 1$, $\beta_{MF} = \nu_{MF} = 1/2 \Rightarrow \boxed{d_c = 4}$

Significance of prefactor R

Mean-field approximation may oK even for $d < d_c$,

if $1 \gg t \gg R^{1/(\gamma+2\beta-d\nu)} = R^{1/\nu(d_c-d)}$: mean-field range

if $t \ll R^{1/(\gamma+2\beta-d\nu)} = R^{1/\nu(d_c-d)}$: critical range

(Example: Superconductivity - Critical range $\sim 10^{-14}K$
One practically always sees mean-field behavior.

Remark: Argument applies only if the direct interactions decay fast enough (faster than $1/r^d$)!

4.3.6 Conclusion: Relevance of Ginzburg-Landau theory

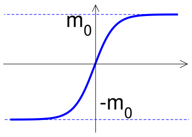
⋆ Ginzburg-Landau functional

- In principle "exact" starting point for perturbation expansions, field theoretic renormalization etc.
  Contruction from symmetry considerations → Universality
- Allows assessment of validity of mean-field approximation (previous section)

⋆ Treatment of inhomogeneous systems

e.g., surfaces, thin films, interfaces

Interface



Problem: Minimize $\mathscr{F}[m(\vec{r})]$ with boundary condition $\lim\limits_{x\to\pm\infty} = \pm m_0$ (with m_0: Bulk order parameter)

$$\mathscr{F}[m(\vec{r})] = \int \mathrm{d}^d r \Big[\tfrac{1}{2} g(\nabla m)^2 + \tfrac{1}{2} b m^2 + \tfrac{1}{4} c m^4\Big]$$

$$\Rightarrow \text{Equation: } bm + cm^3 - g\Delta m = 0,\ m_0 = \sqrt{|b|/c},\ \xi = \sqrt{\tfrac{g}{2|b|}}$$

$$\Rightarrow \text{Solution: } m = m_0 \tanh(x/2\xi) \quad \text{(Check by insertion)}$$

⋆ Allows description of modulated phases

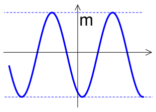
("incommensurable phases", magnetic screw structures, lamellar phases in microemulsions or block copolymers)

Special case $\boxed{g < 0}$. In this case, $\mathscr{F}[m(\vec{r})]$ must include a stabilizing term of higher order

$$\text{e.g., } \mathscr{F} = \int \mathrm{d}^d r \Big[f(m) + \tfrac{1}{2} g(\nabla m)^2 + \tfrac{1}{2} k(\Delta m)^4\Big]$$

$$\text{(or } \tfrac{1}{4} k'(\nabla m)^4\text{)}$$

If g is sufficiently small, $\mathscr{F}$ is minimized by a modulated order parameter.

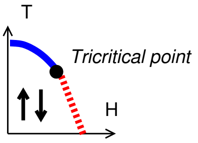


4.4 Multicritical phenomena

4.4.1 Examples

(a) Tricritical point

Example: Strongly anisotropic uniaxial antiferromagnet in a homogeneous external field (discussed earlier in Sec. 4.4.2)

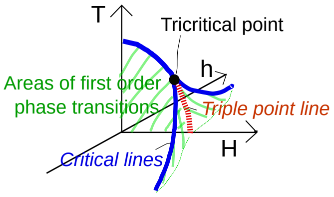


Red dashed: First order transition
Blue solid: Second order transition
Black point: Tricritical point

Why is this point called ”tricritical”?

In an extended phase space, three critical lines meet there.

E.g., antiferromagnet: Choose as additional intensive variable the field h that couples to the order parameter (a staggered field)



Additional characteristics:

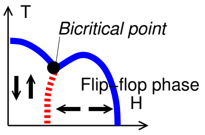
– In mean-field approximation different critical exponents than in the Ising model (see Sec. 4.4.2).
One obtains: $\alpha = 1/2,\ \beta = 1/4,\ \gamma = 1$, but still $\nu = 1/2,\ \eta = 0$.

⇒ Different upper critical dimension according to the Ginzburg criterion: $d_c = (\gamma + 2\beta)/\nu = 3!$

(b) Bicritical point

Two critical lines meet each other

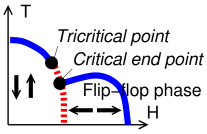
Example: Weakly anisotropic uniaxial antiferromagnet in a homogeneous external field (discussed earlier in Sec. 4.2.3)



(c) Critical end point

Critical line ends at a line of first order phase transitions

Example: Uniaxial antiferromagnet with intermediate anisotropy in a homogeneous external field



(d) Multicritical points of higher order

Example: Tetracritical point - four critical lines meet.

(e) Lifshitz point

Modulated phases compete with regular phases

(f) and many others ...

We will now illustrate the treatment of multicritical phenomena with the Ginzburg-Landau theory at two examples: The tricritical point and the Lifshitz point.

4.4.2 Tricritical point

(a) Landau expansion (already discussed in Sec. 4.4.2)

$\frac{F}{V} = a + \frac{1}{2}bm^2 + \frac{1}{4}cm^4 + \frac{1}{6}dm^6 - hm$

Tricritical point corresponds to $b = c = 0$

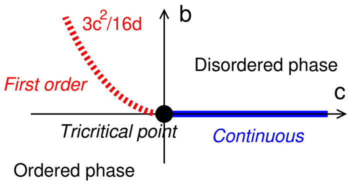
In order for this to happen, b and c should depend on two intensive parameters Δ, T.

$\rightsquigarrow$ $b = c = 0$ defines a point (Δ_t, T_t) in the (Δ, T)-plane

We already showed:

At $c < 0$, one has a first order phase transition at $b = 3c^2/16d$.

Now we discuss the critical behavior directly at the critical point.



(b) Critical behavior in the Landau theory

Preliminary remark: From $\frac{\partial F}{\partial m} = 0$, one concludes at $h = 0$:

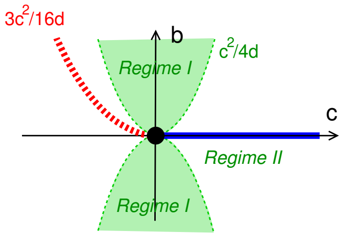
$$bm + cm^3 + dm^5 = 0 \quad \overset{(c<0)}{\Rightarrow} \quad m^2 = \frac{|c|}{2d}\Big(1 + \sqrt{1 - \frac{4bd}{c^2}}\Big)$$

$\rightsquigarrow$ Behavior different for the cases $|4bd/c^2| \ll 1$ and $|4bd/c^2| \gg 1$ "critical" and "tricritical" regime!

Graphical illustration:

I: "Tricritical regime"
II: "Critical regime"

Approaches to the tricritical point:
in I: $b \propto (T - T_t)$, $c \propto (T - T_t)$
in II: $b \ll (T - T_t)^2$, $c \propto (T - T_t)$



- Order parameter

  (I) Approach tricritical point with a finite angle to the phase transition line → in the tricritical region
  $\Rightarrow \frac{4bd}{c^2} \gg 1$ (since b, c approach zero linearly)
  $\Rightarrow m \approx (\frac{-b}{d})^{1/4} \qquad \Rightarrow \qquad \boxed{\beta_t = 1/4}$

  (II) Approach tricritical point in the critical regime such that $1 \ll \frac{4bd}{c^2}$
  $\Rightarrow m \approx (\frac{|c|}{2d})^{1/2} \qquad \Rightarrow \qquad \boxed{\beta_u = 1/2}$

- Specific heat c_H: $\frac{F}{V} = a + \frac{1}{2}bm^2 + \frac{1}{4}cm^4$ and $c_H = -T\frac{\partial^2 F}{\partial T^2}$

  (I) In the tricritical regime: $m \propto (T_t - T)^{1/4}$ and $b \propto (T - T_t)$
  $\Rightarrow c_H \sim \frac{\partial^2}{\partial T^2}(T_t - T)^{3/2} \sim (T_t - T)^{-1/2} \qquad \Rightarrow \qquad \boxed{\alpha_t = 1/2}$

  (II) In the critical regime: $m \propto (T_t - T)^{1/2}$, $b \ll |T - T_t|^2$, $c \propto (T - T_t)$
  $\Rightarrow c_H \sim \frac{\partial^2}{\partial T^2}(T_t - T)^3 \sim (T_t - T)^1 \qquad \Rightarrow \qquad \boxed{\alpha_u = -1}$

- Susceptibility

  From $bm + cm^3 + dm^5 - h = 0$, one gets $\frac{\partial m}{\partial h}\big|_{h=0} = \frac{1}{b+3cm^2}\big|_{h=0}$.

  (I) In the tricritical regime:
  $$\frac{\partial m}{\partial h} \sim \frac{1}{b} \sim (T_t - T)^{-1} \qquad \Rightarrow \qquad \boxed{\gamma_t = 1}$$

  (II) In the critical regime: $b \ll |T - T_t|^2$, $c \propto (T - T_t)$
  $$\frac{\partial m}{\partial h} \sim \frac{1}{b+3cm^2} \overset{cm^2 \sim (T-T_t)^2}{\sim} (T - T_t)^{-2} \qquad \Rightarrow \qquad \boxed{\gamma_u = 2}$$

- Correlation functions

  The exponents ν, η do not change at the tricritical point, since the mean-field correlations do not depend on c (e.g., $\xi \sim \sqrt{|g/b|}$)
  $$\Rightarrow \qquad \boxed{\nu_t = 1/2, \ \eta_t = 0}$$

Summary: Mean-field exponents in the tricritical regime:
$$\beta_t = 1/4, \ \gamma_t = 1, \ \alpha_t = 1/2, \ \nu_t = 1/2, \ \eta_t = 0$$

(c) Application: Ginzburg criterion

Recall Sec. 4.3.5: The Landau theory is good, if $d\nu - 2\beta - \gamma > 0$ for the mean-field exponents ν, β, γ. Inserting the values for the critical exponents at the tricritical point, one obtains $d > d_t$ with $\boxed{d_t > 3}$

Thus the upper critical dimension at the tricritical point is only 3!
In three dimensions, critical fluctuations only lead to logarithmic corrections to the behavior predicted by the Landau theory.

4.4.3 Lifshitz point

(a) Ginzburg-Landau theory for modulated phases

Practical relevance: Often used to describe materials that spontaneously form modulated nanostructures, e.g.,

- Modulated magnetic superstructures in crystals
  (Hornreich et al 1975 – lattice spin model: ANNNI model)
- Amphiphilic systems and microemulsions
- Block copolymer nanostructures
- Domains in lipid membranes

Also postulated to exist in the QCD phase diagram by some models

Ginzburg Landau theory

Modulated phases are possible, if the coefficient g of the square gradient term in the Ginzburg-Landau functional becomes negative. In this case, a stabilizing term of higher order must be included, e.g., $\frac{1}{2}v(\Delta m)^2$
$$\rightsquigarrow \quad \mathscr{F} = \int \mathrm{d}^d r \left[\tfrac{1}{2}bm^2 + \tfrac{1}{4}cm^4 - hm + \tfrac{1}{2}g(\nabla m)^2 + \tfrac{1}{2}v(\Delta m)^2\right]$$

Phase behavior: To find the transition to a modulated phase, we calculate the structure factor $S(\vec{k}) \propto \chi(\vec{k})$ ($\vec{k}$-dependent susceptibility)

Minimize $\mathscr{F}$ → Euler-Lagrange equations
$$\Rightarrow \quad b\, m + c\, m^3 - g\Delta m + v\, \Delta^2 m = h$$

Fourier transform $\vec{r} \to \vec{k}$ and linearization in m

$\Rightarrow \quad b\, m(\vec{k}) + g\, \vec{k}^2 m(\vec{k}) + v\, k^4\, m(\vec{k}) = h(\vec{k})$

$\Rightarrow \quad \chi(\vec{k}) \propto \frac{\partial m(\vec{k})}{\partial h(\vec{k})} = \frac{1}{b+gk^2+vk^4}$

Analysis

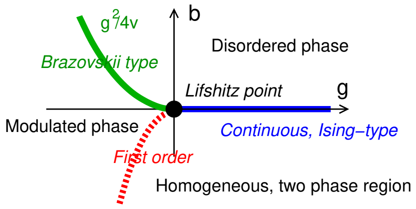
If $g < 0$, then $\chi(\vec{k})$ has a maximum at $k^* = \sqrt{-g/2v}$,

$\Rightarrow \chi(k^*) = \frac{1}{b-g^2/4v}$

In that case, $\chi(k^*)$ diverges at $b = g^2/4v$

⇝ Homogeneous phase is unstable, transition to a modulated structure with characteristic wave vector k^*

Phase diagram



Discussion

– In mean-field approximation: Two types of continuous transitions meet at the multicritical Lifshitz point: A regular Ising-type transition at $g > 0$, $b = 0$ and and a "Brazovskii"-type transition at $g < 0$, $b = \sqrt{g^2/4v}$ between a disordered phase and a modulated structure.

– At the Lifshitz point, the wave vector k^* of the modulated structure becomes zero - i.e., the wave length diverges.

(c) Critical behavior at Lifshitz points

- Exponents $\alpha, \beta, \gamma, \delta$ are the same as in the Ising model, as they do not depend on g.

  $$\boxed{\alpha_L = 0,\ \beta_L = 1/2,\ \gamma_L = q,\ \delta_L = 3}$$

- At the Lifshitz point ($g = 0$), we have $\chi(\vec{k}) \sim \frac{1}{b+vk^4} \sim \frac{1}{b(1+k^4\xi^4)}$

  ⇝ Not a Lorentz curve, but $\xi = (v/b)^{1/4}$ is clearly the characteristic length scale in the system! Diverges as $b \propto (T - T_L) \to 0$.

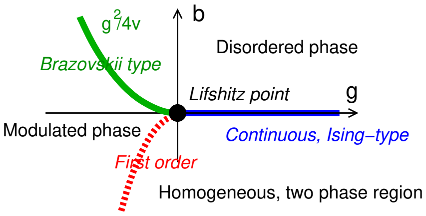
  $\xi \propto b^{-1/4} \quad \Rightarrow \quad \boxed{\nu_L = 1/4}$

  At $b = 0$, we have $\chi(\vec{k}) \propto k^{-4} =: k^{-(2-\eta_L)} \quad \Rightarrow \quad \boxed{\eta_L = -2}$

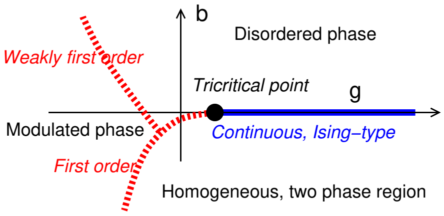
- Upper critical dimension: $d_c \nu_L - 2\beta_L - \gamma_L > 0 \quad \Rightarrow \quad \boxed{d_c = 8}$

(d) Fluctuation effects

- Upper critical dimension is very large ⇝ Fluctuation effects are strong!
- In fact, the lower critical dimension (the minimum dimension where a Lifshitz point exists), is believed to be $d_l = 4$.
- In three dimensions or less, the Lifshitz point becomes unstable and probably turns into a regular tricritical point (Numerical evidence for the case of a block copolymer melt: Vorselaars, Spencer, Matsen, PRL 2020).
- Also, the Brazovskii transition becomes first order due to fluctuations by a mechanism called "Brazovskii mechanism" (ordered modulated domains break up).



Mean-field phase behavior



Real phase behavior in 3D

4.5 Concepts to describe the kinetics of first order phase transitions

4.5.1 Classification of dynamical systems

We focus on a model with a one-component (scalar) order parameter, as in Section 4.1. The dynamic behavior of a system depends crucially on the relevant conserved quantities. The classification below goes back to Hohenberg and Halperin (1977). The simplest cases are:

- Model A: Order parameter is not conserved
  (examples: magnetism)

- Model B: Order parameter is conserved
  (example: demixing)

- Model C: Order parameter is not conserved, but another extensive quantity is conserved which couples to the order parameter.
  (example: order-disorder transition: The overall composition is conserved.)

- Model H (in fluids): Additionally, energy and momentum conservation are important and influence the order parameter kinetics.
  → hydrodynamic modes

- etc.

4.5.2 Field theoretic descriptions

In this chapter, we introduce stochastic partial differential equations that model specifically model A and model B dynamics (the other models are omitted here). This will be done using a sloppy "physicist" approach. The mathematics of stochastic differential equations (SDEs) is actually quite involved and will be discussed in somewhat more depth in chapter 9.

- Starting point: Ginzburg-Landau functional as before:

$$\mathscr{F}[m(\vec{r})] = \int \mathrm{d}^d r \, \big(f(m) + \frac{1}{2} g \, (\nabla m)^2 \big)$$

We define the "effective field" $h_{\text{eff}}(\vec{r}) = -\frac{\delta \mathscr{F}}{\delta m(\vec{r})} = g\Delta m - \frac{\partial f}{\partial m}$

Note: If $h_{\text{eff}}(\vec{r}) = 0$, $\mathscr{F}[m(\vec{r})]$ is extremal.

- Two classes of dynamical models:

(a) Mean-field dynamics: The system is deterministically driven towards a state with $h_{\text{eff}}(\vec{r}) = 0$ according to dynamical equations that respect the relevant local conservation laws (e.g., in model B, a continuity equation for the order parameter field).

(b) Stochastic dynamics: Fluctuating noise is added to the dynamical equations. The noise is chosen to be Gaussian distributed with correlations such that there exists an equilibrium steady-state solution where the field $\{m(\vec{r})\}$ is distributed according to a Boltzmann distribution, $P[m(\vec{r})] \propto \exp\big(-\beta \mathscr{F}[m(\vec{r}]$. The latter is ensured by imposing a so-called "fluctuation-dissipation relation" on the correlations of the noise.

- Specifically:

Model A: No local conservation law, relaxational dynamics.

(a) Deterministic (mean-field) Ansatz: $\frac{\partial m}{\partial t} = L h_{\text{eff}}(\vec{r}, t)$.
with L: relaxation coefficient

(b) Stochastic Ansatz: "Langevin equation"

$$\boxed{\frac{\partial m}{\partial t} = -L \frac{\delta \mathscr{F}}{\delta m(\vec{r})} + \zeta(\vec{r})}$$

with $\zeta(\vec{r}, t)$: Gaussian distributed, uncorrelated white noise with mean zero.

- Mean: $\langle \zeta(\vec{r}, t) \rangle = 0$ (mean zero)
- Fluctuation-dissipation relation:

$$\boxed{\langle \zeta(\vec{r}, t) \zeta(\vec{r}', t') \rangle = 2 k_B T L \, \delta(\vec{r} - \vec{r}') \, \delta(t - t')}$$

$\rightsquigarrow$ White: $\langle \zeta(\vec{r}, t) \zeta(\vec{r}', t') \rangle \propto \delta(t - t')$
Spatially correlated: $\langle \zeta(\vec{r}, t) \zeta(\vec{r}', t') \rangle \propto \delta(\vec{r} - \vec{r}')$
Prefactor: Ensures that the steady-state solution has the desired temperature (see Chapter 9).

- Gaussian distributed: Higher order moments (correlations) of ζ can be derived from the second moment (the fluctuation-dissipation relation) according to the Gaussian distribution.

Model B: Order parameter is conserved, diffusive dynamics.

$\rightsquigarrow$ $m(\vec{r})$ must obey a continuity equation $\boxed{\dfrac{\partial m}{\partial t} = -\nabla \vec{j}}$

with some current density $\vec{j}(\vec{r}, t)$.

(a) Deterministic (mean-field) Ansatz: $\vec{j}(\vec{r}, t) \propto -\nabla h_{\text{eff}}(\vec{r}, t)$

$\Rightarrow$ Cahn-Hilliard equation: $\boxed{\dfrac{\partial m}{\partial t} = L\Delta \dfrac{\delta \mathscr{F}}{\delta m} + \zeta(\vec{r}, t)}$

with L: "Onsager coefficient"

Note: The Cahn-Hilliard equation is also intensely studied in the applied mathematics community.

(b) Stochastic Ansatz: Fluctuating current $\vec{j} = -L\nabla \frac{\delta \mathscr{F}}{\delta m(\vec{r},t)} + \vec{\eta}(\vec{r})$

$$\Rightarrow \quad \boxed{\frac{\partial m}{\partial t} = L\Delta \frac{\delta \mathscr{F}}{\delta m} + \zeta(\vec{r}, t)}$$

with $\zeta(\vec{r}, t) = -\nabla \cdot \vec{\eta}$: Gaussian distributed, Δ-correlated white noise with mean zero.

- Mean: $\langle \zeta(\vec{r}, t) \rangle = 0$ (mean zero)
- Fluctuation-dissipation relation:

$$\boxed{\langle \zeta(\vec{r}, t)\zeta(\vec{r}', t') \rangle = -2k_{_B}TL\, \Delta\delta(\vec{r} - \vec{r}')\, \delta(t - t')}$$

$\rightsquigarrow$ White: $\langle \zeta(\vec{r}, t)\zeta(\vec{r}', t') \rangle \propto \delta(t - t')$

Δ-correlated: $\langle \zeta(\vec{r}, t)\zeta(\vec{r}', t') \rangle \propto \Delta\delta(\vec{r} - \vec{r}')$

NB: Corresponds to uncorrelated white current noise with $\langle \eta_i(\vec{r}, t)\eta_j(\vec{r}', t') = 2Lk_{_B}T\, \delta_{ij}\, \delta(\vec{r} - \vec{r}')\, \delta(t - t')$.

(Check: $\langle \zeta(\vec{r}, t)\zeta(\vec{r}', t') \rangle = \sum_{i,j} \langle (\partial_i \eta_i(\vec{r}, t)) (\partial'_j \eta_j(\vec{r}', t')) \rangle$

$= \sum_{i,j} \partial_i \partial'_j \langle \eta_i(\vec{r}, t)\eta_j(\vec{r}', t') \rangle$

$= 2Mk_{_B}T \sum_{i,j} \partial_i \partial'_j \delta_{ij}\, \delta(\vec{r} - \vec{r'})\, \delta(t - t')$

$= -2Mk_{_B}T \sum_{i,j} \partial_i \partial_j \delta_{ij}\, \delta(\vec{r} - \vec{r'})\, \delta(t - t')$

$= -2Mk_{_B}T\Delta\, \delta(\vec{r} - \vec{r'})\, \delta(t - t')$ ✓)

Prefactor: Ensures that the steady-state solution has the desired temperature (see Chapter 9).

- Gaussian distributed: Same as model A.

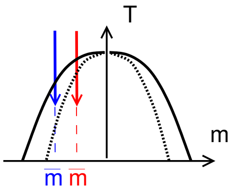
* Physical motivation: Distinction between "fast" and "slow" degrees of freedom, e.g., phonons versus diffusive modes

"Fast" degrees of freedom are projected out
→ Onsager coefficients and noise

The Ansatz is obviously problematic, if one does not really know, which degrees of freedom are "fast" or "slow", or if the time scales are not well separated. Possible strategies to deal with such cases is to either include further fields (as in model C and H) or allow for memory effects ("generalized Langevin equation", not covered in this lecture).

4.5.3 Early-stage phase separation in model B dynamics

Starting point: We consider a system that is suddenly quenched from the disordered phase into the two-phase region. Initially, it is homogeneous with order parameter $m \equiv \overline{m}$ and disordered.
Question: How does phase separation proceed?



- General considerations

  Even in the two-phase region, the system may remain trapped in the disordered state for a while. The reason is that most small deviations $m(\vec{r})$ from the homogeneous state are driven back towards $m \equiv \overline{m}$ – primarily due to the interfacial term $(\nabla m)^2$ in the free energy, but sometimes also because $f(m)$ is convex in the vicinity of $\overline{m}$, see below.

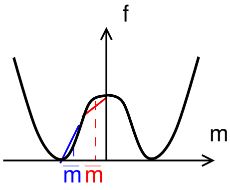
- Stability analysis

  Due to the square gradient term $(\nabla m)^2$ in the Ginzburg-Landau energy, the fluctuations that become unstable first are the ones with long wavelength.

  Consider a "homogeneous" fluctuation where m is enhanced by δm_1 in a volume fraction a_1 of the system and reduced by δm_2 in a fraction a_2 $(m_i = \overline{m} + \delta m_i)$. Since the overall composition does not change, we have $\sum_i a_i \delta m_i = 0$.

  ⇒ Change of (Ginzburg-Landau) free energy:

$$\frac{1}{V}\Delta\mathscr{F} = \sum_i a_i \big(f(\overline{m}+\delta m_i) - f(\overline{m})\big) = f'(\overline{m}) \underbrace{\sum_i a_i \delta m_i}_{0} + \frac{1}{2} f''(\overline{m}) \underbrace{\sum_i a_i \delta m_i^2}_{>0}$$



  ⇝ For $f''(\overline{m}) > 0$, fluctuations are driven back.
  For $f''(\overline{m}) < 0$, fluctuations grow, unstable

  ⇒ Crossover between regimes at $f''(\overline{m}) = 0$: Spinodal.

- Discussion:

  In mean field theory, the spinodal line separates a region where phase separation occurs spontaneously from a region where it can only proceed by an activated nucleation process.

  In reality, the separation between metastable and stable regions is not sharp. However, the mean-field concepts can still qualitatively explain differences in the observed phase separation behavior for deep and shallow quenches.

4.5.3.1 Unstable regime:
Cahn-Hilliard theory of spinodal decomposition

We first consider quenches in regions with $f''(\overline{m}) < 0$. In this case, the homogeneous phase is unstable after the quench. The process of phase separation is a driven process which also takes place in the absence of noise, provided the initial configuration is slightly noisy. The Cahn-Hilliard theory describes how this process is initiated.

- $*$ Approximations:
  (i) Linearize $h_{\text{eff}}(\vec{r}) = -\frac{\delta\mathscr{F}}{\delta m} \approx g\Delta m - f'(\overline{m}) - f''(\overline{m})(m(\vec{r}) - \overline{m})$
  (ii) Neglect noise (OK, since the transition is driven).

- $*$ Solution of the linearized equation:
  Fourier transform $m(\vec{r}) \to m(\vec{k})$ $(\vec{k} \neq 0)$
  $\Rightarrow \quad \frac{\partial m(\vec{k})}{\partial t} = -Mk^2\big(gk^2 + f''(\overline{m})\big)\, m(\vec{k}) \equiv -\omega(\vec{k})\, m(\vec{k})$
  with $\omega(\vec{k}) = \omega(k) = Mk^2\big(gq^2 + f''(\overline{m})\big)$.
  $\Rightarrow \; m(\vec{k}, t) = m(\vec{k}, 0)\, \exp(-\omega(\vec{k})t)$

- $*$ Analysis of the result:

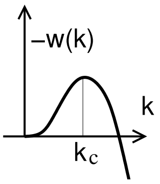
  Consider the time evolution of a small fluctuation $m(\vec{k}, 0)$

  $\omega(\vec{k}) > 0 \Rightarrow m(\vec{k}, t)$ shrinks, the mode $\vec{k}$ is stable.

  $\omega(\vec{k}) < 0 \Rightarrow m(\vec{k}, t)$ grows, the mode $\vec{k}$ is unstable.

  Instability condition: $\omega(\vec{k}) < 0$ for at least one $\vec{k}$.
  $\Rightarrow \quad gk^2 + f''(\overline{m}) < 0$: Possible for $f''(\overline{m}) < 0$
  $\rightsquigarrow$ Recover spinodal.

  Expected time evolution in the unstable regime:
  Consider $\omega(k)$ at $f''(\overline{m}) < 0$
  $\rightsquigarrow$ Long wave-length modes become unstable first, but they grow most slowly. (Reason: Diffusion – Restructuring on large scales takes time ...)
  $\rightsquigarrow$ Fastest growing modes: $k_c = \sqrt{-f''(\overline{m})/2g}$ (maximum of $\omega(k)$).



- $*$ Discussion:

  Cahn-Hilliard theory prediction: After the quench into the unstable regime, modes with wave vector $k_c \propto \sqrt{-f''(\overline{m})}$ grow fastest.

  $\rightsquigarrow$ A network structure with a characteristic wave length $2\pi/k_c$ emerges. This is indeed observed in experiments and simulations.

  $\rightsquigarrow$ However, different from the prediction of the linearized theory, the modes do not grow independently, instead, the pattern coarsens. → the characteristic wave vector decreases with time. The coarsening sets in immediately after the quench.

  $\rightsquigarrow$ The linearized Cahn-Hilliard theory provides a qualitative picture of the patterns forming during demixing in the spinodal regime, but it fails quantitatively. Including Gaussian noise in the linear theory does not help (not shown here). The coarsening is a nonlinear effect.

4.5.3.2 Metastable regime: Nucleation and classical nucleation theory

In the metastable regime, the transition from a homogeneous state into an inhomogeneous state is a thermally activated process which involves overcoming a free energy barrier. This requires thermal noise.
Typically, the transition is initiated by the (thermally activated) spontaneous nucleation of small domains of the competing phase, which then grow with time. Here, we discuss the simplest theoretical description of this process, the classical nucleation theory.

∗ Starting point and setup:

Ginzburg-Landau functional $\mathscr{F}_\lambda[m(\vec{r})] = \int \mathrm{d}^d r \, \big(f(m) + \frac{1}{2} g \, (\nabla m)^2 - \lambda m \big)$,
with $f(m)$: Double well potential with minima at $m = \pm m^*$
(e. g., $f(m) = a + \frac{b}{2} m^2 + \frac{c}{4} m^4$ with $b < 0$, and $m^* = \sqrt{|b|/c}$)

Mean order parameter $\overline{m}$ chosen in the phase separating, but metastable regime with $f''(\overline{m}) > 0$.
(our example: $|b|/3c < |\overline{m}| < |b|/c$)

Geometry: To study droplets, we consider idealized finite, but spherically symmetric systems, which may contain one droplet centered at the origin.

∗ Constrained Ginzburg Landau free functional:

We consider systems where the spatial average of $m(\vec{r})$, $M = \int \mathrm{d}^d r \, m(\vec{r})$, is constrained at $M/V = \overline{m}$. To account for this in the Ginzburg-Landau functional, we introduce a Lagrange parameter λ,

$$\mathscr{F}_\lambda[m(\vec{r})] = \int \mathrm{d}^d r \, \big(f(m) + \tfrac{1}{2} g \, (\nabla m)^2 - \lambda m \big),$$

where λ is chosen such that $\frac{\delta \mathscr{F}_\lambda}{\delta m(\vec{r})}\Big|_{M/V = \overline{m}} = 0$.

In homogeneous systems, $\lambda = f'(\overline{m})$. In inhomogeneous systems containing droplets, $|\lambda|$ will be smaller, $|\lambda| < |f'(\overline{m})|$

∗ Calculation procedure:

Introducing the Lagrange-parameter amounts to replacing $f(m)$ by $f_{\text{eff}}(m) = f(m) - \lambda m$ in the Ginzburg-Landau functional.
$\rightsquigarrow$ Tilted potential with two minima:
One minimum at $m_1 = \lambda$
A second, lower one at m_2

$\Rightarrow$ Solutions of the Euler-Lagrange equation with $M/V = \overline{m}$

- Homogeneous solution $m(\vec{r}) \equiv \overline{m}$
- Spherical droplet solution: $m(\vec{r}) = m_d(r)$ with $m_d(\infty) = m_1$, $m_d(0) \approx m_2$, and an interface at some $r = R$.
  Note: Since λ depends on R, m_1 and m_2 also depend on R.

∗ Free energy considerations:

Rewrite mean-field free energy of droplet
as $F_d(R) = V\, f(m_1) - \frac{4\pi}{3} R^3 \Delta\mu + F_{\text{excess}}(R)$
with $\Delta\mu := f(m_1) - f(m_2) > 0$. This defines F_{excess}.

Assume, that the dominant contribution to F_{excess} comes from the droplet surface, and that it is hence roughly proportional to the surface area $A_d = 4\pi R^2$ of the droplet.

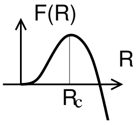
$\rightsquigarrow$ define surface tension $\sigma = F_{\text{excess}}/A_d \approx$ const.

$$\rightsquigarrow \quad \boxed{F_d(R) = \text{const.} + 4\pi\sigma R^2 - \frac{4\pi}{3} R^3 \Delta\mu}$$

$\Rightarrow$ $F_d(R)$ grows as R^2 for small R, decays as $-R^3$ for large R, and has a maximum at $\boxed{R_c = 2\sigma/\Delta\mu}$. (critical nucleus size).

∗ Central assumption of Classical nucleation theory:

Nucleation is described as an (overdamped) Kramers escape process, see Section 9.3.3: The dynamic evolution of $R(t)$ corresponds to overdamped Brownian motion in the potential $F_d(R)$.



– Droplets with $R < R_c$ are driven back to $R = 0$ and shrink.

– Droplets with $R > R_c$ grow.

– A nucleation events takes place if $R(t)$ manages to reach R_c due to thermal fluctuations. According to the Kramers theory, the average time required for this to happen is $\tau \propto \exp(\beta \Delta F(R))$
with $\Delta F = F(R_c) - R(0) = \frac{2\pi}{3} R_c^3$.

Note: As the droplet keeps growing, m_1 and m_2 gradually approach $\pm m^*$ and $\Delta\mu$ approaches zero. This implies that the critical nucleus size increases with time and that new nucleation events are increasingly unlikely.

⋆ Summary and discussion

– According to the classical nucleation theory, the process of phase separation is triggered by the spontaneous nucleation of droplets with critical nucleus size R_c. The nucleation rate I grows exponentially with ΔF according to $I = I_0 \exp(-\beta \Delta F)$.

Dynamic properties of the model (Onsager coefficients etc.) enter I_0.

– Remark: Close to the spinodal, the upper minimum m_1 becomes very shallow, which implies that the interface becomes very broad. In this case, the separation of $F_d(R)$ in terms of volume and surface terms is no longer justified and the droplet concept becomes questionable.

On the other hand, the spinodal decomposition concept also becomes questionable, because the only unstable fluctuations have wavelengths

k very close to zero and grow very slowly compared to the "critical droplets".

$\rightsquigarrow$ Near the spinodal, it becomes very difficult to distinguish between droplets and spinodal fluctuations. The transition between regimes is not sharp. Strictly speaking, the spinodal is not well-defined.

4.5.4 Late stage phase separation in model B dynamics:

4.5.4.1 Droplet regime: Oswald ripening, Lifshitz-Slyozov theory

After the initial droplet nucleation, droplets grow and interact with each other, and possibly collide and merge. At late stages, a regime is entered where the evolution of the morphologies can be described by a scaling law.

Characteristics of the late stage of phase separation in model B:

- Nucleation events are no longer important.
  (since the nucleation rate goes down, see 4.5.3.2)
- Only few droplets remain in the system and do not interact directly with each other
- Indirect interactions: Large droplets grow, small droplets shrink (since R_c grows with time, see 4.5.3.2).
  $\rightsquigarrow$ Number of droplets reduces further, average size increases
  $\rightsquigarrow$ Further coarsening of length scales: Oswald ripening

Droplet growth and derivation of Lifshitz-Slyozov coarsening

TODO

4.5.4.2 Generalization: Lifshitz-Slyozov $t^{1/3}$- scaling

TODO
David Huse, Phys. Rev B 34, 7845 (1986).

4.5.5 Late stage ordering in model A dynamics

TODO

Chapter 5

Critical Phenomena and Scaling Hypothesis

5.1 Scaling relations

Summary of some critical exponents

(Quantity)				Mean-field		
		2D Ising	3D Ising	Ising	Tricritical point	Lifshitz point
(Specific heat)	α	0	0.1	0	1/2	0
(Order parameter)	β	1/8	0.33	1/2	1/4	1/2
(Susceptibility)	γ	7/4	1.24	1	1	1
(OP ↔ field at T_c)	δ	15	4.8	3		
(Correlation length)	ν	1	0.63	1/2	1/2	1/4
(Correlations at T_c)	η	1/4	0.04	0	0	2
(Upper critical dimension)	d_c			4	3	8

Question: Are these exponents really independent?

Closer look: Some general relations seem to be fulfilled:

e.g.: $\beta + \gamma = \beta\delta$

$\alpha + 2\beta + \gamma = 2$ (Rushbrooke law)

$$2 - \alpha = \begin{cases} \nu\, d & : d < d_c \quad \text{(Josephson law)} \\ \nu\, d_c & : d \geqslant d_c \quad \text{(Mean-field case)} \end{cases}$$

$\gamma = \nu\,(2 - \eta)$

$\rightsquigarrow$ Scaling relations

History: Main discoveries around 1963

- Rushbrooke: Thermodynamic stability $\Rightarrow$ inequality $\alpha + 2\beta + \gamma \geqslant 2$
- Essam, Fisher: Numerical results suggest $\alpha + 2\beta + \gamma = 2$
  (for arbitrary models and dimensions)
- Widom: Scaling hypothesis

5.2 Widom's scaling hypothesis

Provides a framework that helps to classify and "derive" scaling relations. First introduced in a heuristic manner. A more formal derivation will be provided in chapter 6.

Of great practical use

Scaling analyses are fast ("back of the envelope" calculations).
Can be applied to a variety of problems/systems
(e.g., finite size scaling, polymers, dynamical systems, ...)

Often give correct relations without lengthy calculations

Here: "Static scaling hypothesis" for Ising-type systems

5.2.1 Scaling hypothesis for the order parameter

(Widom, 1963)

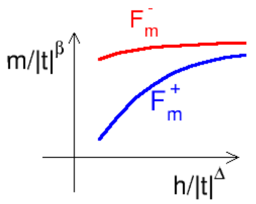
Order parameter is a function of $t = (T - T_c)/T_c$ and $h = H/k_B T$

We know: $m(t, h = 0) = \begin{cases} 0 & : t > 0 \\ \pm A|t|^\beta & : t < 0 \end{cases}$ and $m(t = 0, h) = \pm B|h|^{1/\delta}$

Question: Can one combine both formulae?

Widom's Ansatz: $\boxed{m(t,h) = \begin{cases} t^\beta\, F_m^+(h/t^\Delta) & : t > 0 \\ (-t)^\beta\, F_m^-(h/(-t)^\Delta) & : t < 0 \end{cases}}$

β, Δ: Universal exponents (Δ: "gap exponent")
$F_m^\pm$: Scaling functions:



Data for different fields H should lie on the same curve
$\rightsquigarrow$ "data collapse"

(NB: In order to implement this type of plot, one must either know or fit β, Δ, and T_c!)

To derive relations between exponents, consider limiting cases

- $h \to 0,\ t \neq 0$ ($|t|$ small)

$$m(t, h \to 0) = |t|^\beta\, F_m^\pm(h/|t|^\Delta) \overset{!}{=} \begin{cases} 0 & : t > 0 \\ \pm A|t|^\beta & : t < 0 \end{cases}$$

$$\Rightarrow \quad F_m^+(0) = 0, \quad F_m^-(0) = \pm A \neq 0 \text{ (finite)}$$

$$\chi(h \to 0, t) = \frac{\partial m}{\partial h}\Big|_{h\to 0} = \frac{|t|^\beta}{|t|^\Delta} \frac{\mathrm{d}}{\mathrm{d}x} F_m^\pm(x)\Big|_{x\to 0} = |t|^{\beta-\Delta} F_m^{\pm\prime}(0) \overset{!}{\propto} |t|^{-\gamma}$$

$$\Rightarrow \ \gamma = \Delta - \beta, \quad \text{i.e., } \Delta = \beta + \gamma$$

- $\underline{t \to 0,\ h \neq 0}$ $\quad (|h|$ small)

  $m(t \to 0, h) = |t|^{\beta}\, F_m^{\pm}(h/|t|^{\Delta}) \overset{!}{\propto} |h|^{1/\delta}$ $\underline{\text{independent}}$ of t!

  $\Rightarrow$ Since $\Delta > 0$: $F_m^{\pm}(x) \sim |x|^{\lambda}$ for $x \to \infty$

  where λ has to be chosen such that $|t|^{\beta}\big|h/|t|^{\Delta}\big|^{\lambda}$ is independent of $|t|$ $\Rightarrow$ $\beta - \Delta\lambda = 0$, i.e., $\lambda = \beta/\Delta$

  Insert: $m(t \to 0, h) \sim |h|^{\lambda} = |h|^{\beta/\Delta} \overset{!}{\propto} |h|^{1/\delta}$

  $\rightsquigarrow \ \beta/\Delta = 1/\delta \quad \Rightarrow \quad \Delta = \beta\,\delta$

<u>Together</u>: $\boxed{\Delta = \gamma + \beta = \beta\,\delta}$

Thus we have determined the gap exponent Δ <u>and</u> deduced a scaling relation!

Derivation of other scaling relations is not yet possible, since the exponents α, ν, η do not appear in the critical behavior of the order parameter

$\rightsquigarrow$ Must find other, similar scaling hypotheses!

5.2.2 Scaling hypothesis for the free energy

Alternative to 5.2.1: Write <u>singular part</u> of the free energy density as

$$\boxed{f_s(t,h) = |t|^{2-\alpha} F_f^{\pm}(h/|t|^{\Delta})}$$

$\Rightarrow$ Specific heat at $h = 0$: $\quad c_H \sim \frac{\partial^2 f_s}{\partial t^2} \sim |t|^{-\alpha} F_f^{\pm}(0) + 0 \quad \checkmark$

Order parameter: $\quad m \sim \frac{\partial f_s}{\partial h}\Big|_{h=0} \sim |t|^{2-\alpha-\Delta} F_f^{\pm\prime}(0) \overset{!}{\sim} |t|^{\beta}$

$\Rightarrow\ 2 - \alpha - \Delta = \beta$

Susceptibility: $\quad \chi \sim \frac{\partial m}{\partial h}\Big|_{h=0} \sim |t|^{2-\alpha-2\Delta} F_f^{\pm\prime\prime}(0) \overset{!}{\sim} |t|^{-\gamma}$

$\Rightarrow\ 2 - \alpha - 2\Delta = -\gamma$

Taking everything together, we obtain again $\Delta = \beta + \gamma$ and an additional scaling relation $\boxed{\alpha + 2\beta + \gamma = 2}$

NB: The relation $m \sim |t|^{2-\alpha-\Delta} F_f^{\pm\prime}(h/|t|^{\Delta})$ also reproduces the scaling hypothesis 5.2.1 for the order parameter!

5.2.3 Scaling hypothesis for the correlation function

In the same spirit, one also constructs a scaling form for the two-point correlation function $G(\vec{r}) = \langle m(\vec{r}_0) m(\vec{r}_0 + \vec{r})\rangle - \langle m\rangle^2$.

$$\boxed{G(\vec{r}, t, h) = \frac{1}{r^{d-2+\eta}} F_G^{\pm}(r|t|^{\nu}, h/|t|^{\Delta})}$$

This yields scaling relations for η and ν

Example: $\chi|_{h=0} \sim \int \mathrm{d}^d r\, G(\vec{r}, t, h) \sim \int \mathrm{d}r\, r^{1-\eta} F_G^{\pm}(r|t|^{\nu}, 0)$

$\sim |t|^{-(2-\eta)\nu} \int \mathrm{d}y\, y^{1-\eta} F_G^{\pm}(y) \overset{!}{\propto} |t|^{-\gamma}$

$$\Rightarrow \quad \boxed{\gamma = \nu(2 - \eta)}$$

5.3 Scaling hypothesis and dimensional analysis

Question: How can we physically motivate the scaling hypothesis?

Rough answer (not quite correct, see Section 5.4):
At $T \to T_c$, the correlations length ξ diverges with $\xi \sim |t|^{-\nu}$. This divergence drives all other singularities: Close to T_c, the correlation length is the only relevant length scale.

$\rightsquigarrow$ "Dimensional analysis"

- ⋆ Dimensions:
  - – Singular part of the free energy density: $[f_s] = [\text{length}]^{-d} = [\xi]^{-d}$
  - – Order parameter density: $[m] = [\xi]^{d_m}$
    (d_m is an independent exponent!)
  - – Conjugate field h: $[h] \cdot [m] = [f_s] \;\Rightarrow\; [h] = [\xi]^{-d-d_m}$
- ⋆ Scaling functions: Composed of "dimensionless" quantities!
  - – Free energy density: $\boxed{f_s(t,h) \sim \xi^{-d}\, F_f^{\pm}(h\,\xi^{d+d_m})}$
    Specifically $h = 0$: $f_s \sim \xi^{-d} \overset{!}{\sim} |t|^{2-\alpha}$
    With $\xi \sim |t|^{-\nu}$, one obtains the Josephson relation: $\boxed{2-\alpha = d\nu}$
  - – Order parameter density: $\boxed{m(t,h) \sim \xi^{d_m}\, F_m^{\pm}(h\,\xi^{d+d_m})}$
    Specifically $h = 0$: $m \sim \xi^{d_m} \sim |t|^{\beta} \;\Rightarrow\; d_m = -\beta/\nu$
    Generally: $m \overset{!}{\sim} |t|^{\beta}\, F_m^{\pm}(h/|t|^{\Delta})$
    $\Rightarrow\; \Delta = \nu(d + d_m) = \nu d - \beta = 2 - \alpha - \beta$
    Also, following 5.2 a): $\Delta = \gamma + \beta = \beta\,\delta \;\Rightarrow\; \alpha + 2\beta + \gamma = 2$
  - – Correlation functions in Fourier space:
    $G(\vec{k}) = \int \mathrm{d}^d r\, G(\vec{r})\, \mathrm{e}^{i\vec{k}\cdot\vec{r}}$ with $G(\vec{r}-\vec{r}') = \langle m(\vec{r}) m(\vec{r}')\rangle - \langle m\rangle^2$
    Dimension: $[G(\vec{r})]:\; [m]^2 = [\xi]^{2d_m} = [\xi]^{-2\beta/\nu}$
    $[G(\vec{k})]:\; [m]^2[\text{length}]^d = [\xi]^{2d_m+d} = [\xi]^{d-2\beta/\nu}$
    $[k]:\; [\text{length}]^{-1} = [\xi]^{-1}$
    $\rightsquigarrow$ Scaling Ansatz: $\boxed{G(\vec{k}) \sim \xi^{d-2\beta/\nu}\, F_G^{\pm}(k\xi)}$
    Specifically $\xi \overset{|t|\to 0}{\to} \infty$: Result should not depend on ξ!
    $\Rightarrow\; F_G(x) \overset{x\to\infty}{\sim} x^{2\beta/\nu-d} \;\Rightarrow\; G(\vec{k}) \overset{\xi\to\infty}{\to} k^{2\beta/\nu-d} \overset{!}{\propto} k^{-2+\eta}$
    $\Rightarrow\; 2-\eta = d - 2\beta/\nu = \frac{1}{\nu}(d\nu - 2\beta) = \frac{1}{\nu}(2-\alpha-2\beta) = \gamma/\nu$
    $\Rightarrow\; \boxed{\gamma = \nu(2-\eta)}$

Conclusion: General recipe to construct scaling forms

- – Find dimensions of the (dependent and independent) variables
- – Construct scaling form from "dimensionless" quantities

In practice very successful. However, unfortunately, does not always work.

Problems that are already apparent at this point:

- Relations that contain the spatial dimension d (e.g., the Josephson relation) are obviously no longer valid at $d > d_c$ (in the mean-field regime). So what is going on here ?
- It is not clear a priori, why the dimension d_m should be independent of the other dimensions. (Not at all obvious, see next section!)

5.4 Influence of additional length scales

Preliminary consideration:

Rescale singular part of the Ginzburg-Landau free energy

$$\beta\mathscr{F}_{\text{sing}} = \int \mathrm{d}^d r \, \Big(\tfrac{1}{2}g(\nabla m)^2 + \tfrac{1}{2}bm^2 + \tfrac{1}{4}cm^4\Big) =: \int \mathrm{d}^d r \, f_s$$

Rescale: $\Phi = \sqrt{g}\, m$ and set $r_0 = b/g \propto (T - T_c)$, $u_0 = c/g^2$

$$\Rightarrow \quad \boxed{\beta\mathscr{F}_{\text{sing}} = \int \mathrm{d}^d r \, \Big(\frac{1}{2}(\nabla\Phi)^2 + \frac{1}{2} r_0 \, m^2 + \frac{1}{4} u_0 \, \Phi^4\Big)}$$

$\leadsto$ "Φ^4 theory": Typical starting point for field theories of Ising type phase transitions More generally – one of the favorite toy models in statistical field theory and quantum field theory

Dimensional analysis: $\beta\mathscr{F}_{\text{sing}}$ dimensionless

$$\begin{aligned} \rightarrow \quad & [f_s] = [\text{length}]^{-d}, \quad [\Phi] = [\text{length}]^{1-d/2} \\ & [r_0] = [\text{length}]^{-2}, \quad [u_0] = [\text{length}]^{d-4} \end{aligned}$$

Remark: If the correlation length ξ is the only length that matters, then one would always have

$$\begin{aligned} & r_0 \sim \xi^{-2} \Rightarrow \xi \sim (T - T_c)^{-1/2} \Rightarrow \nu = 1/2 \\ & f_s \sim \xi^{-d} \Rightarrow (2 - \alpha) = d\nu \end{aligned}$$

However, in fact, neither $\nu = 1/2$ nor $(2 - \alpha) = d\nu$ are always valid, and both together are only valid at $d = d_c = 4$!

Question: Where does the argument go wrong?

Answer: The correlation length is not the only length scale that matters!

In addition, other length scales come in: Microscopic length scales and a mean-field length scale. Depending on the spatial dimension, one of the two modifies the critical exponents.

5.4.1 Microscopic length scales and anomalous dimensions

⋆ Correlation length

As shown before: If the correlation length is the only relevant length scales, one would have $\xi \sim 1/\sqrt{|r_0|} \sim |T - T_c|^{-1/2} \quad \Rightarrow \nu = 1/2$

Now assume, a second length scale $l_0 \ll \xi$ exists (but $\xi \to \infty$ still drives the singularity).
→ New scaling Ansatz for ξ: $\xi \sim \frac{1}{\sqrt{|r_0|}} f_\xi^\pm(\underbrace{|r_0|\, l_0^2}_{\text{dimensionless}})$

Assume power law behavior: $\lim_{x\to 0} f_\xi^\pm(x) \sim x^\theta$
→ For $r_0 \to 0$, one has: $\xi \sim |r_0|^{-1/2+\theta} \sim |T-T_c|^{-1/2+\theta}$
$\Rightarrow \boxed{\nu = 1/2 - \theta}$

⇒ Introduction of an "anomalous dimension" θ solves our problem: Exponent θ may differ from 1/2.

Important: In order to introduce θ, we needed to assume the existence of a microscopic length l_0. This is an unusual thought in the theory of critical phenomena. However, the exponent θ turns out to be independent of the actual value of l_0!

⋆ Correlation function

A second independent anomalous dimension is hidden in the behavior of the correlation function $G(\vec{r})$

Dimension: $[G(\vec{r})] = [\Phi]^2 = [\text{length}]^{2-d}$,
$[G(\vec{k})] = [G(\vec{r})] \cdot [\text{length}]^d = [\text{length}]^2$
(since $G(\vec{k}) = \int \mathrm{d}^d r\, G(\vec{r}) \mathrm{e}^{i\vec{k}\cdot\vec{r}}$)

Consider specifically $T = T_c \;\Rightarrow\; \xi \to \infty$ is not a relevant length scale. In the absence of another length scale, we must have $G(\vec{k}) \sim k^{-2}$!

Make again a scaling Ansatz assuming that a microscopic length scale l_0 comes into play: $G(\vec{k}) = k^{-2} F_G^{(0)}(k l_0)$

Consider limit $k \to 0$ and assume power law: $\lim_{x\to 0} F_G^{(0)}(x) \sim x^\eta$

Then we have $\boxed{G(\vec{k}) \sim k^{-2+\eta}}$

$\rightsquigarrow$ G acquires an additional anomalous dimension η.
Φ acquires an additional anomalous dimension $\eta/2$.

5.4.2 "Mean-field" length scale

Now address next problem:
Why isn't the Josephson relation $(2-\alpha) = \nu d$ always valid?
(And why does it cross over into the mean-field relation $(2-\alpha) = \nu d_c$?)

To this end: Inspect dimensions of the parameters r_0, u_0.
$[r_0] \sim \text{length}^{-2}$ → length scale ξ
$[u_0] \sim \text{length}^{d-4}$ → new length scale

Corresponding scaling Ansatz for f_{sing}

$$f_s = \xi^{-d}\, \hat{f}(\underbrace{u_0\, \xi^{4-d}}_{\text{dimensionless}})$$

For $d < 4$: Argument of $\hat{f}(x)$: $x \to \infty$ for $T \to T_c$ or $\xi \to \infty$
For $d > 4$: Argument of $\hat{f}(x)$: $x \to 0$ for $T \to T_c$ or $\xi \to \infty$

$\rightsquigarrow$ Suggests solution for our problem:

$$\text{If} \left\{ \begin{array}{lcl} \lim_{x\to\infty} \hat{f}(x) & \sim & \frac{1}{x} \\ \lim_{x\to 0} \hat{f}(x) & \sim & \text{const} \end{array} \right\} \quad \Rightarrow \quad \left\{ \begin{array}{lcll} f_s & \sim & \xi^{-d} & \text{for } d < 4 \\ f_s & \sim & \frac{1}{u_0}\xi^{-4} & \text{for } d > 4 \end{array} \right.$$

$\Rightarrow$ This reproduces crossover from $(2-\alpha) = \nu d$ to $(2-\alpha) = 4\nu$ at $d = d_c = 4$.

5.4.3 Conclusion from Secs. 5.3 and 5.4

On principle, the dimensional analysis is a good method for constructing scaling hypotheses: It helps to derive relations between "dimensionless" and hence scale invariant quantities. However, this approach is not rigorous, since additional length scales apart from the correlation length exist and may influence the critical exponents. A more rigorous approach is provided by the renormalization group, see next chapter 6.

However, scaling arguments can help to derive theoretical predictions without much effort for a variety of problems. Some examples are given below.

5.5 Other applications of scaling arguments

5.5.1 Finite size scaling

Problem: In simulations (and more and more in experiments), system sizes are not macroscopic, but finite

Example: Simulations with periodic boundary conditions
$\rightsquigarrow$ No boundary effects, nevertheless no thermodynamic limit
$\rightsquigarrow$ Order parameter distribution $P(m, L)$

Scaling Ansatz:

Dimensions: $[m] = [\xi]^{d_m}$, $[L] = [\xi]$, $[P] = [\xi]^{-d_m}$ (since $\int \mathrm{d}m\, P(m) = 1$)

$$\Rightarrow \; P(m, L) = \xi^{-d_m} \tilde{P}(m\, \xi^{-d_m}, L/\xi) = L^{-d_m}\, \tilde{\tilde{P}}(m\, L^{-d_m}, L/\xi)$$

(with $\tilde{\tilde{P}}(y, x) = x^{d_m} \tilde{P}(y\, x^{d_m}, x)$)

Rewrite using $\xi = \hat{\xi} t^{-\nu}$ and $d_m = -\beta/\nu$: $P(m, L) = L^{\beta/\nu} \hat{P}(m\, L^{\beta/\nu}, tL^{1/\nu})$

Use this to calculate finite size effects on various quantities

Example: Moments of the order parameter

$$\langle |m| \rangle_L = \int \mathrm{d}m\, P(m, L)\, |m| = L^{-\beta/\nu}\, f_{\langle |m| \rangle}(tL^{1/\nu})$$
$$\langle m^n \rangle_L = \int \mathrm{d}m\, P(m, L)\, m^n = L^{-n\beta/\nu}\, f_{\langle m^n \rangle}(tL^{1/\nu})$$

(with $f_{\langle |m| \rangle}(x) = \int \mathrm{d}y \hat{P}(y, x) |y|$, $\quad f_{\langle m^n \rangle}(x) = \int \mathrm{d}y \hat{P}(y, x)\, y^n$)

Application: Determining T_c and exponents β, ν from simulations of finite systems. Need simulation data for a set of different sizes L

(a) Binder cumulant method to find T_c

Consider specifically $t = 0$, i.e. $T = T_c$: $\Rightarrow$ $\langle m^{2n} \rangle \sim L^{-2n\beta/\nu} \hat{f}_{\langle m^{2n} \rangle}(0)$

$\Rightarrow$ $\boxed{U_L = \frac{\langle m^2 \rangle^2}{\langle m^4 \rangle}}$ is independent of system size L!

$\rightsquigarrow$ Plot U_L vs. T for different L. All curves intersect at $T = T_c$!

(Note: $\langle m^2 \rangle / \langle |m| \rangle^2$ would also work, but is less popular.)

(b) Scaling plot method to find β, ν (after finding T_c via (a))

- Guess β, ν and plot $|m|\, L^{-\beta/\nu}$ versus $|t| L^{-1/\nu}$ for various L
- Vary β and ν until the curves collapse onto one scaling curve (or use a fitting algorithm that does this for you).

5.5.2 Scaling hypothesis in polymer physics

System: Linear macromolecules in "good" solvent

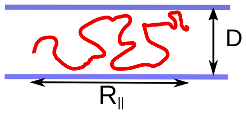
Number of repeat units (monomers): N

Extension: "Gyration radius": $R_g = a N^\nu$,
with ν: Flory exponent ($\nu = 0.588... \approx 3/5$)

Remark: The calculation of ν is an interesting problem of statistical physics in itself which involves advanced methods of statistical field theory. Polymers in good solvent (so-called self-avoiding walks) can be described by a $\vec{\phi}^4$ theory in the limit where the order parameter $\vec{\phi}$ has zero dimensions (de Gennes, 1972)).

Assumption (de Gennes): R_g is the only relevant length scale in such systems. This allows to deduce many relations, which mostly turn out to be correct!

Example: Polymer in a tube of diameter D



Question: What is the lateral extension $R_\|$?

Scaling Ansatz: $R_\|(D R_g) = R_g f_{R_\|}(R_g/D)$

with conditions: $R_\|(D \to \infty, R_g) \sim R_g \quad \to \quad f(x) \xrightarrow[x \to 0]{} 1$

$R_\|(D \to 0, R_g) \propto N \quad \to \quad f(x) \xrightarrow[x \to \infty]{} x^\mu$

with $R_g^{\mu+1} = N^{\nu(\mu+1)} \overset{!}{\sim} N \;\Rightarrow\; \mu = \frac{1}{\nu} - 1$

$\rightsquigarrow$ In case $D \ll R_g$, one obtains $R_\| \sim R_g^{\mu+1}/D^\mu$

and hence $\boxed{R_\| \sim a N (a/D)^{1/\nu - 1}}$

(typical 'back of the envelope' scaling calculation!)

(more examples: Exercises)

Chapter 6

Renormalization

Previous chapter: Focus on behavior of system close to critical points
⇝ Power laws, critical exponents, relations between critical exponents

Could be described in terms of a scaling hypothesis.
However, the physical basis for the scaling hypothesis was not clear

This section: Theoretical framework that explains origin of scaling laws

⇝ Provides a way to calculate critical exponents
But also: A way of thinking about scale-invariant systems which has applications far beyond the theory of phase transitions !

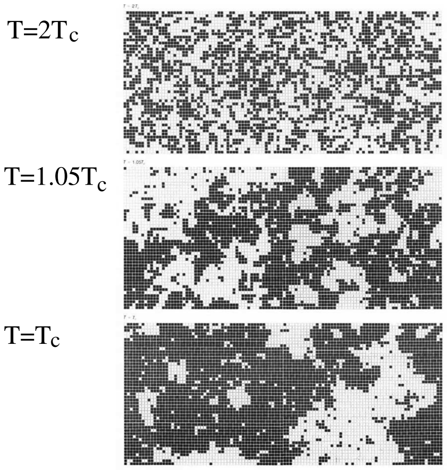
6.1 Kadanoff's argument for the scaling hypothesis[1]

Configurations in the 2D Ising model[1] upon approaching T_c from above: Larger and larger clusters appear, but small clusters are still present.

⇝ Self-similar structure

⇝ Motivates a description in terms of successive coarse-graining steps (Kadanoff, 1966).

⇝ Justifies scaling hypothesis and establishes a connection to the diverging correlation length.



Starting point: Ising model $\beta\mathscr{H} = -\underbrace{\beta J}_{K}\sum_{\langle ij\rangle} S_i S_j - \underbrace{\beta H}_{h}\sum_i S_i$

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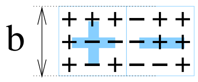
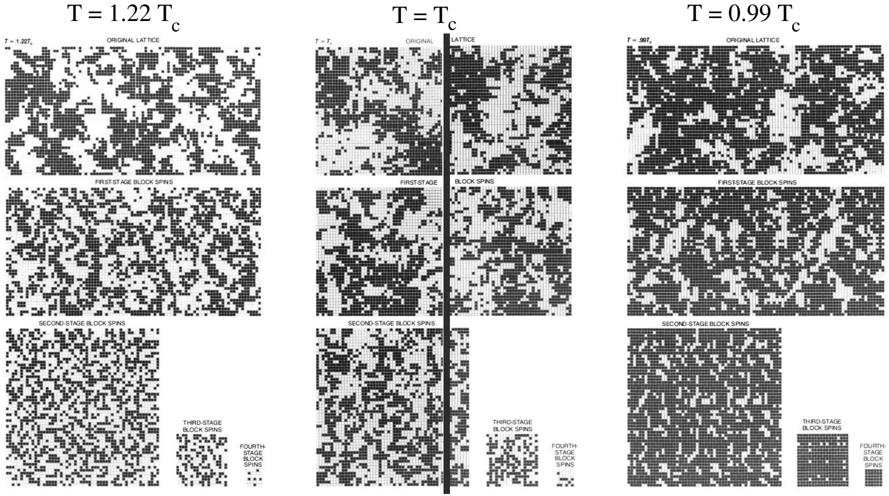
[1] Figures in this section are taken from: Kenneth G. Wilson, Scientific American 1979, 158, *Problems in Physics with Many Scales of Length*

Block spins: Combine spins in blocks with side length b.



$\rightsquigarrow$ "Coarse-graining": Every block is characterized by one block spin variable $S_I = \pm 1$.
(e.g., $S_i = \text{sign} \sum_{i \in I} S_i$)

Example (K. G. Wilson, Scientific American 1979):



Block spins: T' is higher … the same … lower than T

See also Douglas Ashton: https://www.youtube.com/watch?v=MxRddFrEnPc

Assumptions:

(i) "Blockspins have only pairwise interactions with direct neighbors"
$\rightarrow$ one can replace partition function $\sum_{\{S_i\}} \mathrm{e}^{-\beta \mathscr{H}}$ by $\sum_{\{S_I\}} \mathrm{e}^{-\beta \mathscr{H}_l}$
such that $\sum_{\{S_i\}} \mathrm{e}^{-\beta \mathscr{H}} = \sum_{\{S_I\}} \mathrm{e}^{-\beta \mathscr{H}_l}$
with $\beta \mathscr{H}_b = -K_b \sum_{\langle ij \rangle} S_I S_J - h_b \sum_I S_I + \text{const}.$

Then we have:

- ⋆ Correlation length: $\xi_b = \xi / b$
- ⋆ Functional form of singular part of free energy is the same:
  $N b^{-d} f_s(t_b, h_b) = N f_s(t, h)$, i.e., $f_s(t_b, h_b) = b^d f_s(t, h)$

(ii) Close to the critical point, we postulate: $t_b = t\, b^{y_t}$, $h_b = h\, b^{y_h}$
Reasoning: Simplest relation that ensures $t_b = h_b = 0$ for $t = h = 0$
and $(h_b \to -h_b,\ t_b \to t_b)$ for $h \to -h$
Since $\xi_b < \xi$, we must have $y_t, y_h > 0$
(ξ_b smaller $\rightsquigarrow$ (h_b, t_b) further away from critical point)

NB: Assumptions, no proof. In general, only approximately valid.

Consequences:

Free energy assumes the form: $f_s(t, h) = b^{-d}\, f_s(t\, b^{y_t}, h\, b^{y_h})$
Now choose: $b = |t|^{-1/y_t} \Rightarrow f_s(t, h) = |t|^{d/y_t}\, f_s(\pm 1, h|t|^{-y_h/y_t})$

$\rightsquigarrow$ Scaling hypothesis: $f_s(t, h) = |t|^{2-\alpha} F_f^{\pm}(h/|t|^{\Delta})$
with $2 - \alpha = d/y_t$, $\Delta = y_h/y_t$, $F_f^{\pm}(x) = f_s(\pm 1, x)$

NB: Also implies $\nu = 1/y_t$: For $b = |t|^{-1/y_t}$, we have $f_s(t, 0) = b^{-d} f_s(\pm 1, 0)$
and hence $\xi(t) = b\, \xi(\pm 1)$, thus $\xi(t) = |t|^{-1/y_t}\, \xi(\pm 1)$

Conclusions: Another motivation of the scaling hypothesis.
Otherwise, not much new insight

- Idea of self similarity (assumption (i)) not new
  $\widehat{=}$ Idea, that diverging correlation length drives singularities (Chap. 5)
- Exponents y_t, y_h still cannot be calculated.

However: Guides our thinking in a direction that will turn out very fruitful:
Block spin summation → Thinning of degrees of freedom
$\rightsquigarrow$ Will lead to a better understanding of critical phenomena

6.2 Basic idea of renormalization

Here: First schematic sketch. Systematization of Kadanoff's idea.

Consider a system with degrees of freedom $\{\sigma\}$ and coupling constants $\vec{K} = (K_1, \cdots K_n)$

Examples

- Ising model: $\beta\mathscr{H} = +K_1 \sum_i S_i + K_2 \sum_{\langle ij \rangle} S_i S_j + \cdots$
  Degrees of freedom: S_i; Coupling constants: $K_1, K_2, \cdots$
- Ginzburg Landau model: $\beta\mathscr{H} = \int \mathrm{d}^d r \big\{ g + \frac{1}{2}(\nabla\Phi)^2 + \frac{1}{2} r_0 \Phi^2 + \frac{1}{4} u_0 \Phi^4 + \cdots \big\}$
  Degrees of freedom: $\Phi(\vec{r})$; Coupling constants: $r_0, u_0, \cdots$

Coupling constants may be zero. However, the set of coupling constants should be "complete" in a sense to be defined below.

$\rightsquigarrow$ Hamiltonian has the form: $\beta\mathscr{H} = \text{const.} + \sum K_\alpha \, \psi_\alpha(\{\sigma\})$

6.2.1 Renormalization group (RG) transformation

Two basic steps

(i) Thinning out: Replace locally b^d degrees of freedom by one
e.g., $\{S_i\}_{i \in I} \to S_I$ (block spin); $\Phi(\vec{r}) \to \Phi(\vec{R}) = \int_{\vec{r} \in \Omega_{\vec{R}}} \mathrm{d}^d r \; \Phi(\vec{r})$

(ii) Rescale such that the new system with the new degrees of freedom has locally the same structure than the old one (possibly with new coupling constants) $\rightsquigarrow$ $N \to N/b^d$, i.e., $V \to V/b^d$

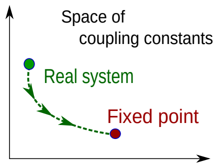
⇒ New Hamiltonian: $\beta\mathscr{H}' = \text{const.}' + \sum K'_\alpha \Psi_\alpha(\{\sigma'\})$ with $\sum\limits_{\{\sigma\}} \mathrm{e}^{-\beta\mathscr{H}} = \sum\limits_{\{\sigma'\}} \mathrm{e}^{-\beta\mathscr{H}'}$

Set of coupling constants "complete" → no new coupling constants

$\rightsquigarrow$ Free energy: $(\sum_{\{\sigma\}} \mathrm{e}^{-\beta\mathscr{H}} = \mathrm{e}^{-\beta N(g + f_s(\vec{K})} \overset{!}{=} \sum_{\{\sigma'\}} \mathrm{e}^{-\beta\mathscr{H}'} = \mathrm{e}^{-\beta(N(g+g') + \frac{N}{b^d} f_s(\vec{K}'))})$
⇒ $f_s(\vec{K}) = f_s(\vec{K}') \frac{1}{b^d} + g'(\vec{K})$
with $g'(\vec{K})$: Regular contribution from local integration,
does not contribute to the singular behavior

Together: Defines map: $\vec{K} \to R_b(\vec{K})$
with the properties of a semi-group: $R_{b_1} \circ R_{b_2} = R_{b_1 \cdot b_2}$
(no full group because in general, R cannot be inverted)

6.2.2 Fixed points, RG flow, and critical behavior



Idea: Critical behavior is associated with fixed points $\vec{K}^*$

of the RG transformation: $R_b(\vec{K}^*) = \vec{K}^*$

Fixed point $\widehat{=}$ Self similar system

In general reached after infinitely many iterations

(Local self similarity is not assumed!)

Consequences for the correlation length ξ

- At the fixed point, one has either $\xi^* = 0$ or $\xi^* \to \infty$

  (Reason: $\xi^* \xrightarrow{R_b} \xi^*/b = \xi^*$ only possible for $\xi^* = 0, \infty$)

  $\xi^* = 0$: Trivial fixed point

  $\xi^* = \infty$: Critical fixed point

- All points attracted by critical fixed point have $\xi \to \infty$

  (Reason: $\xi(\vec{K}) = b\xi(R_b(\vec{K})) = \cdots = b^n \xi(R_b^n(\vec{K}))$

  $= \cdots = b^\infty \xi(\vec{K}^*) = \infty$, since $b > 1$)

Behavior in the vicinity of a critical fixed point

Consider isolated fixed points (generalization is not difficult)

Expand about fixed point: $\vec{K} = \vec{K}^* + \delta\vec{K}$, $\delta\vec{K}$ small

RG transformation: $\vec{K}' = R_b(\vec{K}^* + \delta\vec{K}) = \underbrace{R_b(\vec{K}^*)}_{\vec{K}^*} + \underbrace{\sum_\alpha \frac{\partial R_b(\vec{K})}{\partial K_\alpha}\delta K_\alpha}_{=:M_b\delta\vec{K}}$

$\Rightarrow$ $\vec{K}' = \vec{K}^* + \delta\vec{K}'$ with $\boxed{\delta\vec{K}' = M_b\,\delta\vec{K}}$

linearized RG transformation

Assume M_b can be diagonalized and has real Eigenvalues

(usually correct at critical points. Otherwise, statements below are not correct)

Eigenvalue equation: $M_b\vec{e}^{(\nu)} = \lambda_b^{(\nu)}\vec{e}^{(\nu)}$

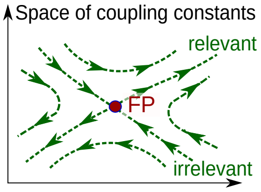
We have: $M_b^n\vec{e}^{(\nu)} = (\lambda_b^{(\nu)})^n\vec{e}^{(\nu)} \quad \Rightarrow \quad \lambda_{b^n}^{(\nu)} = (\lambda_b^{(\nu)})^n$

$M_1 = \mathbb{1} \;\Rightarrow\; \lambda_1^{(\nu)} = \lambda_{b^0}^{(\nu)} = 1$

Together: $\boxed{\lambda_{b^n}^{(\nu)} = b^{n y_\nu}}$ with $y_\nu = \ln\lambda_b^{(\nu)}/\ln b$

Insert: $\delta\vec{K} = \sum_\nu a^{(\nu)}\,\vec{e}^{(\nu)}$

$\Rightarrow$ $\delta\vec{K}' = M_b\delta\vec{K} = \sum_\nu a^{(\nu)}\lambda_b^{(\nu)}\vec{e}^{(\nu)} = \sum_\nu a^{(\nu)}\vec{e}^{(\nu)}b^{y_\nu}$



$\Rightarrow$ Some components of $\delta\vec{K}$ grow, others shrink

$y_\nu > 0$: growth – ”relevant” directions

$y_\nu < 0$: shrink – ”irrelevant” directions

$y_\nu = 0$: ”marginal” directions

6.2.3 Relation to scaling hypothesis

Express f_s in Eigendirections of M in the vicinity of the fixed point:

$$f_s(\delta\vec{K}) = \tfrac{1}{b^d}\, f_s(b^{y_1}\,\delta K_1, b^{y_2}\,\delta K_2, \cdots) = b^{-nd}\, f_s(b^{ny_1}\delta K_1, b^{ny_2}\delta K_2, \cdots)$$

Assume we have two relevant scaling fields t and h (e.g., Ising type systems)

$$\Rightarrow\ f_s(t, h, \delta K_3, \cdots) = b^{-nd}\, f_s(b^{ny_t}t, b^{ny_h}h, b^{ny_3}\delta K_3, \cdots)$$

Consider $t \to 0$ and choose $b^n = |t|^{-1/y_t}$ (OK since $b > 1$)

$$\begin{aligned}\Rightarrow\ f_s(t, h, \delta K_3, \cdots) &= t^{d/y_t}\, f_s(\pm 1, t^{-y_h/y_t}h, t^{-y_3/y_t}\delta K_3, \cdots)\\ &\approx t^{d/y_t}\, f_s(\pm 1, t^{-y_h/h_t}h, 0, \cdots)\end{aligned}$$

$\rightsquigarrow$ Motivates again a scaling hypothesis, however, more systematic approach than before. Points at a way to actually calculate critical exponents!

Remark: Here we have made the assumption that one can take the limit $f_s(\cdots, \delta K_3 \to 0, \cdots) \overset{t\to 0}{\to} f_s(\cdots, \delta K_3 = 0, \cdots)$ without introducing a new t-dependence. This is not always the case for irrelevant variables. If $f_s \sim \delta K_x^\alpha$ for certain irrelevant variables, the critical exponents may change (see Sec. 5.4). Such irrelevant variable are called dangerous.

(Example: In the Ginzburg-Landau theory, u_0 is irrelevant at $d > 4$, but it still makes a difference whether $u_0 = 0$ or $u_0 > 0$, see Sec. 6.5)

6.2.4 Final Remarks

⋆ Differential form of the RG equations: Consider $\vec{K} \to R_{b^n}(\vec{K}) =: \vec{K}(l = b^n)$

$$\Rightarrow\ \text{RG flow equations: } \frac{\mathrm{d}\vec{K}}{\mathrm{d}l} = \frac{1}{l}\underbrace{\lim_{\epsilon\to 0}\frac{1}{\epsilon}(R_{l(1+\epsilon)}(\vec{K}) - R_l(\vec{K}))}_{\beta(\vec{K}),\text{independent of } l}$$

$$\Rightarrow\ \frac{\mathrm{d}\vec{K}}{\mathrm{d}s} = \beta(\vec{K}) \text{ with } s = \ln l \qquad \text{Beta function}$$

⋆ Universality:

Many different systems are attracted by the same fixed point. Every fixed point defines a universality class. In combination with the Ginzburg-Landau theory, this explains why the universality class (the fixed point), in general, only depends on the spatial dimension, the symmetry of the order parameter, and the range of the interactions.

(The assumption that most parameters in the Ginzburg-Landau expansions correspond to irrelevant dimensions can be made plausible by dimensional considerations, similar to Sec. 5.4.2, see Sec. 6.5.)

⋆ In practice ... it is often not possible to do exact RG transformations. Numerical approximations and/or expansions are necessary. Nevertheless, the RG approach is valuable because it ...

- Gives physical explanation for the existence of critical exponents, scaling behavior, and universality
- Provides a starting point for systematic investigations
- Represents a new way of thinking about critical phenomena

6.3 Examples of exact RG transformations

Illustration of RG procedure. Exact renormalization is possible, but "boring" results. More complex, nontrivial examples will follow later.

6.3.1 One dimensional Ising model

Example of a renormalization group calculation in real space

System: One dimensional Ising chain with periodic boundary conditions

$\beta\mathscr{H} = -K\sum_{1^N} S_iS_{i+1} - h\sum_i S_i = \tilde{H}(K,h;\{S_i\}) \quad (S_{N+1} = S_1)$

Partition function: $\mathscr{Z} = \sum_{\{S_i\}} \mathrm{e}^{-\beta H}$

RG transformation

(i) Thinning: Average over spins S_i with odd index i

(ii) Rescaling: $S'_j = S_{2j}$

$$\Rightarrow\ \mathscr{Z} = \sum_{\{S_i\}} \mathrm{e}^{-\beta\mathscr{H}\{S_i\}} \overset{!}{=} \sum_{\{S'_j\}} \mathrm{e}^{-\beta\mathscr{H}'\{S'_j\}}$$

Hence: $\sum_{S_2}\sum_{S_4}\cdots\{\sum_{S_1}\sum_{S_3}\cdots \mathrm{e}^{K\sum S_iS_{i+1}+h\sum S_i}\}$

$$= \sum_{S_2}\mathrm{e}^{hS_2}\sum_{S_4}\mathrm{e}^{hS_4}\cdots\big[\sum_{S_1}\mathrm{e}^{S_1(h+K(S_N+S_2))}\big]\big[\sum_{S_3}\mathrm{e}^{S_3(h+K(S_1+S_3))}\big]\cdots$$

$$= \sum_{S_2}\mathrm{e}^{hS_2}\sum_{S_4}\mathrm{e}^{hS_4}\cdots\big[2\cosh(h+K(S_N+S_2))\big]\big[2\cosh(h+K(S_2+S_4))\big]\cdots$$

$$\overset{S'_j=S_{2j}}{=} \sum_{\{S'_j\}}\mathrm{e}^{h'\sum S'_j+K'\sum S'_jS'_{j+1}+Ng} = \sum_{\{S'_j\}}\mathrm{e}^{-\tilde{H}(K',h',\{S'_j\})+Ng(K,h)}$$

where we choose K', h', g such that for all $x, y = \pm 1$:

$$\mathrm{e}^{\frac{h}{2}(x+y)}2\cosh(h+K(x+h)) =: \mathrm{e}^{2g+h'\frac{x+y}{2}+K'\,xy}$$

$$\Rightarrow \left\{\begin{array}{lll} x=-y & : 2\cosh(h) = \mathrm{e}^{2g-K'} & (i) \\ x=y=1 & : \mathrm{e}^{h}2\cosh(h+2K) = \mathrm{e}^{2g+h'+K'} & (ii) \\ x=y=-1 & : \mathrm{e}^{-h}2\cosh(-h+2K) = \mathrm{e}^{2g-h'+K'} & (iii) \end{array}\right\}$$

$\rightsquigarrow$ Three equations for three unknowns

$$\Rightarrow\ \mathscr{Z} = \sum_{\{S'_j\}}\mathrm{e}^{-\tilde{H}(K',h',\{S'_j\})+Ng(K,h)}$$

$$\text{with}\quad \begin{array}{rcl} g &=& \frac{1}{8}\ln\big(2^4\cosh^2(h)\cosh(2K+h)\cosh(2K-h)\big) \\ K' &=& \frac{1}{4}\ln\big(\cosh(2K+h)\cosh(2K-h)/\cosh^2(h)\big) \\ h' &=& h+\frac{1}{2}\ln\big(\cosh(2K+h)/\cosh(2K-h)\big) \end{array}$$

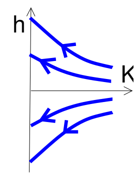
Transformation $(K,h) \to (K',h') = R(K,h)$ defines RG flow

Function $g(K,h)\ \widehat{=}$ regular contribution due to integration

Needed in order to calculate the free energy $\beta F = -\ln\mathscr{Z}$

$(-\frac{\beta F}{N} = g(K,h) + \frac{1}{2}g(R(K,h)) + \frac{1}{4}g(R^2(K,h)) + \cdots = \sum_{j=0}^{\infty}(\frac{1}{2})^j g(R^j(K,h)))$

Analysis of RG flow



- ⋆ $h = 0 \Rightarrow h' = 0$
  $h > 0 \Rightarrow h' > h$
  $h < 0 \Rightarrow h' < h$
- ⋆ For all h: $K' \leqslant K$

(Check: Set $x = \mathrm{e}^{-4K}$, $y = \mathrm{e}^{-2h}$

$0 < x < 1 \Rightarrow 1 + xy < 1 + y,\ x + y < 1 + y$

$\Rightarrow x' = \frac{(1+y)^2}{(1+xy)(x+y)}\,x > x \quad ✓$)

Fixed points:

- ⋆ $K = 0,\ h$ arbitrary ($\widehat{=}\ T \to \infty$): $\xi = 0$
  Trivial fixed points, volume phase
- ⋆ $K = \infty,\ h = 0$ ($\widehat{=}\ T = 0$): $\xi \to \infty$ according to Sec. 3.2
  Critical fixed point, but unreachable at $T \neq 0$

Critical exponents and scaling behavior: Use scaling variables h and $x = \mathrm{e}^{-4K}$
$\Rightarrow$ Critical fixed point at $(x^*, h^*) = (0, 0)$
Linearization: $\binom{x}{h} = \binom{x^*}{h^*} + \binom{\delta x}{\delta h} \ \Rightarrow\ \binom{\delta x'}{\delta h'} = \mathbf{M} \binom{\delta x}{\delta h}$
with $\mathbf{M} = \begin{pmatrix} 4 & 0 \\ 0 & 2 \end{pmatrix} = \begin{pmatrix} 2^{y_x} & 0 \\ 0 & 2^{y_h} \end{pmatrix} \ \Rightarrow\ y_x = 2,\ y_h = 1$
$\Rightarrow$ Free energy scaling: $f_s(x, h) = x^{d/y_x}\, F_f(h\, x^{-y_h/y_x}) = x^{1/2}\, F_f(h\, x^{-1/2})$

6.3.2 The Gaussian model

Example for a renormalization in Fourier space

System: Ginzburg Landau model (Φ^4 model) with $u_0 = 0$

$$\beta\mathscr{F} = \int \mathrm{d}^d r\, \left\{\tfrac{1}{2}(\nabla\Phi)^2 + \tfrac{1}{2} r_0 \Phi^2 - h\Phi\right\}$$

Makes sense only for $r_0 > 0$ (otherwise, $\mathscr{Z}$ diverges)
In that case, exactly soluble ("trivial")
Consider this system in Fourier space, with microscopic cutoff Λ

$$\beta\mathscr{F} = \tfrac{1}{V} \textstyle\sum_{|\vec{k}|<\Lambda} \left\{\tfrac{1}{2}|\Phi_{\vec{k}}|^2 (r_0 + k^2)\right\} - h\Phi_0$$

(Prefactor: Discretize $\frac{1}{(2\pi)^d} \int \mathrm{d}^d k \to \frac{1}{(2\pi)^d} \sum_{\vec{k}} v_{\vec{k}}$ with $v_{\vec{k}} = \frac{(2\pi)^d}{V}$)

Partition function: $\mathscr{Z} = \int \mathscr{D}[\Phi] \mathrm{e}^{-\beta\mathscr{F}} = \Big[\prod\limits_{|\vec{k}|<\Lambda} \frac{1}{V} \int \mathrm{d}\Phi_{\vec{k}}\Big] \mathrm{e}^{\frac{1}{V} \sum\limits_{\vec{k}} \frac{1}{2}|\Phi_{\vec{k}}|^2 (r_0 + k^2) - h\Phi_0}$

RG transformation

(i) Thinning: Integrate over degrees of freedom with short wavelengths
$\rightsquigarrow$ Calculate partial trace for components $\Phi_{\vec{k}}$ with $\Lambda/l < |\vec{k}| < \Lambda$
Easy here, since different $\vec{k}$ modes decouple in $\beta\mathscr{F}$

$$\begin{aligned} \Rightarrow\ \mathscr{Z} &= \textstyle\prod_{|\vec{k}|<\Lambda/l} \frac{1}{V} \int \mathrm{d}\Phi_{\vec{k}} \{ \prod_{\Lambda/l<|\vec{k}|<\Lambda} \frac{1}{V} \int \mathrm{d}\Phi_{\vec{k}} \mathrm{e}^{\frac{1}{V} \sum_{\vec{k}} \frac{1}{2}|\Phi_{\vec{k}}|^2 (r_0+k^2) - h\Phi_0} \} \\ &= \textstyle\prod_{|\vec{k}|<\Lambda/l} \frac{1}{V} \int \mathrm{d}\Phi_{\vec{k}} \mathrm{e}^{\frac{1}{V} \sum_{|\vec{k}|<\Lambda/l} \frac{1}{2}|\Phi_{\vec{k}}|^2 (r_0+k^2) - h\Phi_0} \prod\limits_{\Lambda/l<|\vec{k}|<\Lambda} \underbrace{\tfrac{1}{V} \int \mathrm{d}\Phi_{\vec{k}} \{\mathrm{e}^{\frac{1}{V}\frac{1}{2}|\Phi_{\vec{k}}|^2 (r_0+k^2)}\}}_{\pi/(r_0+k^2)} \\ &= \textstyle\prod_{|\vec{k}|<\Lambda/l} \frac{1}{V} \int \mathrm{d}\Phi_{\vec{k}} \mathrm{e}^{\frac{1}{V} \sum_{|\vec{k}|<\Lambda/l} \frac{1}{2}|\Phi_{\vec{k}}|^2 (r_0+k^2) - h\Phi_0} \exp(V g(r_0)) \end{aligned}$$

with $g(r_0) = \frac{1}{V} \sum_{\Lambda/l<|\vec{k}|<\Lambda} \ln\left(\frac{\pi}{r_0+k^2}\right) \approx \frac{1}{(2\pi)^d} \int_{\Lambda/l}^{\Lambda} \mathrm{d}^d k \ln\left(\frac{\pi}{r_0+k^2}\right)$: regular

(ii) Rescaling such that new system looks like old system (same cutoff Λ)
$\vec{r}' = \vec{r}/l,\ \vec{k}' = \vec{k}l,\ V' = V/l^d,\ \Phi'_{\vec{k}} = l^\theta \Phi_{\vec{k}'}$ (with θ: to be determined)

$$\Rightarrow\ \mathscr{Z} = \mathrm{e}^{V g(r_0)} \textstyle\prod_{|\vec{k}'|<\Lambda} \frac{l^{-2\theta-d}}{V'} \int \mathrm{d}\Phi'_{\vec{k}'} \mathrm{e}^{\frac{1}{V'} l^{-2\theta-d} \sum_{|\vec{k}'|<\Lambda} |\Phi'_{\vec{k}'}|^2 (r_0 + k'^2/l^2) - h l^{-\theta} \Phi'_0}$$

| Same structure $\Rightarrow$ term $\frac{1}{2}(\nabla\Phi)^2 \sim |\Phi_{\vec{k}}|^2 k^2$ must look the same
| $\Rightarrow\ l^{-d-2\theta-2} \overset{!}{=} 1 \ \Rightarrow\ \theta = -(1 + d/2)$

$$= \mathrm{e}^{V g(r_0)} \textstyle\prod_{|\vec{k}'|<\Lambda} \frac{l^2}{V'} \int \mathrm{d}\Phi'_{\vec{k}'} \mathrm{e}^{\frac{1}{V'} \sum_{|\vec{k}'|<\Lambda} |\Phi'_{\vec{k}'}|^2 (r_0 l^2 + k'^2) - h l^{1+d/2} \Phi'_0}$$

$\Rightarrow$ Recursion relations: $\boxed{r' = r_0 l^2,\ h' = h\, l^{1+d/2}}$

Differential form: for the flow $r(s)$, $h(s)$ with $s = \ln l$

Consider infinitesimal RG step $l \approx 1$ (but $l > 1$): $l = \exp(\mathrm{d}s) \approx 1 + \mathrm{d}s$

$$(r_0 = r(s) \overset{\mathrm{RG}}{\to} r' = r(s + \mathrm{d}s) = r(s)\,\mathrm{e}^{2\mathrm{d}s} = r(s) + 2r(s)\,\mathrm{d}s + \mathscr{O}(\mathrm{d}s^2)$$
$$h = h(s) \overset{\mathrm{RG}}{\to} h' = h(s + \mathrm{d}s) = h(s)\,\mathrm{e}^{(1+d/2)\mathrm{d}s} = h(s) + (1 + \tfrac{d}{2})\,h(s)\,\mathrm{d}s + \mathscr{O}(\mathrm{d}s^2)$$

$$\Rightarrow \boxed{\mathrm{d}r/\mathrm{d}s = 2r} \quad \text{and} \quad \boxed{\mathrm{d}h/\mathrm{d}s = (1 + d/2)h}$$

Fixed point: $r^* = 0,\ h^* = 0$

Expansion about fixed point:

$$r_0 = r^* + \delta r \ \Rightarrow \delta r'(s) = \delta r\,\mathrm{e}^{2s} = \delta r\, l^2$$
$$h = h^* + \delta h \ \Rightarrow \delta h'(s) = \delta h\,\mathrm{e}^{(1+d/2)s} = \delta h\, l^{1+d/2}$$

$\Rightarrow$ $r(\propto t)$ and h are relevant directions (only $t > 0$ is possible) with exponents $y_r = y_t = 2,\ y_h = 1 + \frac{d}{2}$

Critical exponents and scaling forms

Correlation length: $\nu = 1/y_t = \frac{1}{2}$

Free energy: $f_s(t, h) = l^{-d} f_s(t\,l^{y_t}, h\,l^{y_h}) \overset{cf.\,6.1}{=} t^{d/y_t} F_f^{+}(h t^{-y_h/y_t})$

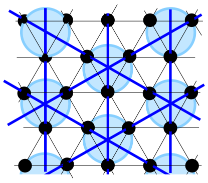
$$\Rightarrow \alpha = 2 - d/y_t = 2 - \tfrac{d}{2}, \quad \Delta = y_h/y_t = \tfrac{1}{2} + \tfrac{d}{4}$$
$$\beta = 2 - \alpha - \Delta = \tfrac{d}{4} - \tfrac{1}{2}, \quad \gamma = 2 - \alpha - 2\beta = 1,$$
$$\delta = \Delta/\beta = \tfrac{d+2}{d-2}, \quad \eta = 2 - \gamma/\nu = 0$$

6.4 Renormalization of the 2D Ising model

Example for an approximate RG treatment in real space (Niemeijer, van Leeuwen, 1974)

System: Ising model on the triangular lattice: $\beta\mathscr{H} = -K \sum_{\langle ij \rangle} S_i S_j - h \sum_i S_i$

RG transformation



(i) Thinning: Combine three spins $\{S_1^I, S_2^I, S_3^I\}$

$\to$ New triangular lattice

New spin: Majority rule $S_I' = \mathrm{sign}(S_1^I + S_2^I + S_3^I)$

(ii) Rescaling: Shrink lattice by factor $b = \sqrt{3}$

$\Rightarrow$ Exact RG transformation would read $\mathscr{Z} = \sum_{\{S_I'\}} \mathrm{e}^{-\beta\mathscr{H}'} = \sum_{\{S_i\}} \mathrm{e}^{-\beta\mathscr{H}}$

$$\Rightarrow \beta\mathscr{H}'(\{S_I\}) = \ln\Big[\sum_{\{S_i\}} \mathrm{e}^{-\beta\mathscr{H}} \prod_I \delta_{S_I, \mathrm{sign}(\sum_\alpha S_\alpha^I)}\Big]$$

Approximate evaluation of RG recursion relations

Separate $\mathscr{H}$ into $\mathscr{H} = \mathscr{H}_0 + V$ such that

$\mathscr{H}_0$: Contains no couplings between blocks

$$\mathscr{H}_0 = -K \textstyle\sum_I (S_1^I S_2^I + S_1^I S_3^I + S_2^I S_3^I) - h \sum S_i$$

V : Rest ($\mathscr{H} - \mathscr{H}_0$), treated as "perturbation"

Define $\langle O\rangle_0 = \dfrac{\sum_{\{S_i\}} O\, \mathrm{e}^{-\beta\mathscr{H}_0} \prod_I \delta_{S_I,\mathrm{sign}(\sum_\alpha s^I_\alpha)}}{\sum_{\{S_i\}} \mathrm{e}^{-\beta\mathscr{H}_0} \prod_I \delta_{S_I,\mathrm{sign}(\sum_\alpha s^I_\alpha)}}$

Expectation value with respect to $\mathscr{H}_0$ for fixed blockspins S'_I

Then we have exactly: $\boxed{\mathrm{e}^{-\beta\mathscr{H}'} = \mathrm{e}^{\frac{N}{3}A+B\sum_I S'_I}\,\langle \mathrm{e}^{-\beta V}\rangle_0}$

with $\binom{A}{B} = \frac{1}{2}\ln(\mathrm{e}^{3K+3h}+3\mathrm{e}^{-K-h}) \pm \frac{1}{2}\ln(\mathrm{e}^{3K-3h}+3\mathrm{e}^{-K-h})$

(Calculation: Since the individual blocks decouple in $\mathscr{H}_0$, we have

$\Rightarrow \sum_{\{S_i\}} \mathrm{e}^{-\beta\mathscr{H}_0}\prod_I \delta_{S_I,\mathrm{sign}(\sum_\alpha s^I_\alpha)} = \prod_I \mathscr{Z}_0(K,S'_I)$

with $\mathscr{Z}_0(K,S'_I) = \sum_{S_1,S_2,S_3} \mathrm{e}^{K(S_1S_2+S_1S_3+S_2S_3)+h(S_1+S_2+S_3)}\delta_{S_I,\mathrm{sign}(S_1+S_2+S_3)}$

$= \left\{\begin{array}{ll} \mathrm{e}^{3K+3h}+3\mathrm{e}^{-K+h} & : S'_I = 1 \\ \mathrm{e}^{3K-3h}+3\mathrm{e}^{-K-h} & : S'_I = -1 \end{array}\right\} \equiv \exp(A+BS_I) \quad \checkmark)$

Now approximation: Cumulant expansion $\boxed{\langle \mathrm{e}^{-\beta V}\rangle_0 \approx \mathrm{e}^{-\beta\langle V\rangle_0}}$

Then $\mathscr{H}'$ has the same form as $\mathscr{H}$ with new coupling constants:

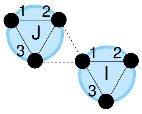
$$\boxed{\begin{array}{rcl} K' &=& 2KD(K,h)^2 \\ h' &=& B(K,h)+12K\,C(K,h)\,D(K,h) \end{array}}$$

where $\binom{C(K,h)}{D(K,h)} = \frac{1}{2}\left(\frac{\mathrm{e}^{3K+3h}+\mathrm{e}^{-K+h}}{\mathrm{e}^{3K+3h}+3\mathrm{e}^{-K+h}} \mp \frac{\mathrm{e}^{3K-3h}+\mathrm{e}^{-K-h}}{\mathrm{e}^{3K-3h}+3\mathrm{e}^{-K-h}}\right)$

(Calculation: Consider $\langle V\rangle_0$ in the reference system $\mathscr{H}_0$ for given $\{S_I\}$

– V couples only to neighbor blocks: $V = \sum_{IJ} V_{IJ}$

– Averaging: e.g, as in the figure:



$\beta\langle V_{IJ}\rangle_0 = K\langle S_{I,1}(S_{J,2}+S_{J,3})\rangle = K\langle S_{I,1}\rangle_0(\langle S_{J,2}\rangle_0+\langle S_{J,3}\rangle_0)$

$= 2K\langle S_{I,\alpha}\rangle_0\langle S_{J,\alpha}\rangle_0$ (averages are independent of α)

Define $\Phi(S'_I) = \langle S_{I,\alpha}\rangle_0$ (is independent of α)

– One can write $\Phi(S)$ as $\Phi(S) = C + DS$

(must be possible: Two equations $\Phi(\pm 1)$ for two unknowns C, D)

Specifically: $\langle S_{I,\alpha}\rangle_0 = \dfrac{\sum\limits_{S_{1,2,3}} S_\alpha \mathrm{e}^{K(S_1S_2+S_1S_3+S_2S_3)+h(S_1+S_2+S_3)}\delta_{S'_I,\,\mathrm{sign}(S_1+S_2+S_3)}}{\sum\limits_{S_{1,2,3}} \mathrm{e}^{K(S_1S_2+S_1S_3+S_2S_3)+h(S_1+S_2+S_3)}\delta_{S'_I,\,\mathrm{sign}(S_1+S_2+S_3)}}$

$= \left\{\begin{array}{ll} \frac{\mathrm{e}^{3K+3h}+\mathrm{e}^{-K+h}}{\mathrm{e}^{3K+3h}+3\mathrm{e}^{-K+h}} & : S'_I = 1 \\ \frac{-\mathrm{e}^{3K-3h}-\mathrm{e}^{-K+h}}{\mathrm{e}^{3K-3h}+3\mathrm{e}^{-K-h}} & : S'_I = -1 \end{array}\right\} =: C + DS'_I$

$\Rightarrow \beta V_{IJ} = 2K(C+DS'_I)(C+DS'_J) = 2KC^2 + 4KCD(S_I+S'_J) + 2KD^2S'_IS'_J$

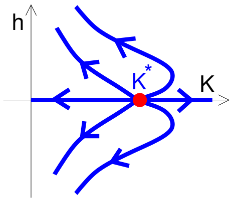
$\Rightarrow \beta\mathscr{H}' = \frac{N}{3}A + B\sum_I S'_I - \beta\sum_{IJ}V_{IJ}$

$= \underbrace{\frac{N}{3}(A+6KC^2)}_{Ng\text{ regular}} + \underbrace{B+12KCD}_{h'}\sum_I S'_I + \underbrace{2KD^2}_{K'}\sum_{\langle IJ\rangle} S_IS_J \quad \checkmark\ )$

Recursion relations in special cases:

- $\star$ $h=0$: $K' = 2\left(\frac{\mathrm{e}^{3K}+\mathrm{e}^{-K}}{\mathrm{e}^{3K}+3\mathrm{e}^{-3K}}\right)^2 K \approx \left\{\begin{array}{ll} K/2 & \text{for } K\to 0\text{: shrinks} \\ 2K & \text{for } K\to\infty\text{: grows} \end{array}\right.$
- $\star$ $h\to\infty$: $K' = 2D^2K = \frac{8}{9}K$ shrinks

$\Rightarrow$ Fixed points and RG Flow diagram



Trivial fixed points:

$(h,K) = (0,0),\ (0,\infty),\ (\pm\infty,0)$

Critical fixed point:

$(h,K) = (0,K^*)$ with $\left(\frac{\mathrm{e}^{3K^*}+\mathrm{e}^{-K^*}}{\mathrm{e}^{3K^*}+3\mathrm{e}^{-K^*}}\right)^2 = \frac{1}{2}$

Analysis of RG results

⋆ Critical point: $K_c = K^* = \dots = \frac{1}{4}\ln(1+2\sqrt{2}) = 0.33$
(Compare exact value: $K_c = 0.27$, Bragg-Williams: $K_c = \frac{1}{6} = 0.17$)

⋆ Phase diagram: Follows from flow diagram

⋆ Critical exponents

Expand about critical point: $\binom{\delta K}{\delta h} = \binom{K}{h} - \binom{K^*}{h^*} \to \binom{\delta K'}{\delta h'}$

$$\Rightarrow \binom{\delta K'}{\delta h'} = \mathbf{M}\binom{\delta K}{\delta h} \text{ with } \mathbf{M} = \begin{pmatrix} \frac{\partial K'}{\partial K} & \frac{\partial K'}{\partial h} \\ \frac{\partial h'}{\partial K} & \frac{\partial h'}{\partial h} \end{pmatrix}_{(K^*,h^*)}$$

For symmetry reasons ($h^* = 0$), we have $\left.\frac{\partial K'}{\partial h}\right|_{h^*} = \left.\frac{\partial h'}{\partial K}\right|_{h^*}$

$\Rightarrow$ $\mathbf{M}$ is already diagonal!

Eigenvalues of $\mathbf{M}$:

$$\Lambda_K = \left(\frac{\partial K'}{\partial K}\right)_{(K^*,h^*)} = \dots = 1.62 =: b^{y_t} \quad \Rightarrow \; y_t = 0.882$$

$$\Lambda_h = \left(\frac{\partial h'}{\partial h}\right)_{(K^*,h^*)} = \dots = 3.06 =: b^{y_h} \quad \Rightarrow \; y_h = 2.034$$

Compare exact values: $y_t = 1$, $y_h = 15/8 = 1.875$

Remarks

⋆ RG treatment allows calculating phase diagrams and critical exponents.
Not exact, but can be improved systematically – e.g. by taking the cumulant expansion up to second order!

(In that case, RG transformation generates additional interactions
→ have to be cut off, further approximations become necessary.
Result is nevertheless much better: $K_c = 0.26$, $y_t = 1.04$.)

⋆ Important: RG transformation must be analytic! (Singularities should emerge when approaching the fixed point, not prior to that!)
Non-trivial requirement! Among other, it implies that the RG transformation must maintain the symmetries of the system.

(For example, an RG transformation that maps a Heisenberg model on an Ising model is not allowed!)

6.5 Renormalization of the Φ^4-model

Recall (Φ^4 theory and related)

Section 5.4 – Φ^4 theory: $\beta\mathscr{F} = \mathrm{d}^d r \,\{\frac{1}{2}(\nabla\Phi)^2 + \frac{1}{2}r_0\Phi^2 + \frac{1}{4}u_0\Phi^4\}$

Rescale: $\varphi = \Phi\sqrt{r_0}^{1-d/2}$, $\vec{y} = \vec{r}\,\sqrt{r_0}$

$\Rightarrow$ $\beta\mathscr{F} = \mathrm{d}^d y\,\{\frac{1}{2}(\nabla\varphi)^2 + \frac{1}{2}\varphi^2 + \frac{1}{4}\bar{u}_0\Phi^4\}$ with $\bar{u}_0 = u_0\,\sqrt{r_0}^{d-4}$

At the phase transition, r_0 vanishes: $r_0 \to 0$

$\Rightarrow$ φ^4-term diverges for $d < 4$, vanishes for $d > 4$

(NB: Dimensional analysis: In the latter case ($d > 4$), higher order terms vanish as well. For example, prefactor of φ^6 scales as r_0^{d-3}.

Section 6.3.2 – Exact renormalization of Gaussian model with $u_0 = 0$

$\beta\mathscr{F} = \mathrm{d}^d r\,\{\frac{1}{2}(\nabla\Phi)^2 + \frac{1}{2}r_0\Phi^2\}$

Treatment of Φ^4 term in Φ^4- theory

a) $d > 4$: u_0 irrelevant, effectively Gaussian model ("Gaussian fixed point").

b) $d < 4$: u_0 becomes relevant at the Gaussian fixed point.
$\rightsquigarrow$ Gaussian fixed point unstable,
new fixed point ("Wilson-Fisher fixed point").
Perturbation expansion about u_0 and $\epsilon = d - 4$.

Problems:

- Expansion diverges ! (already clear from the fact that expansion must diverge for $u_0 < 0$! $\Rightarrow$ Convergence radius $u_0 = 0$)
  But: First terms of the expansion still improve the results. Beyond that, Borel resummation is possible.
- Individual terms of perturbation expansion diverge in the limit $\Lambda \to 0$ (Λ: microscopic cutoff): "Ultraviolet divergences"!
  $\rightsquigarrow$ suggests sensitive dependence on Λ

Ways out

- Fourier space renormalization (shown here)
  $\rightsquigarrow$ Degrees of freedom in $[\Lambda, \Lambda/l]$ are gradually integrated out $\to$ RG equations. Fixed point is independent of Λ
- Direct elimination of ultraviolet divergences by field theoretic renormalization (not covered here, detailed treatment, e.g., in Binney, Dorwick, Fisher, Newman: *The theory of critical phenomena.*

6.5.1 Φ^4-theory in $d > 4$ dimensions

Question:

u_0 irrelevant $\to$ RG group should correspond to that of Gaussian model (Sec. 6.3.2).

Critical exponents of the Gaussian model:
$\alpha = 2 - \frac{d}{2}$, $\beta = \frac{d}{4} - \frac{1}{2}$, $\gamma = 1$, $\delta = \frac{d+2}{d-2}$

But: In fact, critical exponents are quite different!
Mean-field exponents, independent of dimension (cf. Sec. 4.3.5)
$\alpha = 0$, $\beta = \frac{1}{2}$, $\gamma = 1$, $\delta = 3$

$\rightsquigarrow$ How does this fit together?

Answer: u_0 is a dangerous irrelevant variable (cf. Sec. 6.2.3).

Scaling form of the free energy in mean-field approximation (according to dimensional analysis, Sec. 5.3): $f_s(t, h, u_0) = l^{-d} f_s(t l^{y_t}, h l^{y_h}, u_0 l^{y_u})$ with $y_t = 2$, $y_h = 1 + \frac{d}{2}$, $y_u = 4 - d$.

Specifically: Mean-field solution $f_s = \frac{1}{2}r_0\Phi^2 + \frac{1}{4}u_0\Phi^4 - h\Phi$

$$\text{with } \Phi = \left\{ \begin{array}{ll} \sqrt{r_0/u_0} + h/2|r_0| & : r_0 < 0 \\ (h/u_0)^{1/3} & : r_0 \sim 0 \\ h/r_0 & : r_0 > 0 \end{array} \right\}$$

$$\Rightarrow\ f_s = \left\{ \begin{array}{ll} -\frac{1}{4}\, r_0^2/u_0 - h\sqrt{r_0/u_0} - h^2/2r_0 & : r_0 < 0 \\ -\frac{3}{4}u_0^{-1/3}h^{4/3} & : r_0 \sim 0 \\ -h^2/2r_0 & : r_0 > 0 \end{array} \right\}$$

$\Rightarrow$ for $u_0 > 0$, we can generally write $f_s(t,h,u_0) = \frac{1}{u_0}\hat{f}_s(t, h\sqrt{u_0})$

$$\text{with } \hat{f}_s(t,x) = \left\{ \begin{array}{ll} -\frac{1}{4}r_0^2 - x\sqrt{r_0} - x^2/2r_0 & : t < 0 \\ -\frac{3}{4}x^{4/3} & : t \sim 0 \\ -x^2/2r_0 & : t > 0 \end{array} \right\} \text{ where } r_0 \propto t$$

$$\begin{aligned} \Rightarrow f_s(t,h,u_0) &= l^{-d} f_s(tl^{y_t}, hl^{y_h}, u_0 l^{y_u}) \\ &\overset{l=|t|^{-1/y_t}}{=} |t|^{d/y_t} f_s(\pm 1, h|t|^{-y_h/h_t}, u_0|t|^{-y_u/y_t}) \\ &= |t|^{\frac{d+y_u}{y_t}} \frac{1}{u_0}\hat{f}_s(\pm 1, h\sqrt{u_0}|t|^{-\frac{2y_h+y_u}{y_t}}) \\ &\Big| \quad \text{Use } y_t = 2,\ y_h = 1 + \tfrac{d}{2},\ y_u = 4 - d \\ &= |t|^2 \frac{1}{u_0}\hat{f}_s(\pm 1, h\sqrt{u_0}|t|^{-3/2}) = |t|^2\, F_f^{\pm}(h|t|^{-3/2}) \end{aligned}$$

(Replaces $F_f^{\pm}(h|t|^{-y_h/h_t}) = F_f^{\pm}(h|t|^{-(d+2)/4})$)

$$\begin{array}{llll} \Rightarrow & \text{Specific heat:} & c_H \sim \left.\frac{\partial^2 f_s}{\partial t}\right|_{h=0} \sim |t|^0 & \Rightarrow \alpha = 0 \\ & \text{Order parameter:} & m \sim -\frac{\partial f_s}{\partial h} \sim |t|^{1/2} F_f^{\pm}(h|t|^{-3/2}) & \Rightarrow \beta = 1/2 \\ & & t = 0:\ m \sim h^{1/3} & \Rightarrow \delta = 3 \end{array}$$

(Last line: $t \to 0, h \neq 0 \ \Rightarrow\ m$ independent of $t \Rightarrow\ F_f^{\pm}(x) \overset{|x|\to\infty}{\sim} x^{1/3}$

Conclusion:

Since u_0 is irrelevant, the RG-calculation still gives the Gaussian fixed point (Sec. 6.3.2). However, u_0 is dangerous and changes the critical exponents. To obtain the correct critical exponents, one needs additional information (i.e., mean-field solution and Ginzburg criterion!)

6.5.2 Φ^4-theory in $d < 4$ dimensions: ϵ-expansion

At the Gaussian fixed point, u_0 becomes relevant, new RG treatment necessary (Gaussian fixed point becomes unstable.
→ new fixed point: Wilson-Fisher fixed point.)

System: Ginzburg-Landau theory (Φ^4 theory) with $u_0 > 0$

$$\beta\mathscr{F} = \int \mathrm{d}^d r\, \{\tfrac{1}{2}(\nabla\Phi)^2 + \tfrac{1}{2}r_0\Phi^2 + \tfrac{1}{4}u_0\Phi^4 + \cdots - h\Phi\}$$

In Fourier representation $\quad \left(\frac{1}{(2\pi)^d}\int \mathrm{d}^d k = \frac{1}{V}\sum_{\vec{k}}\right)$

$$\begin{aligned} \beta\mathscr{F} = {} & \tfrac{1}{V}\textstyle\sum_{|\vec{k}|<\Lambda} \left\{\tfrac{1}{2}|\Phi_{\vec{k}}|^2(r_0 + k^2)\right\} - h\Phi_0 && \text{(Gaussian model)} \\ & + \tfrac{1}{4}u_0\, \tfrac{1}{V^4} \sum_{\vec{k}_1,\vec{k}_2,\vec{k}_3,\vec{k}_4} \Phi_{\vec{k}_1}\Phi_{\vec{k}_2}\Phi_{\vec{k}_3}\Phi_{\vec{k}_4}\, V\delta_{\sum_1^4 \vec{k}_i,0} && (\Phi^4 \text{ term}) \\ & + \tfrac{1}{6}w_0\, \tfrac{1}{V^6} \sum_{\vec{k}_1,\cdots,\vec{k}_6} \Phi_{\vec{k}_1}\cdots\Phi_{\vec{k}_6}\, V\delta_{\sum_1^6 \vec{k}_i,0} + \cdots && (\Phi^6 \text{ term and higher}) \end{aligned}$$

Higher order terms (Φ^6 etc.) must be included for now, because they might be generated by RG transformation.

RG transformation (same as 6.3.2)

(i) Thinning: Integrate out $\Phi_{\vec{k}}$ for $\Lambda/l < |\vec{k}| < \Lambda$

(ii) Rescale: $\vec{k} \to \vec{k}l$, $\Phi_{\vec{k}} \to l^\theta \Phi_{\vec{k}}$, such that $\beta\mathscr{F}$ retains its form
$\rightsquigarrow$ term $\frac{1}{2}(\nabla\Phi)^2$ remains unchanged.

First (i): Thinning: Integrate out short wavelength modes $\Phi_{\vec{k}}$

Separate $\mathscr{F} = \mathscr{F}_0 + \mathscr{F}_1 + \mathscr{V}$ with

$$\beta\mathscr{F}_0 = \frac{1}{V}\sum_{|\vec{k}|<\Lambda/l} \frac{1}{2}|\Phi_{\vec{k}}|^2(r_0+k^2) - h\Phi_0$$

$$\beta\mathscr{F}_1 = \frac{1}{V}\sum_{\Lambda/l\leqslant|\vec{k}|<\Lambda} \frac{1}{2}|\Phi_{\vec{k}}|^2(r_0+k^2)$$

$$\beta\mathscr{V} = \frac{1}{4}u_0\,\frac{1}{V^4}\sum_{\vec{k}_1\cdots\vec{k}_4}\Phi_{\vec{k}_1}\cdots\Phi_{\vec{k}_4}V\delta_{\sum_1^4\vec{k}_i,0} + \text{higher order terms}$$

$$\Rightarrow\ \mathscr{Z} = \prod_{|\vec{k}|<\Lambda/l}\frac{1}{V}\int \mathrm{d}\Phi_{\vec{k}}\mathrm{e}^{-\beta\tilde{\mathscr{F}}+Vg(r_0)} \quad \text{with} \quad \mathrm{e}^{-\beta\tilde{\mathscr{F}}} = \big\langle \mathrm{e}^{-\beta\mathscr{V}}\big\rangle_1 \mathrm{e}^{-\beta\mathscr{F}_0}$$

where $Vg(r_0) = \ln\Big[\prod_{\Lambda/l<|\vec{k}|<\Lambda}\frac{1}{V}\int\mathrm{d}\Phi_{\vec{k}}\mathrm{e}^{-\beta\mathscr{F}_1}\Big] = \sum_{\Lambda/l<|\vec{k}|<\Lambda}\ln\Big(\frac{\pi}{r_0+k^2}\Big)$
(see Sec. 6.3.2)

and $\big\langle O\big\rangle_1 = \dfrac{\prod_{\Lambda/l<|\vec{k}|<\Lambda}\int\mathrm{d}\Phi_{\vec{k}}\mathrm{e}^{-\beta\mathscr{F}_1}O}{\prod_{\Lambda/l<|\vec{k}|<\Lambda}\int\mathrm{d}\Phi_{\vec{k}}\mathrm{e}^{-\beta\mathscr{F}_1}}$,

Cumulant expansion:

$$\big\langle \mathrm{e}^{-\mathscr{V}}\big\rangle_1 \approx \exp\Big(-\beta\langle\mathscr{V}\rangle_1 + \frac{\beta^2}{2}(\langle\mathscr{V}^2\rangle_1 - \langle\mathscr{V}\rangle_1^2) + \cdots\Big)$$

$\Rightarrow$ Expand $\beta\tilde{\mathscr{F}}$ in powers of u_0.

Here: Only very rudimentary sketch of the calculation

For a more systematic treatment involving Feynman diagrams etc. and better assessment of the approximations below see N. Goldenfeld *Lectures on Phase Transitions and the Renormalization Group*

⋆ First order: Calculate contribution of Φ^4-term to $\langle\mathscr{V}\rangle_1$

Separate the contributions to $\frac{u_0}{4}\frac{1}{V^4}\sum_{\vec{k}_1\cdots\vec{k}_4}\Phi_{\vec{k}_1}\cdots\Phi_{\vec{k}_4}V\delta_{\sum_1^4\vec{k}_i,0}$

- $|\vec{k}_i| > \frac{\Lambda}{l}\ \forall\, i\ (i=1,...4)$: Can be integrated out completely → regular term
- $|\vec{k}_i| < \frac{\Lambda}{l}\ \forall\, i\ (i=1,...4)$: No integration (term remains).
- One or three $|\vec{k}_i| > \frac{\Lambda}{l}$: → Terms vanish for symmetry reasons ($\langle\Phi_{\vec{k}}\rangle_1 = 0$)
- Two $|\vec{k}_i| > \frac{\Lambda}{l}$, e.g., $|\vec{k}_{1,2}| < \frac{\Lambda}{l}$, $|\vec{k}_{3,4}| > \frac{\Lambda}{l}$.
  $\Rightarrow$ Contributes only if $\vec{q} := \vec{k}_3 = -\vec{k}_4$ (implying $\vec{k}_1 = -\vec{k}_2 =: \vec{k}$)
  ($\vec{k}_3 \neq \pm\vec{k}_4 \Rightarrow \langle\Phi_{\vec{k}_3}\Phi_{\vec{k}_4}\rangle_1 = \langle\Phi_{\vec{k}_3}\rangle_1\langle\Phi_{\vec{k}_4}\rangle_1 = 0$,
  $\vec{k}_3 = \vec{k}_4$ not possible, incompatible with $\sum\vec{k}_i = 0$ & $|\vec{k}_{1,2}| < \Lambda/l$)
  Every single such term contributes $\frac{u_0}{4}\Big(\frac{1}{V^2}\sum_{q>\Lambda/l}\Gamma(q)\Big)\frac{1}{V}\sum_{k<\Lambda/l}\Phi_{\vec{k}}\Phi_{-\vec{k}}$
  with $\Gamma(q) = \langle|\Phi_{\vec{q}}|^2\rangle_1 = \cdots = \frac{V}{r_0+q^2}$ (Gaussian integral)
  In total: $\binom{4}{2} = 6$ such terms ($\binom{4}{2}$ ways to distribute $(\pm\vec{k},\pm\vec{q})$ on $\vec{k}_{1\ldots4}$)

Summary: Φ^4 term in $\langle\mathscr{V}\rangle_1$ gives additional contribution to r_0

$r_0 \to \tilde{r} = r_0 + 3u_0\frac{1}{V^2}\sum_{q>\Lambda/l}\Gamma(q)$ (not yet rescaled)

Coefficient u_0 remains unchanged in first order of $\mathscr{V}$

⋆ Second order: Consider again Φ^4-term

– Contribution of order $\mathscr{O}(u_0^2)$ to $\tilde{r}$ → neglected
(keep only leading contributions of expansion in u_0)

– Contribution to u_0: Leading correction, must be accounted for

... lengthy calculation ...

$$\to \tfrac{1}{V^4} \sum \Phi_{\vec{k}_1} \cdots \Phi_{\vec{k}_4} V \delta_{\sum_1^4 \vec{k}_i, 0} \, \tfrac{1}{4} \, \tilde{u}$$
$$= \tfrac{1}{V^4} \sum \Phi_{\vec{k}_1} \cdots \Phi_{\vec{k}_4} V \delta_{\sum_1^4 \vec{k}_i, 0} \tfrac{1}{4} u_0 \big(1 - 9u_0 \tfrac{1}{V^4} \sum_{q,q' > \Lambda/l} \Gamma(q)\Gamma(q') V \delta_{\vec{k}_3 + \vec{k}_4 - \vec{q} - \vec{q}'}\big)$$

$\to$ Approximation: $\tilde{u} \approx u_0 \big(1 - 9u_0 \frac{1}{V^3} \sum_{q>\Lambda/l} \Gamma(q)^2\big)$

$\star$ Higher order terms in Φ (Φ^6 etc.) give higher order contributions to $\tilde{r}$ and $\tilde{u}$ (e.g., $\Phi^6 \to \mathscr{O}(u^3)$). Shall be neglected here.

Now (ii): Rescaling – analogous to Sec. 6.3.2:

$\vec{k} \to \vec{k}l$, $\Phi_{\vec{k}} \to \Phi'_{\vec{k}} = l^{-(1+d/2)} \Phi_{\vec{k}l}$, $V \to V' = V/l^d$

$\Rightarrow$ $r' = \tilde{r}\, l^2$, $u' = \tilde{u}\, l^{4-d}$, $h' = h\, l^{1+d/2}$

$\big(\rightsquigarrow \frac{1}{V'} r' \Phi'^2 \sim l^0,\ \frac{1}{V'^3} u' \Phi'^4 \sim l^0,\ h'\Phi' \sim l^0\big)$

Together: Recursion relations (recalling $\Gamma(q) = V/(r_0 + q^2)$)

$$\boxed{r' = l^2(r_0 + 3u_0 I_1(r_0)),\ u' = u_0\, l^{4-d}(1 - 9u_0 I_2(r_0)),\ h' = h l^{1+d/2}}$$

with $I_1(r_0) = \frac{1}{V^2} \sum_{\Lambda/l \leqslant q < \Lambda} \Gamma(q) \approx \frac{1}{(2\pi)^d} \int_{\Lambda/l \leqslant < \Lambda} \mathrm{d}^d q \, \frac{1}{r_0 + q^2}$

$I_2(r_0) = \frac{1}{V^3} \sum_{\Lambda/l \leqslant q < \Lambda} \Gamma(q)^2 \approx \frac{1}{(2\pi)^d} \int_{\Lambda/l \leqslant q < \Lambda} \mathrm{d}^d q \, \frac{1}{(r_0 + q^2)^2}$

Differential form of the RG flow equations

for the flow $r(s)$, $u(s)$, $h(s)$ with $s = \ln l$

Consider infinitesimal RG step $l \approx 1$ (but $l > 1$): $l = \exp(\mathrm{d}s) \approx 1 + \mathrm{d}s$

$\Rightarrow$ $I_1(r_0) \approx \frac{\Lambda \mathrm{d}s}{r_0 + \Lambda^{-2}} \Lambda^{d-1} C_d = \mathrm{d}s \frac{\Lambda^{d-2} C_d}{1 + r_0 \Lambda^{-2}}$

$I_2(r_0) \approx \frac{\Lambda \mathrm{d}s}{(r_0 + \Lambda^{-2})^2} \Lambda^{d-1} C_d = \mathrm{d}s \frac{\Lambda^{d-4} C_d}{(1 + r_0 \Lambda^{-2})^2}$

where $C_d = \Omega_d \frac{1}{(2\pi)^d} = \frac{2^{1-d}}{\pi^{d/2} (\frac{d}{2} - 1)!}$ (Ω_d: Surface of unit sphere)

Specifically: $C_4 = 1/8\pi^2$

$$(r_0 = r(s) \overset{\mathrm{RG}}{\to} r' = r(s + \mathrm{d}s) = \mathrm{e}^{2\mathrm{d}s}(r(s) + 3u(s) I_1) = r + \mathrm{d}s\,(2r + 3uI_1) + \mathscr{O}(\mathrm{d}s^2)$$
$$u_0 = u(s) \overset{\mathrm{RG}}{\to} u' = u(s + \mathrm{d}s) = \mathrm{e}^{(4-d)\mathrm{d}s} u(s)\,(1 - 9u(s) I_2) = u + \mathrm{d}s\, u\,((4-d) - 9u\, I_2) + \mathscr{O}(\mathrm{d}s^2)$$
$$h = h(s) \overset{\mathrm{RG}}{\to} h' = h(s + \mathrm{d}s) = h(s)\, \mathrm{e}^{(1+d/2)\mathrm{d}s} = h + (1 + \tfrac{d}{2})\, h\, \mathrm{d}s + \mathscr{O}(\mathrm{d}s^2))$$

$$\Rightarrow \quad \boxed{\begin{aligned} \tfrac{\mathrm{d}r}{\mathrm{d}s} &= \Big(2r + 3u \tfrac{C_d}{(1 + r\Lambda^{-2})} \Lambda^{d-2}\Big) \\ \tfrac{\mathrm{d}u}{\mathrm{d}s} &= u\Big((4-d) - 9u \tfrac{C_d}{(1 + r\Lambda^{-2})^2} \Lambda^{d-4}\Big) \\ \tfrac{\mathrm{d}h}{\mathrm{d}s} &= h\Big(1 + \tfrac{d}{2}\Big) \end{aligned}}$$

Fixed points

Gaussian fixed point: $\boxed{r^* = u^* = h^* = 0}$

Wilson-Fisher fixed point:

$u^* = (4-d) \frac{(1 + r^* \Lambda^{-2})^2}{9C_d} \Lambda^{4-d}$, $r^* = -\frac{3}{2} \frac{C_d}{(1 + r^* \Lambda^{-2})} \Lambda^{d-2} u^*$, $h^* = 0$.

NB: Approaches $r^* = u^* = 0$ for $4 - d \to 0$

$\rightsquigarrow$ Motivates expansion in $\boxed{\epsilon = 4 - d}$

$$\boxed{u^* = \epsilon\,\frac{1}{9C_4} = \frac{8\pi^2}{9}\,\epsilon, \quad r^* = -\epsilon\Lambda^2\frac{1}{6}, \quad h^* = 0}$$

Linearized RG equations and scaling exponents

Consider recursion relations
$\frac{\mathrm{d}r}{\mathrm{d}s} = f_r(r,u,h)$ $\frac{\mathrm{d}u}{\mathrm{d}s} = f_u(r,u,h)$ $\frac{\mathrm{d}h}{\mathrm{d}s} = f_h(r,u,h)$

Expansion about fixed point: $r = r^* + \delta r, \; u = u^* + \delta u, \; h = h^* + \delta h$

$$\Rightarrow \frac{\mathrm{d}}{\mathrm{d}s}\begin{pmatrix}\delta r\\ \delta u\\ \delta h\end{pmatrix} = \mathbf{L}\begin{pmatrix}\delta r\\ \delta u\\ \delta h\end{pmatrix} \text{ with } \mathbf{L} = \frac{\partial(f_r,f_u,f_h)}{\partial(r,u,h)} = \begin{pmatrix}2-\frac{\epsilon}{3} & \star & 0\\ 0 & -\epsilon & 0\\ 0 & 0 & 3-\frac{\epsilon}{2}\end{pmatrix} + \mathcal{O}(\epsilon^2)$$

where $\star = \Lambda^2 C_4(3 + \frac{\epsilon}{2})$

(Calculations:

$$L_{rr} = \frac{\mathrm{d}f_r}{\mathrm{d}r} = 2 - 3u^*\Lambda^{d-2}C_d\frac{1}{(1+r^*\Lambda^{-2})^2}\Lambda^{-2} = 2 - 3u^*C_4 + \mathcal{O}(\epsilon^2) = 2 - \tfrac{1}{3}\epsilon + \mathcal{O}(\epsilon^2)$$
$$L_{ru} = \frac{\mathrm{d}f_r}{\mathrm{d}u} = 3\Lambda^{d-2}C_d\frac{1}{(1+r^*\Lambda^{-2})} = 3\Lambda^2C_4(1+\epsilon/6) + \mathcal{O}(\epsilon^2)$$
$$L_{ur} = \frac{\mathrm{d}f_u}{\mathrm{d}r} = 18u^{*2}\Lambda^{d-4}C_d\frac{1}{(1+r^*\Lambda^{-2})^3}\Lambda^{-2} = \mathcal{O}(\epsilon^2)$$
$$L_{uu} = \frac{\mathrm{d}f_u}{\mathrm{d}u} = ((4-d) - 18u^*C_d\frac{1}{(1+r^*\Lambda^{-2})^2}\Lambda^{d-4} = \epsilon - 18u^*C_4 + \mathcal{O}(\epsilon^2)$$
$$= -\epsilon + \mathcal{O}(\epsilon^2)$$
$$L_{rh} = L_{hr} = L_{uh} = L_{hu} = 0$$
$$L_{hh} = \frac{\mathrm{d}f_h}{\mathrm{d}h} = 1 + \frac{d}{2} = 3 - \tfrac{1}{2}\epsilon\;)$$

$$\Rightarrow \text{ Solution: } \begin{pmatrix}\delta r\\ \delta u\\ \delta h\end{pmatrix} = \exp(\mathbf{L}s)\begin{pmatrix}\delta r\\ \delta u\\ \delta h\end{pmatrix} = l^{\mathbf{L}}\begin{pmatrix}\delta r\\ \delta u\\ \delta h\end{pmatrix}$$

$\Rightarrow$ Scaling exponents and scaling fields are the Eigenvalues and Eigenvectors of $\mathbf{L}$

$$\Rightarrow \boxed{y_r = 2 - \epsilon/3, \quad y_2 = -\epsilon, \quad y_h = 3 - \epsilon/2}$$

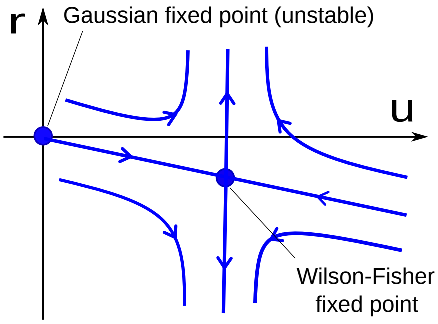
with scaling fields $\vec{e}_r \propto \begin{pmatrix}1\\0\\0\end{pmatrix}$, $\vec{e}_2 \propto \begin{pmatrix}-\star/2\\1\\0\end{pmatrix}$, $\vec{e}_h \propto \begin{pmatrix}0\\0\\1\end{pmatrix}$.

$\rightsquigarrow$ $y_r, y_h > 0$ are relevant scaling fields,
$y_1 < 0$ is irrelevant!

Discussion

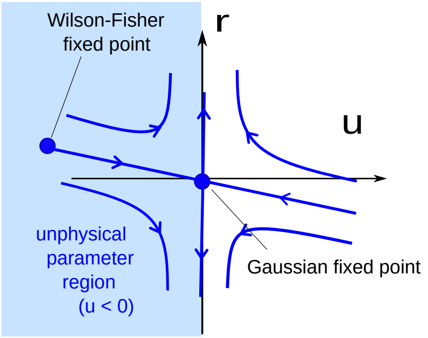
- Flow diagrams

  $\epsilon > 0$ ($d < 4$)



  At $\epsilon = 0$ ($d = 4$), Wilson-Fisher fixed point joins Gaussian fixed point.

  $\epsilon < 0$ ($d > 4$)



  Wilson-Fisher fixed point becomes unstable and moves into unphysical parameter region at $u < 0$.

- Critical exponents at the Wilson-Fisher fixed point, $d < 4$

  Calculation as before from
  $y_t = y_r = 2 - \epsilon/3$ (since $t \sim r$), $y_h = 3 - \epsilon/2$
  $y_u < 0 \;\Rightarrow$ Scaling field u is irrelevant fixed point
  (and also not dangerous)

  Results (numbers for 3 dimensions → $\epsilon = 1$)

  $\nu = 1/y_t = 1/2 + \epsilon/12 + \mathcal{O}(\epsilon^2) \qquad \approx 0.58$
  $\alpha = 2 - d/y_t = \epsilon/6 + \mathcal{O}(\epsilon^2) \qquad \approx 0.16$
  $\Delta = y_y/y_t = 3/2 + \mathcal{O}(\epsilon^2) \qquad \approx 1/5$
  $\beta = 2 - \alpha - \Delta = 1/2 - \epsilon/6 + \mathcal{O}(\epsilon^2) \qquad \approx 0.33$
  $\gamma = \Delta - \beta = 1 + \epsilon/6 + \mathcal{O}(\epsilon^2) \qquad \approx 1.16$
  $\delta = \Delta/\beta = 3 + \epsilon + \mathcal{O}(\epsilon^2) \qquad \approx 4$
  $\eta = 2 - \gamma/\nu = \mathcal{O}(\epsilon^2) \qquad \approx 0$

  $\rightsquigarrow$ Much better than Mean-field!
  (Correct values in 3D: $\alpha = 0.11,\ \beta = 0.32,\ \gamma = 1.24,\ \delta = 4.82$
  $\nu = 0.63,\ \eta = 0.04$)

Part II

Nonequilibrium Statistical Mechanics

The theory of nonequilibrium statistical physics is much less unified than equilibrium statistical physics. The main reason is that one has no equivalent to the central postulates of equilibrium statistical physics - the existence of an equilibrium state where the entropy is maximal. Nevertheless, statistical descriptions are sometimes possible.
Here we will briefly describe a few selected approaches

Linear response theory

Close to equilibrium, equilibrium statistiscal mechanics can be used to describe nonequilibrium systems within first order perturbation theory. Important results are the fluctuation-dissipation theorem and the Green-Kubo relations (already used in section 4.5)

Boltzmann equation

Statistical approach to systems, whose dynamical evolution is dominated by scattering processes (e.g., gases). Assumes

- Only collisions between two particles
- Every collision is a random process
- Description by one particle distribution functions $f(\vec{p}, t)$

In general, the validity of these assumptions is questionable. Nevertheless, the Boltzmann equation has been very successful in many respect, and played an important role in the history of nonequilibrium physics.

Extensions: Equations for hierarchies of N-particle distributions, BBGKY hierarchy, requires ”closure” relations (not covered here).

Stochastic processes

Basic idea: Separation of time scales, slow and fast degrees of freedom
→ Coarse- graining, similar to RG idea

- ”slow” degrees of freedom: Formulate dynamical equations for them
- ”fast” degrees of freedom: Noise

In the simplest case: Langevin equation with white noise

Extensions: Colored noise and memory
Statistical physics framework: Mori-Zwanzig theory (not covered).

Stochastic thermodynamics

TODO

Exact relations for fluctuating driven systems. Entropy production, fluctuation theorems, thermodynamic uncertainty relations.

Chapter 7

Dynamics Close to Equilibrium: Linear Response Theory

Recapitulation: Regarding static properties, we already know that there exists a relation between correlations and response functions (cf. Sec. 3.5.3.4).

Consider generally a Hamiltonian with a small, time independent perturbation that couples to a dynamic variable A: $\mathscr{H} = \mathscr{H}_0 - h_A A$

$\rightsquigarrow$ Response of quantity B to this perturbation:

$$\boxed{\frac{\partial\langle B\rangle}{\partial h_A} = \beta\, C_{BA}} \qquad \text{with} \qquad \boxed{C_{BA} = \langle BA\rangle - \langle B\rangle\langle A\rangle}$$

(Proof: $\mathscr{Z} = \mathrm{Tr}(\mathrm{e}^{-\beta\mathscr{H}_0+\beta h_A A})$; $\langle B\rangle = \frac{1}{\mathscr{Z}}\,\mathrm{Tr}(B\mathrm{e}^{-\beta\mathscr{H}_0+\beta h_A A})$

$$\begin{aligned}\Rightarrow \tfrac{\partial\langle B\rangle}{\partial h_A} &= -\tfrac{1}{\mathscr{Z}^2}\tfrac{\partial\mathscr{Z}}{\partial h_A}\,\mathrm{Tr}(B\mathrm{e}^{-\beta\mathscr{H}_0+\beta h_A A}) + \tfrac{1}{\mathscr{Z}}\tfrac{\partial}{\partial h_A}\,\mathrm{Tr}(B\mathrm{e}^{-\beta\mathscr{H}_0+\beta h_A A})\\ &= -\tfrac{1}{\mathscr{Z}^2}\beta\,\mathrm{Tr}(B\mathrm{e}^{-\beta\mathscr{H}_0+\beta h_A A})\,\mathrm{Tr}(A\mathrm{e}^{-\beta\mathscr{H}_0+\beta h_A A}) + \tfrac{1}{\mathscr{Z}}\beta\,\mathrm{Tr}(BA\mathrm{e}^{-\beta\mathscr{H}_0+\beta h_A A})\\ &= -\beta\langle B\rangle\langle A\rangle + \beta\langle BA\rangle \quad \checkmark\end{aligned}$$

)

This relation is also called ”static fluctuation-dissipation theorem”.

Now: Generalization for time-dependent perturbations

$\rightsquigarrow$ Dynamic fluctuation-dissipation theorem

General relation between dynamical correlations and dynamic response functions.

Particularly relevant in the context of

- Transport close to equilibrium
  (Currents in response to external driving forces)
- Green-Kubo relations and Onsager coefficients
- Friction and entropy production close to equilibrium
  (hence ”dissipation”)

7.1 The fluctuation-dissipation theorem

Shall be derived at the level of quantum theory here.
Pure classical derivation → Exercise!

7.1.1 Fluctuation-dissipation theorem for density fluctuations

First consider important special case: Fluctuation-dissipation theorem relating density fluctuations (i.e., structure factor) with a generalized susceptibility).

Generalization in Sec. 7.1.2

Consider Hamilton operator of a homogeneous many-particle system with a perturbation that couples to the local particle density:

$$H = H_0 + H_{\text{ext}} \quad \text{with} \quad H_{\text{ext}} = \int \mathrm{d}^d r \, n(\vec{r},t)\, \Phi(\vec{r},t) = \sum_i \Phi(\vec{R}_i, t)$$

with $\Phi(\vec{r},t)$: Local time-dependent one-body potential
and $n(\vec{r},t) = \sum_i \delta(\vec{r} - \vec{R}_i(t))$: Operator for particle density

Define:

- ⋆ Dynamic structure factor: (can be measured in scattering experiments)

$$\boxed{S(\vec{q},\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \, \mathrm{e}^{i\omega t} \langle n(\vec{q},t)\, n(-\vec{q},0)\rangle}$$

with $n(\vec{q},t)$: Fourier transform of $n(\vec{r},t)$ $\quad (n(\vec{r},t) = \frac{1}{V}\sum_{\vec{q}} n(\vec{q},t) \mathrm{e}^{i\vec{q}\cdot\vec{r}})$

- ⋆ Generalized susceptibility: χ^R – Characterizes local density change $\delta\langle n(\vec{r},t)\rangle$ in response to an infinitesimal perturbation $\Phi \to 0$.

Translational invariance in space and time → General linear relation

$$\boxed{\delta\langle n(\vec{r},t)\rangle = \int \mathrm{d}^d r' \int_{-\infty}^{\infty} \mathrm{d}t' \, \chi^R(\vec{r}-\vec{r}', t-t')\, \Phi(\vec{r}', t')}$$

(leading order in Φ) or, in Fourier space (convolution theorem):

$$\boxed{\delta\langle n(\vec{q},\omega)\rangle = \chi^R(\vec{q},\omega)\, \Phi(\vec{q},\omega)}$$

with $\chi^R(\vec{q},\omega)$: Generalized susceptibility

(Fourier transform: $f(\vec{r},t) = \frac{1}{2\pi V}\sum_{\vec{q}} \int_{-\infty}^{\infty} \mathrm{d}\omega \, f(\vec{q},\omega)\, \mathrm{e}^{i\vec{q}\cdot\vec{r}}\, \mathrm{e}^{-i\omega t}$)

In this Section, we will derive the following relations:

$$\boxed{\chi^R(\vec{q},t) = -\frac{i}{\hbar V}\, \Theta(t)\, \langle [n(\vec{q},t), n(-\vec{q},0)]\rangle}$$

and the Fluctuation-dissipation theorem

$$\boxed{(1 - \mathrm{e}^{-\beta\hbar\omega})\, S(\vec{q},\omega) = -2\hbar V \,\mathrm{Im}\, \chi^R(\vec{q},\omega)}$$

Classical limit ($\hbar \to 0, \quad \frac{1}{i\hbar}[A,B] \to \{A,B\}$)

$$\boxed{\begin{aligned} &\chi^R(\vec{q},t) = \Theta(t)\, \langle \{n(\vec{q},t), n(-\vec{q},0)\}\rangle \\ &\beta\omega S(\vec{q},\omega) = -2V \,\mathrm{Im}\, \chi^R(\vec{q},\omega) \end{aligned}}$$

This will now be shown in several steps in the next subsections.

7.1.1.1 Linear response and susceptibility

Task: Calculate response of density $\delta\langle n(\vec{r},t)\rangle$ to perturbation Φ

Procedure: Time-dependent perturbation theory

Equations of motion in the Dirac picture
(Heisenberg picture with respect to unperturbed system H_0)
States: $i\hbar\partial_t|\psi_D\rangle = H^D_{\text{ext}}|\psi_D\rangle$, Statistical operator: $i\hbar\partial_T\rho_D = [H^D_{\text{ext}},\rho_D]$
with $H^D_{\text{ext}} = \mathrm{e}^{\frac{i}{\hbar}H_0 t}\, H_{\text{ext}}\, \mathrm{e}^{-\frac{i}{\hbar}H_0 t}$

Solution at lowest order of H_{ext} (first order perturbation theory)

$$\Rightarrow\ |\psi_D(t)\rangle = |\psi_H^{(0)}\rangle - \tfrac{i}{\hbar}\textstyle\int_{-\infty}^t \mathrm{d}t'\, H^D_{\text{ext}}(t')\, |\psi_H^{(0)}\rangle$$

$$\rho_D(t) = \rho_H^{(0)} - \tfrac{i}{\hbar}\textstyle\int_{-\infty}^t \mathrm{d}t'\, [H^D_{\text{ext}}(t'),\rho_H^{(0)}]$$

(with: $|\psi_H^{(0)}\rangle$, $\rho_H^{(0)}$: unperturbed system, Heisenberg picture)

$\Rightarrow$ Time evolution of the density

Density operator in the Dirac picture: $n(\vec{r},t) = \mathrm{e}^{\frac{i}{\hbar}H_0 t} n(\vec{r})\mathrm{e}^{-\frac{i}{\hbar}H_0 t}$
Expectation value:

$$\begin{aligned}\langle n(\vec{r},t)\rangle &= \mathrm{Tr}\left(\rho_D(t)\, n(\vec{r},t)\right)\\ &= \mathrm{Tr}\left(\rho_H^{(0)} n(\vec{r},t)\right) - \tfrac{i}{\hbar}\textstyle\int_{-\infty}^t \mathrm{d}t'\ \underbrace{\mathrm{Tr}\left([H^D_{\text{ext}}(t'),\rho_H^{(0)}]n(\vec{r},t)\right)}_{\mathrm{Tr}\left(\rho_H^{(0)}[n(\vec{r},t),H^D_{\text{ext}}(t')]\right)}\\ &= \langle n(\vec{r},t)\rangle_0 - \tfrac{i}{\hbar}\textstyle\int_{-\infty}^t \mathrm{d}t' \int \mathrm{d}^d r'\, \Phi(\vec{r}',t')\, \langle [n(\vec{r},t), n(\vec{r}',t')]\rangle_0\end{aligned}$$

$\Rightarrow$ Time evolution of the density fluctuation

$$\delta\langle n(\vec{r},t)\rangle = -\tfrac{i}{\hbar}\textstyle\int_{-\infty}^t \mathrm{d}t' \int \mathrm{d}^d r'\ \Phi(\vec{r}',t')\, \langle [n(\vec{r},t), n(\vec{r}',t')]\rangle_0$$

where $\langle\cdot\rangle_0$: Expectation value with respect to unperturbed system!

Result: Generalized susceptibility

Equation for $\delta\langle n(\vec{r},t)\rangle$ can be rewritten as

$$\boxed{\delta\langle n(\vec{r},t)\rangle = \int \mathrm{d}^d r' \int_{-\infty}^{\infty} \mathrm{d}t D^R(\vec{r},t;\vec{r}',t')\ \Phi(\vec{r}',t')}$$

$$\text{with}\quad \boxed{D^R(\vec{r},t;\vec{r}',t') = \frac{i}{\hbar}\Theta(t-t')\,\langle [n(\vec{r},t), n(\vec{r}',t')]\rangle_0}$$

Specifically: Homogeneous system H_0: D^R depends only on $(\vec{r}-\vec{r}')$ and $(t-t')$.
$\rightsquigarrow$ Fourier transform: $\chi^R(\vec{q},\omega) = \frac{1}{V}\int \mathrm{d}^d r \int \mathrm{d}^d r' \int \mathrm{d}t \mathrm{e}^{-i\vec{q}\cdot(\vec{r}-\vec{r}')}\mathrm{e}^{i\omega t} D^R(\vec{r},t;\vec{r}',0)$
Then we have: $\delta\langle n(\vec{q},\omega)\rangle = \chi^R(\vec{q},\omega)\ \Phi(\vec{q},\omega)$ ✓

$$\begin{aligned}\text{with } \chi^R(\vec{q},\omega) &= -\tfrac{i}{\hbar V} \textstyle\int \mathrm{d}t\, \mathrm{e}^{i\omega t}\, \Theta(t)\, \langle [\int \mathrm{d}^d r\, \mathrm{e}^{-i\vec{q}\cdot\vec{r}} n(\vec{r},t), \int \mathrm{d}^d r'\, \mathrm{e}^{i\vec{q}\cdot\vec{r}'} n(\vec{r}',0)]\rangle\\ &= -\tfrac{i}{\hbar V} \textstyle\int \mathrm{d}t\, \mathrm{e}^{i\omega t}\, \Theta(t)\, \langle [n(\vec{q},t), n(-\vec{q},0)]\rangle \quad \checkmark\end{aligned}$$

7.1.1.2 Relation to structure factor

Task: Establish connection between χ^R and number density fluctuations

Procedure: Starting from expression for $\chi^R(\vec{q},\omega)$ in the previous section

⋆ Insert integral representation of the Heaviside Theta function

$\Theta(t) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} \mathrm{d}\omega'\, \mathrm{e}^{i\omega' t}\frac{1}{\omega' - i\eta}\Big|_{\eta\to 0^+}$ (Proof: Theorem of residues)

$\Rightarrow\ \chi^R(\vec{q},\omega) = -\frac{1}{2\pi\hbar V}\int_{-\infty}^{\infty}\mathrm{d}t\int_{-\infty}^{\infty}\mathrm{d}\omega'\,\mathrm{e}^{it(\omega+\omega')}\,\frac{\langle[n(\vec{q},t),n(-\vec{q},0)]\rangle}{\omega'-i\eta}$

$\Big|$ Substitute $\omega'' = \omega + \omega'$, exploit time invariance

$= -\frac{1}{\hbar V}\int\frac{\mathrm{d}\omega''}{2\pi}\,\frac{1}{(\omega''-\omega)-i\eta}\int\mathrm{d}t\,\mathrm{e}^{i\omega'' t}\,\big(\langle n(\vec{q},t)\,n(-\vec{q},0)\rangle - \underbrace{\langle n(-\vec{q},0)\,n(\vec{q},t)\rangle}_{\langle n(-\vec{q},-t)\,n(\vec{q},0)\rangle}\big)$

$\Big|$ Substitute $t' = -t$

$= -\frac{1}{\hbar V}\int\frac{\mathrm{d}\omega''}{2\pi}\,\frac{1}{(\omega''-\omega)-i\eta}\big(\int\mathrm{d}t\mathrm{e}^{i\omega'' t}\langle n(\vec{q},t)n(-\vec{q},0)\rangle - \int\mathrm{d}t'\mathrm{e}^{-i\omega'' t'}\langle n(-\vec{q},t')n(\vec{q},0)\rangle\big)$

⇝ Establishes general connection with structure factor
(for homogeneous steady states)

$$\boxed{\chi^R(\vec{q},\omega) = \frac{1}{\hbar V}\int\frac{\mathrm{d}\omega'}{2\pi}\,\frac{S(\vec{q},\omega') - S(-\vec{q},-\omega')}{(\omega-\omega')+i\eta}\Big|_{\eta\to 0^+}}$$

⋆ Now consider a reference (unperturbed) state at thermal equilibrium

⇒ Statistical operator: $\rho = \frac{1}{Z_{GK}}\mathrm{e}^{-\beta(H_0-\mu N)}$ (grand canonical)

Consequences:

- $S(\vec{q},\omega) = S(-\vec{q},\omega)$ is real.
- $\boxed{S(-\vec{q},-\omega) = S(\vec{q},-\omega) = \mathrm{e}^{-\beta\hbar\omega}\,S(\vec{q},\omega)}$ ("detailed balance")

(Proof:

$S(\vec{q},\omega) = \int\mathrm{d}t\,\mathrm{e}^{i\omega t}\ \mathrm{Tr}\,\big(\rho_H^{(0)}\,n(\vec{q},t)\,n(\vec{q},0)\big)$

$\Big|$ Choose Eigenbasis $|m\rangle$ of H_0 and N
with $H_0|m\rangle = E_m|m\rangle,\ (H_0-\mu N)|m\rangle = K_m|m\rangle$

$= \int\mathrm{d}t\,\mathrm{e}^{i\omega t}\ \sum_m\langle m|\rho_H^{(0)}\ \mathrm{e}^{\frac{i}{\hbar}H_0 t}\ n(\vec{q},0)\,\mathrm{e}^{-\frac{i}{\hbar}H_0 t}\ n(-\vec{q},0)\,|m\rangle$

$\Big|$ Insert $\mathbf{1} = \sum_{m'}|m'\rangle\langle m'|$

$= \int\mathrm{d}t\mathrm{e}^{i\omega t}\frac{1}{Z_{GK}}\sum_{m,m'}\langle m|\mathrm{e}^{-\beta(H_0-\mu N)}\mathrm{e}^{\frac{i}{\hbar}H_0 t}n(\vec{q},0)\mathrm{e}^{-\frac{i}{\hbar}H_0 t}|m'\rangle\langle m'|n(-\vec{q},0)|m\rangle$

$= \frac{1}{Z_{GK}}\sum_{m,m'}\mathrm{e}^{-\beta K_m}\underbrace{\int\mathrm{d}t\,\mathrm{e}^{i\omega t}\,\mathrm{e}^{\frac{i}{\hbar}E_m t}\,\mathrm{e}^{-\frac{i}{\hbar}E_{m'}t}}_{2\pi\hbar\delta(\hbar\omega+E_m-E_{m'})}\underbrace{\langle m|\,n(\vec{q},0)\,|m'\rangle\,\langle m'|\,n(-\vec{q},0)\,|m\rangle}_{|\langle m|n(\vec{q},0)|m'\rangle|^2}$

$= \frac{1}{Z_{GK}}\sum_{m,m'}\mathrm{e}^{-\beta K_m}\ 2\pi\hbar\delta(\hbar\omega + E_m - E_{m'})\ |\langle m|n(\vec{q},0)|m'\rangle|^2$

$S(\vec{q},-\omega) = \frac{1}{Z_{GK}}\sum_{m,m'}\mathrm{e}^{-\beta K_m}\ 2\pi\hbar\delta(-\hbar\omega + E_m - E_{m'})\ |\langle m|n(\vec{q},0)|m'\rangle|^2$

$\Big|$ $E_{m'} = E_m - \hbar\omega,\ |\langle m|n(\vec{q},0)|m'\rangle|^2 = |\langle m'|n(\vec{q},0)|m\rangle|^2$

$= \frac{1}{Z_{GK}}\sum_{m,m'}\mathrm{e}^{-\beta K_{m'}-\beta\hbar\omega}\ 2\pi\hbar\delta(\hbar\omega + E_{m'} - E_m)\ |\langle m'|n(\vec{q},0)|m\rangle|^2$

$= \mathrm{e}^{-\beta\hbar\omega}\ S(\vec{q},\omega)\quad\checkmark$)

Remark: Interpretation of the factor $\mathrm{e}^{-\beta\hbar\omega}$

$S(\vec{q},\omega) \triangleq$ Average over transitions between states m and m'. The transition probability $\omega \leftrightarrow \omega'$ is symmetric, but the occupation probability of the states depends on temperature.

Result: Collect all ⇒ $\boxed{(1-\mathrm{e}^{-\beta\hbar\omega})\,S(\vec{q},\omega) = -2\hbar V\,\mathrm{Im}\,\chi^R(\vec{q},\omega)}$ ✓

(Proof: $\chi^R(\vec{q},\omega) = \frac{1}{\hbar V}\int\frac{\mathrm{d}\omega'}{2\pi}\ \frac{1}{\omega-\omega'+i\eta}\Big|_{\eta\to 0^+}S(\vec{q},\omega)\,(1-\mathrm{e}^{-\beta\hbar\omega'})$

$\Big|$ $\frac{1}{\omega+i\eta}\Big|_{\eta\to 0^+} = P(\frac{1}{\omega}) - i\pi\,\delta(\omega)$ with P: Principal value

$= \frac{1}{2\pi\hbar V}\underbrace{P\int\frac{\mathrm{d}\omega'}{\omega-\omega'}S(\vec{q},\omega')\,(1-\mathrm{e}^{-\beta\hbar\omega'})}_{\text{real}} - \frac{i}{2\hbar V}\underbrace{S(\vec{q},\omega)\,(1-\mathrm{e}^{-\beta\hbar\omega})}_{\text{real}}$)

7.1.2 General fluctuation-dissipation theorem

Generalize results from Sec. 7.1.1 to general case of a small perturbation that couples to a dynamical quantity $A \rightsquigarrow H = H_0 + \Phi_A(t)\,A$. (Proofs as before).

(a) Generalized susceptibility:

The response of a quantity $B(t)$ to $\Phi_A(t')$ is given by

$$\boxed{\delta\langle B(t)\rangle = \int_{-\infty}^{t} \mathrm{d}t'\,\chi^R_{BA}(t,t')\,\Phi_A(t')}$$

where

$$\boxed{\chi^R_{BA}(t,t') = -2i\chi''_{BA}(t)\,\Theta(t-t') \quad \text{with} \quad \chi''_{BA}(t) = \frac{1}{2\hbar}\,\langle[B(t),A(0)]\rangle}$$

NB: – Rationale to introduce $\chi''_{BA}(t)$: Analytic function
– Relation between χ^R_{BA} and χ''_{BA} in Fourier space:

$$\boxed{\chi^R_{BA}(\omega) = \frac{1}{\pi}P\int \mathrm{d}\omega'\,\frac{\chi''_{BA}(\omega')}{\omega-\omega'} - i\chi''_{BA}(\omega)}$$

(Proof: Insert $\Theta(t) = \frac{1}{2\pi i}\int \mathrm{d}\omega'\,\frac{\mathrm{e}^{i\omega' t}}{\omega' - i\eta}\Big|_{\eta\to 0^+}$

$$\begin{aligned}\Rightarrow \chi^R(\omega) &= -2i\int \mathrm{d}t\mathrm{e}^{i\omega t}\Theta(t)\chi''(t) = -\tfrac{1}{\pi}\int \mathrm{d}\omega'\,\tfrac{\mathrm{e}^{i\omega' t}}{\omega'-i\eta}\int \mathrm{d}t\,\mathrm{e}^{i\omega t}\,\chi''(t)\\ &= -\tfrac{1}{\pi}\int \mathrm{d}\omega'\,\tfrac{1}{\omega'-i\eta}\chi''(\omega+\omega') = \tfrac{1}{\pi}\int \mathrm{d}\omega'\,\tfrac{1}{\omega-\omega'+i\eta}\chi''(\omega')\end{aligned}$$

and use $\frac{1}{\omega+i\eta}\Big|_{\eta\to 0^+} = P(\frac{1}{\omega} - i\pi\delta(\omega)\ \ )$

(b) Generalized correlation function and detailed balance

$\boxed{C_{BA}(t) = \langle B(t)\,A(0)\rangle}$ with $\boxed{C_{BA}(\omega) = \mathrm{e}^{\beta\hbar\omega}C_{AB}(\omega)}$ at equilibrium

(Proof of detailed balance property same as in Sec. 7.1.1.2

(c) Fluctuation-dissipation theorem

$$\boxed{(1-\mathrm{e}^{-\beta\hbar\omega})\,C_{BA}(\omega) = 2\hbar\,\chi''_{BA}(\omega)}$$

Specifically: If $B = A^+ \ \Rightarrow\ C_{BA}$ real $\Rightarrow \chi''_{BA}(\omega) = -\mathrm{Im}\chi^R_{BA}(\omega)$
(e.g., Sec. 7.1.1: $A = n(\vec{q},t),\ B = n(-\vec{q},t) = A^+$)

(d) Classical limit – Simplest via $\hbar \to 0$ and $[B,A] \to i\hbar\{B,A\}$

$\Rightarrow$ $\boxed{\chi''_{BA}(\omega) = \frac{\beta\omega}{2}C_{BA}(\omega)}$ respectively $\boxed{\chi''_{BA}(t) = i\frac{\beta}{2}\frac{\mathrm{d}}{\mathrm{d}t}C_{BA}(t)}$

$\Rightarrow$ $\boxed{\chi^R_{BA}(t) = -2i\chi''_{BA}(t)\,\Theta(t) = \beta\,\Theta(t)\,\frac{\mathrm{d}}{\mathrm{d}t}C_{BA}(t)}$

and further $\boxed{\chi''_{BA}(t) = \frac{i}{2}\langle\{B(t),A(0)\}\rangle}$ (from $\chi''(t) = \frac{1}{\hbar}\langle[B(t),A(0)]\rangle$)

(Can also be calculated directly without quantum mechanics → Exercise!)

7.1.3 Other exact relations

Famous relations. Useful in practice, e.g., for evaluating approximations.

7.1.3.1 Kramers-Kronig relations

Relations between real and imaginary part of response functions:

$$\boxed{\begin{array}{l} \mathrm{Re}\chi^R(\omega) = -P\displaystyle\int \frac{\mathrm{d}\omega'}{\pi}\,\frac{\mathrm{Im}\chi^R(\omega')}{\omega-\omega'} \\ \mathrm{Im}\chi^R(\omega) = +P\int \frac{\mathrm{d}\omega'}{\pi}\,\frac{\mathrm{Re}\chi^R(\omega')}{\omega-\omega'} \end{array}}$$

This is a consequence of causality, i.e., $\chi^R(t) = 0$ for all $t > 0$

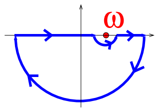
($\chi^R(t) = \frac{1}{2\pi} \in \mathrm{d}\omega\, \mathrm{e}^{-i\omega t}\, \chi^R(\omega) = 0$ for $t > 0$

$\rightsquigarrow$ $\chi^R(\omega)$ does not have poles in the lower complex half plane

Assume further:

- No poles on the real axis (would correspond to dissipationless resonances)
- $\chi^R(\omega)$ decays "sufficiently rapidly" for $\omega \to \pm\infty$

Choose integration path as in picture



and consider the integral $\frac{1}{2\pi i} \oint \mathrm{d}\omega'\, \frac{\chi^R(\omega')}{\omega'-\omega}$

- Contribution large circle: 0
- Contribution small circle: $(\omega' = \omega + \varepsilon \mathrm{e}^{i\varphi})$

  $\frac{1}{2\pi i}\chi^R(\omega) \int_\pi^{2\pi} \mathrm{d}[\epsilon \mathrm{e}^{i\varphi}]\,/\epsilon \mathrm{e}^{i\varphi} = \frac{1}{2}\chi^R(\omega)$
- Contribution straight part: $-i\frac{1}{2\pi} P \int \mathrm{d}\omega'\, \frac{\chi^R(\omega')}{\omega'-\omega}$ ✓)

7.1.3.2 Sum rules

Exact relations for moments of response functions.

Here: Specifically for structure factor and density fluctuations (Sec. 7.1.1).
Similar relations can be derived for for other response functions

⋆ If the interaction potentials do not depend on the velocity, one has

$$\Big\langle\big[[n(\vec{q}, H], n(-\vec{q})\big]\Big\rangle = \Big\langle\big[[n(\vec{q}), T], n(-\vec{q})\big]\Big\rangle = \frac{\hbar^2 q^2}{m}\langle N\rangle$$

(Proof: $n(\vec{q}) = \sum_j \mathrm{e}^{i\vec{q}\cdot\vec{R}_j}$

$\Rightarrow$ $[n(\vec{q}), \sum_j \frac{P_j^2}{2m}] = \sum_j [\mathrm{e}^{-i\vec{q}\cdot\vec{R}_j}, \frac{P_j^2}{2m}] = \cdots = \sum_j \mathrm{e}^{-i\vec{q}\cdot\vec{R}_j} (-\frac{\hbar^2}{2m}\, q^2 + \frac{\hbar}{m}\vec{q}\cdot\vec{P}_j)$

$\Rightarrow$ $[[n(\vec{q}), \sum_j \frac{P_j^2}{2m}], n(-\vec{q})] = \sum_j \frac{\hbar\vec{q}}{m} \cdot [\mathrm{e}^{-i\vec{q}\cdot\vec{R}_j}\vec{P}_j, \mathrm{e}^{i\vec{q}\cdot\vec{R}_j}] = \cdots = \frac{\hbar^2 q^2}{m}\, \underbrace{\sum_J 1}_{N}$)

⋆ This results in the f-sum rule for the density response function

$$\boxed{\int \frac{\mathrm{d}\omega}{\pi}\, \omega\, \mathrm{Im}\chi^R(\vec{q},\omega) = -\frac{q^2}{mV}\,\langle N\rangle}$$

with m: particle mass, N: particle number, T: kinetic energy

(Proof: With the notation of 7.1.2, we have $\mathrm{Im}\chi^R(\vec{q},\omega) = -\chi''(\vec{q},\omega)$
with $\chi''(\vec{q},t) = \frac{1}{2\hbar V}\langle[n(\vec{q},t), n(-\vec{q},0)]\rangle$

$$\Rightarrow \int \frac{\mathrm{d}\omega}{\pi}\omega\chi^R(\vec{q},\omega) = -\int \frac{\mathrm{d}\omega}{\pi}\omega\chi''(\vec{q},\omega) = -\int \frac{\mathrm{d}\omega}{\pi}\omega \int \mathrm{d}t \mathrm{e}^{i\omega t}\chi''(\vec{q},t) = \int \mathrm{d}t\chi''(\vec{q},t) \underbrace{\int \frac{\mathrm{d}\omega}{\pi}\frac{1}{i}\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{i\omega t}}_{2i\frac{\mathrm{d}}{\mathrm{d}t}\,\delta(t)}$$

$$= -2i\frac{\mathrm{d}}{\mathrm{d}t}\chi''(\vec{q},t)\Big|_{t=0} = \frac{1}{i\hbar V}\frac{\mathrm{d}}{\mathrm{d}t}\langle[n(\vec{q},t), n(-\vec{q},0)]\rangle\Big|_{t=0}$$

$$= \frac{1}{i\hbar V}\langle[\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}n(\vec{q},t)\Big|_{t=0}}_{\frac{1}{i\hbar}[n(\vec{q},0),H]}, n(-\vec{q},0)]\rangle\Big|_{t=0} = -\frac{1}{\hbar^2 V}\langle[[n(\vec{q}), H], n(-\vec{q})]\rangle = -\frac{q^2}{m}\frac{\langle N\rangle}{V}$$ ✓)

⋆ In the same way one can derive sum rules from higher order commutators.

7.2 Transport

Topic in this section: Stationary currents that build up in response to constant external driving fields in the linear response regime, i.e., small fields

Starting point:

- Densities ρ_k of conserved quantities K (mass, energy, charge, ...)
  $\Rightarrow$ Continuity equations $\partial_t \rho_k = -\nabla \cdot \vec{j}_k$
- Associated generalized potentials Φ_k
  Physical origin (e.g., electrostatic potential) or thermodynamic origin (e.g., chemical potential)

Remarks:

- One can distinguish between two types of transport
  - (i) Convective transport in a flowing medium.
    Flow velocity $\vec{v} \;\rightarrow\;$ Current $\vec{j}_k^{\,\mathrm{conv}} = \vec{v}\,\rho_k$
  - (ii) Diffusive transport in the local rest system of the medium in response to an external generalized force $\vec{Z}_k$
    $\rightsquigarrow$ This is the transport type of interest here.

  Usually, a diffusive transport law is associated with a diffusion law.
- Nature of generalized forces $\vec{Z}_k$
  - Similar to generalized potentials, can have "physical" origin (e.g., electric field) or "thermodynamic" origin (e.g., chemical potential gradient, temperature gradient)
  - Can be associated with a perturbation H' of the Hamiltonian

    At constant temperature: $H = H_0 + H'$
    $\vec{Z}_k = -\nabla\,\Phi_k$
    $H' = \sum_k \int \mathrm{d}^d r\; \rho_k(\vec{r})\; \Phi_k(\vec{r})$

    In case of temperature gradient $T(\vec{r}) \leftrightarrow \beta(\vec{r}) = \beta_0 + \delta\beta(\vec{r})$
    $T(\vec{r})$ induces gradient in the energy density $\rho_e(\vec{r})$
    Define reference system $\bar{H}_0$ that has same profile $\rho_e(\vec{r})$ at equilibrium: $\bar{H}_0 = H_0 + \int \mathrm{d}^d r\; \frac{\delta\beta(\vec{r})}{\beta_0}\; \rho_e(\vec{r})$

    $$\Phi_k(\vec{r}) \rightarrow \bar{\Phi}_k(\vec{r}) = \frac{\beta(\vec{r})}{\beta_0}\Phi_k(\vec{r}), \qquad \vec{Z}_k = -\nabla\bar{\Phi}_k(\vec{r})$$

    $\Rightarrow$ "Perturbed" system: $H = \bar{H}_0 + H'$

    $$\text{with } H' = \underbrace{-\int \mathrm{d}^d r\; \rho_e(\vec{r})\; \frac{\delta\beta(\vec{r})}{\beta_0}}_{H_0 - \bar{H}_0} + \underbrace{\sum_{k \neq e} \int \mathrm{d}^d r\; \rho_k(\vec{r})\; \frac{\beta(\vec{r})}{\beta_0}\; \Phi_k}_{\text{other perturbations}}$$

  $\rightsquigarrow$ Connection with generalized potentials:

  $$\boxed{\vec{Z}_k = -T_0\,\nabla(\Phi_k/T)} \;\;(\text{ setting } \boxed{\Phi_e := -1}\;)$$
- Consider spatially constant $\vec{Z}_k \Rightarrow \frac{\beta(\vec{r})}{\beta_0}\Phi_k = -\vec{Z}_k \cdot \vec{r} + \text{const.}$

  $\Rightarrow\;\; H' = -\sum_k \vec{Z}_k \cdot \int \mathrm{d}^d r\; \rho_k(\vec{r})\; \vec{r} + \text{const.}$

7.2.1 Green-Kubo relations

Consider locally conserved quantities a, b, where a experiences spatially constant generalized force $\vec{Z}_a$
$\Rightarrow$ Perturbation (see above) $H' = -\vec{Z}_a \int \mathrm{d}^d r \, \vec{r} \, \rho_a \; + \text{const.}$

Question: How does the current density $\vec{j}_b$ respond to this force?

Answer: (as will be shown below)

$\boxed{\langle \vec{j}_b \rangle = \boldsymbol{\lambda}_{ba} \, \vec{Z}_a}$ with $\boldsymbol{\lambda}_{ba}$: Onsager coefficients

Connection to current correlations: Green-Kubo relations

Quantum mechanical:
$$\boldsymbol{\lambda}_{ba} = V \int_0^\infty \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda \, \langle \vec{j}_a(-i\hbar\lambda) \otimes \vec{j}_b(\tau) \rangle$$

Classical:
$$\boldsymbol{\lambda}_{ba} = V\beta \int_0^\infty \mathrm{d}\tau \, \langle \vec{j}_a(0) \otimes \vec{j}_b(\tau) \rangle$$

Derivation of these relations:

- Consider first moments of densities: $\vec{A} = \int \mathrm{d}^d r \, \vec{r} \rho_a(\vec{r})$, $\vec{B} = \int \mathrm{d}^d r \, \vec{r} \rho_b(\vec{r})$

  $\to$ Perturbation: $H' = -\vec{Z}_a \cdot \vec{A}$, Current: $V \, \vec{j}_b = \dot{\vec{B}}$

  (Assume $|\vec{j}_b| \to 0$ at border of volume V
  $\Rightarrow \; V\vec{j}_b = \int \mathrm{d}^d r \, \vec{j}_b = \int \mathrm{d}^d r \, (\vec{j}_b \cdot \nabla)\vec{r} = -\int \mathrm{d}^d r \, \vec{r}(\nabla \cdot \vec{j}_b) = -\int \mathrm{d}^d r \, \vec{r} \partial_t \rho_b = \dot{\vec{B}}$)

  $\rightsquigarrow$ New, equivalent problem:

  Response of a quantity $\dot{\vec{B}}$ to a field coupling to $\vec{A}$
  $V\langle j_{b\alpha} \rangle = \langle \dot{B}_\alpha \rangle = -\sum_\gamma \int_{-\infty}^t \mathrm{d}t \, \chi^R_{\dot{B}_\alpha A_\gamma}(t-t') \, Z_{a\gamma} =: V \sum_\gamma \lambda_{ba}^{\alpha\gamma} \, Z_{a\gamma}$
  $\Rightarrow \; \lambda_{ba}^{\alpha\gamma} = -\frac{1}{V} \int_0^\infty \mathrm{d}\tau \, \chi^R_{\dot{B}_\alpha A_\gamma}(\tau)$ (α, γ: Cartesian coordinates)

- First classical case (simpler). Drop indices α, γ for simplicity.

  Fluctuation-dissipation theorem:
  $$\Rightarrow \; \chi^R_{\dot{B}A}(t) = \beta\Theta(t)\tfrac{\mathrm{d}}{\mathrm{d}t} C_{\dot{B}A}(t) = \beta\Theta(t)\tfrac{\mathrm{d}}{\mathrm{d}t}\langle \dot{B}(t) A(0) \rangle = \beta\Theta(t)\tfrac{\mathrm{d}}{\mathrm{d}t}\langle \dot{B}(0) A(-t) \rangle$$
  $$= -\beta\Theta(t) \, \langle \dot{B}(0) \, \dot{A}(-t) \rangle = -\beta\Theta(t) \, \langle \dot{B}(t) \, \dot{A}(0) \rangle$$
  $$\Rightarrow \; \lambda_{ba} = -\tfrac{1}{V} \int_0^\infty \mathrm{d}\tau \chi^R_{\dot{B}A}(\tau) = \tfrac{\beta}{V} \int_0^\infty \mathrm{d}\tau \langle \dot{B}(\tau) \dot{A}(0) \rangle = V\beta \int_0^\infty \mathrm{d}\tau \langle j_a(0) j_b(\tau) \rangle$$

- Now quantum mechanical version, again without indices α, γ.
  $$\chi^R_{\dot{B}A}(t) = -\tfrac{i}{\hbar}\Theta(t) \, \langle [\dot{B}(t), A(0)] \rangle$$
  $$= -\tfrac{i}{\hbar}\Theta(t) \, \mathrm{Tr}\left(\rho \, [\dot{B}(t), A(0)]\right) = -\tfrac{i}{\hbar}\Theta(t) \, \mathrm{Tr}\left([\dot{B}(t), [A(0), \rho]]\right)$$

  > Side calculation (most general case: grand canonical, $K_0 = H_0 - \mu N$, $[A, N] = 0$)
  > $[A(0), \rho_{GK}] = \frac{1}{Z_{GK}}[A, \mathrm{e}^{-\beta K_0}] = \frac{1}{Z_{GK}}\mathrm{e}^{-\beta K_0}(\mathrm{e}^{\beta K_0} A \mathrm{e}^{-\beta K_0} - A)$
  > $= \frac{1}{Z_{GK}}\mathrm{e}^{-\beta K_0}(\mathrm{e}^{\beta H_0} A \mathrm{e}^{-\beta H_0} - A) =: \rho_{GK} \, \Psi(\beta)$ with $\Psi(\beta = 0) = 0$.
  > $\frac{\partial}{\partial\lambda}\Psi(\lambda) = \mathrm{e}^{\lambda H_0} H_0 A \mathrm{e}^{-\lambda H_0} - \mathrm{e}^{\lambda H_0} A H_0 \mathrm{e}^{-\lambda H_0} = \mathrm{e}^{\lambda H_0} \underbrace{[H_0, A]}_{\frac{\hbar}{i}\dot{A}(t)} \mathrm{e}^{-\lambda H_0}$
  > $= \frac{\hbar}{i}\mathrm{e}^{\lambda H_0} \dot{A} \mathrm{e}^{-\lambda H_0} = \frac{\hbar}{i}\dot{A}(t = -i\hbar\lambda)$
  > $\Rightarrow \; [A(0), \rho] = \rho\Psi(\beta) = \frac{\hbar}{i}\rho_{GK} \int_0^\beta \mathrm{d}\lambda \dot{A}(i\hbar\lambda)$

  $$= -\,\mathrm{Tr}\left(\dot{B}(t)\rho_{GK} \int_0^\beta \mathrm{d}\lambda \dot{A}(-i\hbar\lambda)\right) = -\int_0^\beta \mathrm{d}\lambda \, \mathrm{Tr}\left(\rho_{GK} \dot{A}(-i\hbar\lambda)\dot{B}(t)\right)$$
  $$= -\int_0^\beta \mathrm{d}\lambda \, \langle \dot{A}(-i\hbar\lambda)\dot{B}(t) \rangle$$
  $$\Rightarrow \; \lambda_{ba} = -\tfrac{1}{V}\int_0^\infty \mathrm{d}\tau \, \chi^R_{\dot{B}A}(t) = \tfrac{1}{V}\int_0^\infty \mathrm{d}\tau \, \int_0^\beta \mathrm{d}\lambda \, \langle \dot{A}(-i\hbar\lambda)\dot{B}(t) \rangle$$
  $$= V \int_0^\infty \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda \, \langle j_a(-i\hbar\lambda) \, j_b(\tau) \rangle \quad \checkmark$$

7.2.2 Onsager relations

From microscopic reversibility (invariance of dynamics under time reversal)

one can derive $\boxed{\text{(i)}\lambda_{ba}^{\alpha\gamma} = \lambda_{ab}^{\gamma\alpha};}$ $\boxed{\text{(ii)}\lambda_{aa}^{\alpha\alpha} > 0}$

(Proof (drop again indices α, γ):

- Classical case – almost trivial

  (i) $\lambda_{ab} = V\beta \int_0^\infty \mathrm{d}\tau \langle j_b(0) j_a(\tau)\rangle = V\beta \int_0^\infty \mathrm{d}\tau \langle j_a(0) j_b(-\tau)\rangle \overset{\text{reversi-}\atop\text{bility}}{=} V\beta \int_0^\infty \mathrm{d}\tau \langle j_a(0) j_b(\tau)\rangle$ ✓

  (ii) Consider $\langle \big(\int_0^T \mathrm{d}\tau\, j_a(\tau)\big)^2\rangle = \iint_0^T \mathrm{d}\tau\,\mathrm{d}\tau'\,\langle j_a(\tau)\, j_a(\tau')\rangle = \iint_0^T \mathrm{d}\tau\,\mathrm{d}\tau'\,\langle j_a(0)\, j_a(\tau-\tau')\rangle$

  $\underset{\text{reversi-}\atop\text{bility}}{=} \iint_0^T \mathrm{d}\tau \mathrm{d}\tau' \langle j_a(0) j_a(|\tau-\tau'|)\rangle = 2T \int_0^T \mathrm{d}\tau'' \langle j_a(0) j_a(\tau'')\rangle (1-\tau''/T)$

  $\Rightarrow\ \lambda_{aa} = \frac{V\beta}{2} \lim\limits_{T\to\infty} \frac{1}{T} \langle \big(\int_0^T \mathrm{d}\tau\, j_a(\tau)\big)^2\rangle \geqslant 0$ ✓

- Quantum mechanical case (grand canonical, $K_0 = H_0 - \mu N$, $[N,A] = [N,B] = 0$)

  (i) $\lambda_{ab} = V\int_0^\tau \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda \langle j_b(-i\hbar\lambda)\, j_a(\tau)\rangle = V\int_0^\tau \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda \langle j_b(-\tau - i\hbar\lambda)\, j_a(0)\rangle$

  $\overset{\text{reversibility}}{=} V\int_0^\tau \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda \langle j_b(\tau - i\hbar\lambda)\, j_a(0)\rangle$

  $= V\int_0^\tau \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda \frac{1}{Z_{GK}}\ \mathrm{Tr}\,\big(\mathrm{e}^{-\beta K_0 + \lambda H_0} j_b(\tau)\, \mathrm{e}^{\beta K_0 - \lambda H_0}\ \mathrm{e}^{-\beta K_0}\ j_a(0)\rangle$

  $= V\int_0^\tau \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda \frac{1}{Z_{GK}}\ \mathrm{Tr}\,\big(\underbrace{\mathrm{e}^{-(\beta-\lambda)H_0} j_b(\tau)\, \mathrm{e}^{(\beta-\lambda)H_0}}_{j_b(\tau + i\hbar(\beta-\lambda)}\ \mathrm{e}^{-\beta K_0}\ j_a(0)\big)$

  $\overset{\lambda'=\beta-\lambda}{=} V\int_0^\tau \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda' \langle j_a(0) j_b(\tau + i\hbar\lambda') j_a(0)\rangle = V\int_0^\tau \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda' \langle j_a(-i\hbar\lambda') j_b(\tau)\rangle$ ✓

  (ii) Define $J_T = \int_{-T/2}^{T/2} \mathrm{d}\tau'\, j_a(\tau' - i\hbar\frac{\lambda}{2},\ J_T^+ = \int_{-T/2}^{T/2} \mathrm{d}\tau'\, j_a(\tau' + i\hbar\frac{\lambda}{2}$

  Consider $\langle J_T J_T^+\rangle = \iint \mathrm{d}\tau'\,\mathrm{d}\tau'' \langle j_a(\tau' - i\hbar\frac{\lambda}{2}) j_a(\tau'' + i\hbar\frac{\lambda}{2})\rangle$

  $= 2T \int \mathrm{d}\tau \langle j_a(-i\hbar\lambda) j_a(\tau''-\tau')\rangle \overset{\tau''-\tau'=\tau}{=} \langle j_a(-i\hbar\lambda) j_a(\tau)\rangle (1-\tau/T)$

  $\Rightarrow\ \lambda_{aa} = \frac{V}{2} \lim_{T\to\infty} \frac{1}{T} \int_0^\beta \mathrm{d}\lambda \langle J_T J_T^+\rangle > 0$ ✓)

7.2.3 Entropy production

Starting point: Consider a system characterized by

ρ_k: Densities of conserved quantities with $\partial_t \rho_k = -\nabla\cdot\vec{j}_k$

$\vec{Z}_k, \Phi_k$: Generalized forces and potentials, $\frac{1}{T}\vec{Z}_k = -\nabla(\frac{1}{T}\Phi_k)$

Entropy change: $\mathrm{d}S = \frac{\text{đ}Q}{T}$ with $\text{đ}Q$: Produced heat

First law of thermodynamics: $\mathrm{d}E = \text{đ}Q + \text{đ}W$ with $\text{đ}W$: Work

$\Rightarrow$ Change of entropy density:

$\mathrm{d}s = \frac{1}{T}\mathrm{d}\rho_e - \frac{1}{T}\sum_j \mu_j\, \mathrm{d}n_j - \frac{1}{T}\sum_j X_j\, \mathrm{d}\xi_j - \cdots = -\sum_k \frac{1}{T}\Phi_k\, \mathrm{d}\rho_k$

$\Rightarrow$ Rate of entropy change $\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\partial s}{\partial t} + \nabla\cdot\vec{j}_s$

with $\vec{j}_s = -\sum_k \frac{1}{T}\Phi_k\,\vec{j}_k$, $\quad \frac{\partial s}{\partial t} = -\sum_k \frac{1}{T}\Phi_k\, \frac{\partial\rho_k}{\partial t} = -\sum_k \frac{1}{T}\Phi_k\, (\nabla\cdot\vec{j}_k)$

$\Rightarrow\ \frac{\mathrm{d}s}{\mathrm{d}t} = -\sum_k \nabla(\frac{1}{T}\Phi_k)\cdot\vec{j}_k\ = \frac{1}{T}\ \sum_k \vec{Z}_k\cdot\vec{j}_k$

Insert Onsager coefficients $\vec{j}_k = \boldsymbol{\lambda}_{kk}\, \vec{Z}_k$

$$\Rightarrow\ \boxed{\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\sum_k \vec{Z}_k\cdot\vec{j}_k = \frac{1}{T}\sum_{k,\alpha} \lambda_{kk}^{\alpha\alpha}\, Z_k^{\alpha 2} > 0} \qquad \text{since } \lambda_{kk}^{\alpha\alpha} > 0$$

Conclusion: Diffusive currents generate entropy

$\rightsquigarrow$ The assumption of microscopic reversibility ($\lambda_{kk}^{\alpha\alpha} > 0$)
results in macroscopic irreversibility ($\mathrm{d}s/\mathrm{d}t > 0$: Time arrow) !

7.2.4 Applications

First overview (table), then discuss selected cases separately

Transport coefficient	Conserved quantity	Current	Green-Kubo relation (classical)
Self diffusion D Mobility $1/\mu$	Particle number (one)	Velocity $\vec{v}$	$D = \frac{1}{d}\int\limits_0^\infty \mathrm{d}\tau \, \langle \vec{v}(0)\cdot\vec{v}(\tau)\rangle = \frac{k_BT}{\mu}$
Friction coefficient μ		Force $\vec{F}$ acting on particle at constrained velocity $\vec{v} = 0$	$\mu = \frac{1}{3k_BT}\int\limits_0^\infty \mathrm{d}\tau \, \langle \vec{F}(0)\cdot\vec{F}(\tau)\rangle$
Electrical conductivity σ	Charge	$\vec{j}_q = \frac{1}{V}\sum_i q_i\dot{\vec{r}}_i$	$\sigma = \frac{V}{3k_BT}\int\limits_0^\infty \mathrm{d}\tau \, \langle \vec{j}(0)\cdot\vec{j}(\tau)\rangle$
Thermal conductivity k_T	Energy	$\vec{j}_e = \frac{1}{V}\frac{\mathrm{d}}{\mathrm{d}t}\sum_i \vec{r}_i(e_i - \langle e\rangle)$ $e_i = \frac{p_i^2}{2m} + \frac{1}{2}\underbrace{\sum_j v(\vec{r}_{ij})}_{\text{pair interactions}} + \cdots$	$k_T = \frac{V}{3k_BT^2}\int\limits_0^\infty \mathrm{d}\tau \, \langle \vec{j}_e(0)\cdot\vec{j}_e(\tau)\rangle$
Viscosity	Momentum	Viscous stress tensor (Momentum current) $\boldsymbol{j}_g - \underbrace{\langle \boldsymbol{j}_g\rangle}_{\substack{\text{equilibrium value: } P\,1 \\ \text{with } P\text{: pressure}}} = -\boldsymbol{\sigma}'$ $\boldsymbol{j}_g = \frac{1}{V}\sum_i(m_i\vec{v}_i\otimes\vec{v}_i + \vec{r}_i\otimes\vec{f}_i)$	
Shear viscosity η		Secondary diagonals	$\eta = \frac{V}{6k_BT}\sum\limits_{\alpha\neq\gamma}\int\limits_0^\infty \mathrm{d}\tau \, \langle \sigma'_{\alpha\gamma}(0)\sigma'_{\alpha\gamma}(\tau)\rangle$
Longitudinal viscosity η_l $(\eta_l = \frac{4}{3}\eta + \zeta)$		Main diagonals	$\eta_l = \frac{V}{3k_BT}\sum\limits_{\alpha}\int\limits_0^\infty \mathrm{d}\tau \, \langle \sigma'_{\alpha\alpha}(0)\sigma'_{\alpha\alpha}(\tau)\rangle$

7.2.4.1 Electrical conductivity

- $\star$ Conserved quantity: Charge
  - Density: $\rho_q(\vec{r},t) = \sum_i q_i\,\delta(\vec{r} - \vec{R}_i(t))$
    First moment: $\vec{A}_q(t) = \int \mathrm{d}^d r\,\vec{r}\,\rho_q(\vec{r},t) = \sum_i q_i \vec{R}_i(t)$
  - Current: $\dot{\vec{A}}_q = V\vec{j}_q = \sum_i q_i \dot{\vec{R}}_i$
  - Generalized force $\vec{Z}_q$: Electrical field, $\vec{Z}_q = \vec{E}$
    (Perturbation: $H' = -\vec{E}\cdot\sum_i q_i\vec{R}_i$)
- $\star$ Transport law: $\boxed{\langle\vec{j}_q\rangle = \boldsymbol{\sigma}_q\vec{E}}$

  Onsager coefficients: Conductivity tensor $\boldsymbol{\sigma}_q$
- $\star$ Green-Kubo relation: $\boxed{\boldsymbol{\sigma}_q = V\beta\int_0^\infty \mathrm{d}\tau\,\langle\vec{j}_q(0)\otimes\vec{j}_q(\tau)\rangle}$

  Isotropic medium: $\boldsymbol{\sigma}_q = \sigma\,\mathbb{1}$ and $\boxed{\sigma = \frac{V\beta}{d}\int_0^\infty \mathrm{d}\tau\,\langle\vec{j}_q(0)\cdot\vec{j}_q(\tau)\rangle}$
- $\star$ Entropy production: $\frac{\mathrm{d}S}{\mathrm{d}t} = \int \mathrm{d}^d r\,\frac{1}{T}\,\vec{j}_q\cdot\vec{E} = \frac{V}{T}\,\sigma\,\vec{E}^2 > 0$

7.2.4.2 Thermal conductivity

- $\star$ Conserved quantity: Energy
  - Density: $\rho_e(\vec{r},t) = \sum_i \delta(\vec{r} - \vec{R}_i(t))(e_i - \langle e\rangle)$
    with $e_i = \frac{p_i^2}{2m} + \underbrace{\frac{1}{2}\sum_j v_{ij}}_{\text{pair interactions}} + \cdots$: local energy
    First moment: $\vec{A}_e(t) = \int \mathrm{d}^d r\,\vec{r}\,\rho_e(\vec{r},t) = \sum_i \vec{R}_i(t)\,(e_i - \langle e\rangle)$
  - Current: $\dot{\vec{A}}e = V\vec{j}_e$
  - Generalized force $\vec{Z}_e = T\nabla(\frac{1}{T}) = -\frac{\nabla T}{T}$
- $\star$ Transport law: $\boxed{\langle\vec{j}_e\rangle = -k_T\,\nabla T}$ Fourier law
- $\star$ Green-Kubo relation: $\boxed{k_T = \frac{V}{dk_B T^2}\int_0^\infty \mathrm{d}\tau\,\langle\vec{j}_e(0)\cdot\vec{j}_e(\tau)\rangle}$
- $\star$ Entropy production: $\frac{\mathrm{d}S}{\mathrm{d}t} = -\int \mathrm{d}^d r \frac{1}{T}\vec{j}_e\frac{\nabla T}{T} = k_T\int \mathrm{d}^d r\,(\frac{\nabla T}{T})^2 > 0$
- $\star$ Relation to diffusion law (with c: specific heat, ρ: density)

  Combine $\partial_t\rho_e + \nabla\cdot\vec{j}_e = 0$ and $\partial_t\rho_e = c\rho\partial_t T \;\Rightarrow\; c\rho\partial_t T = -\nabla\cdot\vec{j}_e = k_T\Delta T$

  $\rightsquigarrow$ Thermal equation: $\boxed{\frac{\partial T}{\partial t} = \kappa\,\Delta T}$ with $\boxed{\kappa = k_B T/c\rho}$

7.2.4.3 Mobility and self-diffusion of one particle

- ⋆ <u>Conserved quantity</u>: Particle Number
  - – Density: Distribution $n(\vec{r},t) = \delta(\vec{r} - \vec{R}(t))$
    First moment: $\vec{A}_n(t) = \int \mathrm{d}^d r \, \vec{r} \, n(\vec{r},t) = \vec{R}(t)$
  - – Current: Velocity $\dot{\vec{A}}_n = V \, \vec{j}_n = \dot{\vec{R}} =: \vec{v}$
  - – Generalized force $\vec{Z}_n$: Real external force $\vec{F}_{\text{ext}}$ on the particle
    (Perturbation: $H' = -\vec{F}_{\text{ext}} \cdot \vec{R}$)
- ⋆ <u>Transport law</u>: $\boxed{\langle \vec{v} \rangle = \vec{F}_{\text{ext}}/\mu}$ ($1/\mu$: Mobility constant)
- ⋆ <u>Green-Kubo relation</u>: $\boxed{\dfrac{1}{\mu} = \dfrac{\beta}{d} \displaystyle\int_0^\infty \mathrm{d}\tau \, \langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle}$
- ⋆ <u>Entropy production</u>: $\frac{\mathrm{d}}{\mathrm{d}t} S = \frac{1}{T} \vec{j}_n \cdot \vec{F}_{\text{ext}} = \frac{1}{T} \frac{1}{\mu} \vec{F}^2_{\text{ext}} > 0$
- ⋆ Relation to self-diffusion
  <u>Einstein relation</u>: $\boxed{D := \lim\limits_{t \to \infty} \dfrac{\langle (\vec{R}(t) - \vec{R}(0))^2 \rangle}{2dt} = \dfrac{k_{\scriptscriptstyle B} T}{\mu}}$

$$(\langle (\vec{R}(t) - \vec{R}(0))^2 \rangle = \langle (\textstyle\int_0^t \mathrm{d}\tau \, \vec{v}(\tau))^2 \rangle = \iint_0^t \mathrm{d}\tau \, \mathrm{d}\tau' \, \langle \vec{v}(\tau) \cdot \vec{v}(\tau') \rangle = \iint_0^t \mathrm{d}\tau \, \mathrm{d}\tau' \, \langle \vec{v}(0) \cdot \vec{v}(|\tau - \tau'|) \rangle$$
$$= 2t \textstyle\int_0^t \mathrm{d}\tau \, (1 - \tau/t) \, \langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle$$
$$\Rightarrow \lim_{t \to \infty} \tfrac{1}{2t} \langle (\vec{R}(t) - \vec{R}(0))^2 \rangle = \tfrac{d}{\beta} \, \tfrac{1}{\mu} \; \checkmark \;)$$

Remark: In general, Einstein relations have to be applied with care. Problems, e.g., in the case of rotational diffusion (angle jumps by 2π!)

7.2.4.4 Friction of one particle

Same problem as 7.2.4.3, but from a different perpective: Particle moves with <u>fixed</u> velocity $\vec{v}_{\text{fixed}}$ ($\widehat{=}$ Particle mass $M \to \infty$), experiences friction force $\vec{F}_{\text{friction}}$.

- – <u>Reference system</u>: Zero velocity, $\vec{v}_{\text{fixed}} = 0$
- – Identify <u>Perturbation</u>: Split up particle momentum: $\vec{P} = M \, \vec{v}_{\text{fixed}} + \vec{P}_{\text{int}}$
  ($M \, \vec{v}_{\text{fixed}}$: "external", imposed; $\vec{P}_{\text{int}}$: absorbs collisions with medium)
  $\Rightarrow H' = \frac{\vec{P}^2}{2M} - \frac{\vec{P}^2_{\text{int}}}{2M} = \frac{(\vec{P}_{\text{int}} + M \vec{v}_{\text{fixed}})^2}{2M} - \frac{\vec{P}^2_{\text{int}}}{2M} = \vec{P}_{\text{int}} \cdot \vec{v}_{\text{fixed}} + \mathscr{O}(\vec{v}^2_{\text{fixed}})$

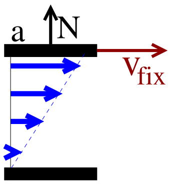
- ⋆ "Conserved quantity": None, apply formalism nevertheless with $\vec{A} = \vec{P}_{\text{int}}$
  - – "Current": Friction force $\vec{F}_{\text{friction}} = \mathrm{d}\vec{P}/\mathrm{d}t = \mathrm{d}\vec{P}_{\text{int}}/\mathrm{d}t = \mathrm{d}\vec{A}/\mathrm{d}t$
  - – Generalized force $\vec{Z} = -\vec{v}_{\text{fixed}}$
- ⋆ <u>Transport law</u>: $\boxed{\langle \vec{F}_{\text{friction}} \rangle = -\mu \, \vec{v}_{\text{fixed}}}$ (same coefficient μ as in 7.2.4.3)
- ⋆ <u>Green-Kubo relation</u>: $\boxed{\mu = \dfrac{\beta}{d} \displaystyle\int_0^\infty \mathrm{d}\tau \, \langle \vec{F}_{\text{friction}}(0) \cdot \vec{F}_{\text{friction}}(\tau) \rangle}$

  Remark: Prerequisite is that the particle really has velocity zero in the reference system (limit $M \to \infty$). Does not work if it diffuses freely. In that case, Green-Kubo integral is found to vanish ⇝ "plateau problem".
- ⋆ <u>Entropy production</u>: $\frac{\mathrm{d}}{\mathrm{d}t} S = \frac{1}{T} \vec{F}_{\text{friction}} \cdot \vec{v}_{\text{fixed}} = \frac{1}{T} \, \mu \, \vec{v}^2_{\text{fixed}} > 0$

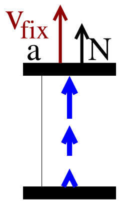
7.2.4.5 Viscosity

Consider the following system: Fluid confined between parallel plates.

Impose a strain rate by moving one plate with velocity $\vec{v}_{\text{fixed}}$ (normal vector $\vec{N}$, area a, mass $M \to \infty$).



Shear flow



Elongational flow

- Flow profile: $\vec{u}(\vec{r})$;
- Local strain rate: $G_{\alpha\beta}(\vec{r}) = \partial_\alpha u_\beta$.
- Global strain rate: $\overline{\boldsymbol{G}} = \frac{1}{V}\int \mathrm{d}^3r\, \boldsymbol{G}(\vec{r})$
  with $\vec{N}^T \overline{\boldsymbol{G}}\, V = a\,\vec{v}_{\text{fixed}}$
- Force on plate: $\vec{F}_{\text{plate}} = \boldsymbol{\sigma}\vec{N}a$
  with $\boldsymbol{\sigma}$: Stress tensor, known to be symmetric!

- Reference system: $\overline{\boldsymbol{G}} = 0$
- Perturbation (similar to 7.2.4.4): Split up plate momentum: $\vec{P} = M\,\vec{v}_{\text{fixed}} + \vec{P}_{\text{int}}$
  with $\frac{\mathrm{d}}{\mathrm{d}t}\vec{P}_{\text{int}} = \vec{F}_{\text{plate}} = -\boldsymbol{\sigma}\vec{N}a$; Define $\vec{P}_{\text{int}} =: \frac{a}{V}\,\boldsymbol{A}\vec{N} \Rightarrow \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{A} = -V\,\boldsymbol{\sigma}$
  $\Rightarrow H' = \frac{\vec{P}^2}{2M} - \frac{\vec{P}^2_{\text{int}}}{2M} = \vec{v}_{\text{fixed}}\cdot\vec{P}_{\text{int}} + \mathscr{O}(\vec{v}^2_{\text{fixed}}) = \vec{N}^T\overline{\boldsymbol{G}}\,\boldsymbol{A}\vec{N}$
  Generalize: Sum over all directions of of $\vec{N}$ and use $\boldsymbol{\sigma} = \boldsymbol{\sigma}^T \Rightarrow \boldsymbol{A} = \boldsymbol{A}^T$
  $\Rightarrow H' = \mathrm{Tr}\,\big(\overline{\boldsymbol{G}}\,\boldsymbol{A}\big) = \mathrm{Tr}\,\big(\overline{\boldsymbol{E}}\,\boldsymbol{A}\big)$ with $\boldsymbol{E} = \frac{1}{2}(\boldsymbol{G} + \boldsymbol{G}^T)$: Strain rate tensor

⋆ Conserved quantity: Momentum

- Density: Momentum density $\vec{g}(\vec{r},t) = \sum_i \delta(\vec{r} - \vec{R}_i(t))\,\vec{p}_i$
  First moment: $\boldsymbol{A}_g(t) = \int \mathrm{d}^d r\, \vec{r}\otimes\vec{g}(\vec{r},t) = \sum_i \vec{R}_i(t)\otimes\vec{v}_i\, m_i$
- Current: $\boldsymbol{j}_g = \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{A}_g = \underbrace{\sum_i (m_i\vec{v}_i\otimes\vec{v}_i + \vec{R}_i\otimes\vec{f}_i)}_{\text{Virial theorem: } -V\boldsymbol{\sigma}}$ since $(\vec{f}_i = m_i\dot{\vec{R}}_i)$
  $\Rightarrow \boldsymbol{A}_g = \boldsymbol{A}$
  NB: Equilibrium $\boldsymbol{\sigma}_{\text{eq}} = -P\mathbb{1}$ must be removed (”response”)
  $\rightsquigarrow \delta\boldsymbol{j}_g = -\boldsymbol{\sigma} - P\mathbb{1} = -\boldsymbol{\sigma}'$ (viscous stress tensor)
- Generalized force $\vec{Z}_g = -\overline{\boldsymbol{E}}$

⋆ Transport law: $\boxed{\boldsymbol{\sigma}' = \boldsymbol{L}\,\overline{\boldsymbol{E}}}$ with $\boldsymbol{L}$: Fourth order tensor

Isotropic media (without proof): $L_{\alpha\beta\gamma\delta} = \eta\,(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) + B\,\delta_{\alpha\beta}\,\delta_{\gamma\delta}$

$$\Rightarrow \boxed{\boldsymbol{\sigma}' = 2\eta\,\overline{\boldsymbol{E}} + B\,\mathbb{1}\,\mathrm{Tr}(\overline{\boldsymbol{E}}) =: 2\eta\,\underbrace{\Big(\overline{\boldsymbol{E}} - \frac{1}{3}\mathbb{1}\,\mathrm{Tr}(\overline{\boldsymbol{E}})\Big)}_{\text{traceless}} + \zeta\,\mathbb{1}\,\underbrace{\mathrm{Tr}(\overline{\boldsymbol{E}})}_{(\nabla\cdot\vec{u})}}$$

η: Shear viscosity - Opposes deformation without volume change

ζ: volume viscosity - Opposes isotropic volume dilation, $\zeta = B + \frac{2}{3}\eta$

⋆ Green-Kubo relation: $L_{\alpha\beta\gamma\delta} = \frac{V}{k_BT}\int_0^\infty \mathrm{d}\tau\,\langle\sigma'_{\alpha\beta}(0)\,\sigma'_{\gamma\delta}(\tau)\rangle$

Specifically: $L_{\alpha\beta\alpha\beta} = \eta$ for $\alpha \neq \beta$ (Onsager: $\eta \geqslant 0$)

$L_{\alpha\alpha\alpha\alpha} = 2\eta + B =: \eta_l$: Longitudinal viscosity ($\eta_l \geqslant 0$)

$$\Rightarrow \boxed{\begin{array}{rcl} \eta & = & \dfrac{V}{6k_BT}\displaystyle\sum_{\alpha\neq\beta}\int_0^\infty \mathrm{d}\tau\,\langle\sigma'_{\alpha\beta}(0)\sigma'_{\alpha\beta}(\tau)\rangle \\ \eta_l & = & \dfrac{V}{3k_BT}\displaystyle\sum_{\alpha}\int_0^\infty \mathrm{d}\tau\,\langle\sigma'_{\alpha\alpha}(0)\sigma'_{\alpha\alpha}(\tau)\rangle \end{array}}$$

Remark: As in 7.2.4.4, these Green-Kubo relations are only valid if the global strain rate is really constrained to zero in the equilibrium reference system (e.g., simulations with periodic boundary conditions). If it is allowed to fluctuate, one may encounter a plateau problem. On the other hand, the resulting viscosity parameters can also be used to describe local stress/strain rate relations in inhomogeneous systems down to the length scales of "fluid elements" (see literature on hydrodynamics).

- ⋆ Relation to <u>diffusion law</u> for velocities

  Consider incompressible case $\mathrm{Tr}(\boldsymbol{E}) = \nabla \cdot \vec{u} = 0 \Rightarrow \boldsymbol{\sigma'} = 2\eta \boldsymbol{E}$ and
  $\rightsquigarrow$ Density of viscous force: $\vec{f_v} = \nabla \boldsymbol{\sigma'} = 2\eta \, \nabla \boldsymbol{E}$
  $\rightsquigarrow$ Associated acceleration of fluid element: $\rho \frac{\mathrm{d}\vec{u}}{\mathrm{d}t} = \vec{f_v}$

  $$\text{with } \frac{\mathrm{d}\vec{u}}{\mathrm{d}t} = \partial_t \vec{u} + (\vec{u} \cdot \nabla)\vec{u} = \partial_t \vec{u} + \mathscr{O}(\boldsymbol{E}^2) \Rightarrow \partial_t \vec{u} = 2\eta \, \nabla \boldsymbol{E} \overset{\nabla \cdot \vec{u} = 0}{=} \eta \, \Delta \vec{u}$$

  $$\Rightarrow \boxed{\partial_t \vec{u} = \nu \, \Delta \vec{u}} \quad \text{with } \nu = \eta/\rho\text{: } \underline{\text{kinematic viscosity}}$$

- ⋆ <u>Local entropy production</u>:

  $$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T} \, \mathrm{Tr}(\boldsymbol{\sigma'} \boldsymbol{E}) = \frac{1}{T} \left(2\eta (\mathrm{Tr}(\boldsymbol{E}^2) - (\mathrm{Tr}\, \boldsymbol{E})^2) + \eta_l (\mathrm{Tr}\, \boldsymbol{E})^2 \right) > 0$$

Chapter 8

The Boltzmann Equation

TODO

8.1 Boltzmann equation for gases

8.2 Homogeneous systems: Equilibrium and H-theorem

8.3 Chapman Enskog expansion for inhomogeneous systems

8.4 Boltzmann equation for electrons

Chapter 9

Stochastic Processes

Equilibrium statistical physics (Sec. 1.2)
→ Probability based approach (Entropy and Jayne's principle)

Here: Consider dynamics, equilibrium and non-equilibrium
→ Choose again descriptions based on probability

First example: Boltzmann equation (Chapter **??**)
⇝ Description in terms of statistics of collisions.
Details of collisions (collision parameter) do not matter.

Second famous example: Brownian motion
⇝ Important additional concept of time scale separation
- "Slow" degrees of freedeom: Formulate dynamical equations
- "Fast" degrees of freedom: Enter as "noise", stochastic forces

This is the topic of the present chapter

Structure of the chapter

- First "quick and dirty"
- Mathematical framework of stochastic processes
- Applications: Brownian motion and Kramer's problem

9.1 Introduction: Brownian motion

System: Observe a particle under the microscope that undergoes thermal motion (one dimension for simplicity). Take a series of pictures (a movie)

⇝ stroposcopic time series $(t_1, t_2, \cdots, t_n)$

⇝ Observation: Series of positions $(x_1(t_1), \cdots x_n(t_n))$ for $t_1 < \cdots < t_n$

Goal: Understand the laws governing this time series

9.1.1 History

1827: Brown (Botanist)

Discovers irregular motion of small particles swimming on water under the microscope (pollen, minerals)

1905: Einstein

Theoretical explanation. Diffusion law $\langle \Delta r^2 \rangle \sim Dt$.

(Actually, Einstein did not know Brown's experiments. He made a theoretical prediction for an experiment designed to prove the atomic structure of matter.)

Very influential work
- Establishes nature of heat as being kinetic motion of particles
- Inspires a new field of mathematics (stochastic processes)

1906: Smoluchowski

Derivation of the same law by a different method

(Although not as "independent" as some claim: Smoluchowski knew Einstein's work and refers to it in his paper).

1908 Langevin – "Langevin equation"

Theoretical description in terms of a stochastic equation

1914 Fokker and 1917 Planck: – Fokker-Planck equation

Theoretical description in terms of equations for distribution functions

1918 - 1921: Smoluchowski and Wiener

Mathematical model for Brownian motion

1948: Feynman: Path integrals

9.1.2 Starting point: Deterministic friction force

Consider a particle in a viscous fluid → friction
(Surrounding molecules slow the particle down and absorb energy.)

Simplest equation: Stokes equation
Friction force: $F_D = -\mu\, v$
Dynamical equation: $m\dot{v} + \mu\, v = 0$ or $\dot{v} + \gamma\, v = 0$ with $\gamma = \frac{\mu}{m} =: \frac{1}{\tau}$

Solution: Velocity decays exponentially
$v(t) \sim \mathrm{e}^{-\gamma\, t} = \mathrm{e}^{-t/\tau}$ (with τ: Relaxation time)

Discussion: Deterministic treatment seems acceptable
as long as $v^2 \gg v^2_{\text{thermal}}$ $\quad (\frac{1}{2} m v^2_{\text{thermal}} = \frac{1}{2} k_B T)$
$\rightsquigarrow$ Only valid for particles with large masses!
Gives information on expectation value of $v(t)$

9.1.3 Motivation of the Langevin equation

Simple sloppy "derivation" of the Langevin equation for Brownian motion.
A more rigorous treatment will be introduced in Sec. 9.2.

If the particle velocity is comparable to thermal velocity v_{thermal}
$\rightsquigarrow$ Add additional stochastic force $F_R(t)$

Interpretation: Coupling to a "heat bath"
Represents an ensemble of possible surrounding systems

⋆ Total force of the medium on the particle: $F(t) = F_D(t) + F_R(t)$

or $\boxed{\dot{v} + \gamma\, v = \eta(t)}$ with $\eta(t) = F_R(t)/m$

Example of a Langevin equation

⋆ Properties of $\eta(t)$ (usual assumptions)

(i) $\langle \eta(t) \rangle = 0$
(ii) $\langle \eta(t)\, \eta(t') \rangle = q\, \delta(t-t')$ – Uncorrelated white noise
("white" → $\delta(t) = \int \mathrm{d}\omega\, \mathrm{e}^{i\omega t} 1$ is independent of ω)
(iii) Higher order correlations: According to Gaussian distribution

Motivation for these assumptions

ad (i): Nonvanishing parts of $\langle F_R \rangle$ would be attributed to the deterministic friction force.

ad (ii): The time scale of correlations ($\sim$ collision time) is taken to be much smaller than the time scale of interest here.
(questionable, but reasonable first order approximation)

ad (iii) Central limit theorem
For reasons of consistency, the functional form of the distribution of η should be the same for different time discretization (RG argument)
$\rightsquigarrow$ If second moment exists ($q < \infty$), this is only possible for the Gaussian distribution

⋆ Determination of remaining free parameter q

Temperature has to be recovered, i.e., $\lim_{t\to\infty} \langle v^2 \rangle = k_B T/m$

$$\Rightarrow \quad \boxed{q = 2\,\gamma\, \frac{k_B T}{m}}$$

(Argument: Quick and dirty solution of Langevin equation
with initial conditions $v(0) = v_0$

$v(t) = v_0 \mathrm{e}^{-\gamma t} + \int_0^t \mathrm{d}t'\, \mathrm{e}^{-\gamma(t-t')} \eta(t')$

$$\langle v(t_1)\, v(t_2) \rangle = v_0^2 \mathrm{e}^{-\gamma(t_1+t_2)} + \int_0^{t_1} \int_0^{t_2} \mathrm{d}t_1' \mathrm{d}t_2'\, \mathrm{e}^{-\gamma(t_1+t_2-t_1'-t_2')} \underbrace{\langle \eta(t_1')\, \eta(t_2') \rangle}_{q\delta(t_1'-t_2')}$$
$$= v_0^2 \mathrm{e}^{-\gamma(t_1+t_2)} + q\, \mathrm{e}^{-\gamma(t_1+t_2)} \underbrace{\int_0^{t_1} \mathrm{d}t_1' \mathrm{e}^{2\gamma t_1'}}_{\frac{1}{2\gamma}(\mathrm{e}^{2\gamma t_1}-1)}$$
$$= v_0^2 \mathrm{e}^{-\gamma(t_1+t_2)} + \tfrac{q}{2\gamma} (\mathrm{e}^{-\gamma(t_2-t_2)} - \mathrm{e}^{-\gamma(t_2+t_1)})$$
$$\xrightarrow{t_1 \to \infty} \tfrac{q}{2\gamma}\, \mathrm{e}^{-\gamma\, |t_2-t_1|}$$

$\Rightarrow \langle v(t)^2 \rangle = \frac{q}{2\gamma} = \frac{1}{2} \frac{k_B T}{m} \quad \Rightarrow \quad q = 2\gamma k_B T/m \quad \checkmark$)

⋆ Discussion:

- Above, we have also calculated the velocity autocorrelation function
  $\langle v(t)\, v(t')\rangle = \frac{k_B T}{m}\, \mathrm{e}^{-\gamma|t_1 - t_2|}$
- Mean square displacement $\langle (x(t) - x(0))^2\rangle$
  Einstein relation (cf. 7.2.4.3):
  $$\langle (x(t)-x(0))^2\rangle = \langle (\textstyle\int_0^t \mathrm{d}t'\ v(t'))^2\rangle = \iint_0^t \mathrm{d}t'\mathrm{d}t''\langle v(t)\, v(t')\rangle$$
  $$= \iint_0^t \mathrm{d}t'\mathrm{d}t''\, \frac{k_B T}{m}\mathrm{e}^{-\gamma|t'-t''|} = \frac{k_B T}{m}\big(\tfrac{2}{\gamma}t - \tfrac{2}{\gamma^2}(1-\mathrm{e}^{-\gamma t})\big)$$
  Limit $\gamma t \to \infty$: $\langle (x(t) - x(0))^2\rangle = 2Dt$ with $\boxed{D = \frac{k_B T}{m\gamma}}$
- This behavior is characteristic for diffusion
  Consider δ-shaped distribution at time $t = 0$ $\big(\, p(x, t = 0) = \delta(x)\, \big)$
  After time t: Broadens according to second moment $\langle x^2\rangle = 2Dt$
  Distribution is Gaussian (proof see later)
  $\rightsquigarrow$ $p(x,t) \sim \mathrm{e}^{-x^2/4DT}\, \sqrt{8\pi Dt}$
  $\rightsquigarrow$ Solves differential equation $\partial_t p(x, t) = D\, \partial_{xx} p(x, t)$
  $\rightsquigarrow$ Dynamical equation without dubious "random force"!

9.1.4 Motivation of the Fokker-Planck equation

The above discussion suggests that it may be of advantage to describe Brownian motion in terms of dynamical equations for distribution functions.

Here: Consider velocity distribution $p(v, t)$ (since the previously discussed Langevin equation describes the evolution of the velocity).

It turns out (next chapter) that this equation has the form

$$\boxed{\frac{\partial p}{\partial t} = \gamma\, \frac{\partial (vp)}{\partial v} + \gamma\, \frac{k_B T}{m}\, \frac{\partial^2 p}{\partial v^2}}$$

Example of a Fokker-Planck equation

"Drift term" "Diffusion term"

⋆ Discussion of the different terms

- "Drift term": Originates in friction force F_D
  Consider pure Stokes equation, without stochastic force: $\dot{v} = -\gamma\, v$
  → Evolution of v, dv after time dt: $v \to v - \gamma\, v\, \mathrm{d}t$, $\mathrm{d}v \to \mathrm{d}v(1 - \gamma\, \mathrm{d}t)$
  $$\to\ \mathrm{d}v\, p(v,t) = \big[\mathrm{d}v(1-\gamma\,\mathrm{d}t)\big]\, \big[p(v - \gamma v\mathrm{d}t, t + \mathrm{d}t)$$
  $$= \mathrm{d}v\, \big[p(v,t) \underbrace{-\gamma\, \mathrm{d}t\, p(v,t) - \gamma\, v\, \tfrac{\partial p}{\partial v}\, \mathrm{d}t}_{-\gamma \frac{\partial (vp)}{\partial v}\, \mathrm{d}t} + \tfrac{\partial p}{\partial t}\, \mathrm{d}t\big]$$
- "Diffusion term": Originates in stochastic force F_R
  Consider Langevin equation without friction force: $\dot{v} = \eta$
  → Diffusion in velocity space
  (Again quick and dirty: $\langle (v(t) - v(0))^2\rangle = \iint_0^t \mathrm{d}t'\mathrm{d}t''\langle \eta(t')\eta(t'')\rangle = 2\gamma \frac{k_B T}{m}\, t = q\, t$
  Initial condition $p(v, 0) = \delta(v - v_0)$ → Gaussian distribution: $p(v,t) \sim \exp(\frac{-(v-v_0)^2}{2qt})$
  Arbitrary initial distributions → Linear superposition of Gaussians
  satisfies differential equation $\frac{\partial p}{\partial t} = \gamma\, \frac{k_B T}{m}\, \frac{\partial^2 p}{\partial v^2}$)

For a clean treatment beyond "quick and dirty" see Section 9.2

9.1.5 Final remarks

⋆ General form of a Fokker-Planck equation

- One variable, $p(x,t)$
  $$\frac{\partial}{\partial t} p(x,t) = \big(- \frac{\partial}{\partial x} D^{(1)}(x) + \frac{1}{2} \frac{\partial^2}{\partial x^2} D^{(2)}(x) \big)\, p(x,t)$$
- Several variables, $p(\{x\},t)$
  $$\frac{\partial}{\partial t} p(\{x\},t) = \big(- \sum_i \frac{\partial}{\partial x_i} D^{(1)}_i(\{x\}) + \frac{1}{2} \sum_{ij} \frac{\partial^2}{\partial x_i \partial x_j} D^{(2)}_{ij}(\{x\}) \big) p(\{x\},t)$$

⋆ Interpretation: Describes distribution of fluctuating "slow" variables.
$\rightsquigarrow$ Hierarchy of modelling levels:

Microscopic ⟶	Stochastic ⟶	Deterministic
All degrees of freedom (DoFs)	Mesoscopic DoFs Microscopic DoFs are integrated out (fluctuations and friction)	"Macroscopic" Fluctuations are neglected. (e.g., no diffusion)

NB: Assumes perfect separation of time scales. Usually not correct (approximation). In the more general case, memory comes into play at the level of the stochastic description $\rightsquigarrow$ "Generalized Langevin equation"

⋆ Approaches to connect between levels

- Ideally: Exact calculation of $D^{(1)}$, $D^{(2)}$ from "first principles" (i.e., from microscopic theory). Usually not possible.
- Close to equilibrium: Linear response theory
- Often just heuristic: Start from from known deterministic equations (e.g., Navier-Stokes equations), add stochastic Langevin force

⋆ Comparison of Fokker-Planck equation and Boltzmann equation

In both cases: Equations for distribution functions

Boltzmann equation: All particles treated on equal footing
Approximation: Particles are uncorrelated

Fokker-Planck equation: Degrees of freedom could be anything
(e.g., Laser modes, currents, ...)
Approximation: Separation of time scales

9.2 Mathematical background: Stochastic processes

Problems with the discussion of Brownian motion so far:

Heuristic postulation of an "equation of motion" $\dot{v} + \lambda v = \eta(t)$

Many "quick and dirty proofs" relied on calculations involving integrals of the form $\int \mathrm{d}t'\, \dot{v} \sim \cdots + \int \mathrm{d}t' \eta(t')$

However, $\eta(t')$ (white noise) is uncorrelated, i.e., different at all times t
$\rightsquigarrow$ $\dot{v}$ is not well-defined ($v(t)$ is continuous, but not differentiable).
$\rightsquigarrow$ Currently, $\int \mathrm{d}t'\, \eta(t') \cdots$ is not well-defined.

(Example: $\langle \int_{t_1}^{t_2} \mathrm{d}t\, \eta(t)^2 \rangle = \int_{t_1}^{t_2} \mathrm{d}t \langle \eta(t)^2 \rangle = \int_{t_1}^{t_2} \mathrm{d}t\, \frac{k_B T}{m} \delta(0)$ always diverges!)

Now: More rigorous mathematical formulation

9.2.1 Definition of a stochastic process

⋆ Recall: stochastic variable

- Probability space $(\Omega, \mathscr{F}, \mu)$
  with Ω: Set of "outcomes" of a random process or experiment
  $\mathscr{F}$: σ-algebra on Ω ("event space")
  μ: Probability measure
- Random variable: μ integrable function $X : \Omega \to \mathbb{R}$
  Distributed according to a distribution function $f(x)$
  Expectation value: $\langle g(x) \rangle = \int g(x(\omega))\, \mathrm{d}\mu(\omega) = \int g(x)\, f(x)\, \mathrm{d}x$
- Notions of conditional probabilities, statistical independence etc.

⋆ Stochastic process: "Time dependent random variable"

- Family (X_t) of random variables with $t \in \mathbb{R}$ or $\mathbb{N}$ (index set)
  ($\mathbb{R}$: Continuous time; $\mathbb{N}$: Discrete time steps)
  below: often use notation for discrete processes for simplicity
- Corresponding distribution function
  - "One-point" distribution for one time t: $p(x,t) = \langle \delta(x - X_t) \rangle$
  - "N-point" distributions
    $p\big((x_1,t_1), \cdots, (x_N,t_N)\big) = \langle \delta(x_1 - X_{t_1}) \cdots \delta(x_N - X_{t_N}) \rangle$
  - Conditional probabilities etc. defined as usual
    e.g., $P(x_n|x_i)$: Conditional probability for $X_n = x_n$ given $X_i = x_i$
    $E(x_n|x_i)$: Corresponding expectation value

⋆ Special stochastic processes

- Stationary process:
  $p\big((x_1,t_1), \cdots, (x_N,t_N)\big) = p\big((x_1,t_1+\tau), \cdots, (x_N,t_N+\tau)\big)$ for all τ
  $\rightsquigarrow$ Invariant against time translations, homogeneity of time
  (not to confuse with stationary state in a dynamical system)

- Martingale process: (Discrete case): Process with $E(x_{n+1}|x_1 \cdot\cdot\, x_n) = x_n$
  (Actual value is the best estimate for the next value)
  Examples:
  - Sum of random variables with mean zero, $x_n = \sum_1^n y_i$ with $\langle y_i \rangle = 0$,
  - Diffusion in the absence of drift,
  - Weather forecast (well, sort of)
- Markov process: Process without memory
  $$p\big((x_n,t_n)|(x_1,t_1),\cdots,(x_{n-1},t_{n-1})\big) = p\big((x_n,t_n)|(x_{n-1},t_{n-1})\big) \quad \text{for } t_1 < t_2 \cdots < t_n$$
  Such processes are fully characterized by two distributions:
  $p(x,t)$ and $p\big((x_1,t_1)|(x_0,t_0)\big)$
  (Examples: Monte Carlo simulation in Chapter 3.6,
  Brownian dynamics,
  Deterministic Hamiltonian dynamics)

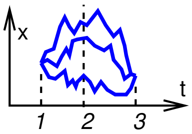
In the following, we will focus on stationary Markov processes

9.2.2 Dynamical equations for Markov processes

9.2.2.1 Transition rate and master equation

⋆ Chapman-Kolmogorov equation

Consider a Markov Process.
Then we have for $t_3 \geqslant t_2 \geqslant t_1$:



$$\boxed{p\big((x_3,t_3)|(x_1,t_1)\big) = \int \mathrm{d}x_2\, p\big((x_3,t_3)|(x_2,t_2)\big)\, p\big((x_2,t_2)|(x_1,t_1)\big)}$$

For stationary Markov processes, $p\big((x',t+\tau)|(x,t)\big)$ is independent of t.
This motivates the definition of a Transition rate

$$\boxed{R(x',x) = \lim_{\tau\to 0} \frac{1}{\tau}\; p\big((x',t+\tau)|(x,t)\big)}$$

Using the Chapman-Kolmogorov equation, one can use this to construct every other conditional probability for finite τ.

⋆ Master equation (for stationary Markov processes)

$$\boxed{\frac{\partial}{\partial t} p(x,t) = \underbrace{\int \mathrm{d}x'\, p(x',t)\, R(x,x')}_{\text{Flow in}} - \underbrace{\int \mathrm{d}x'\, p(x,t)\, R(x',x)}_{\text{Flow out}}}$$

(Example again: Monte Carlo simulations, chapter 3.6)

9.2.2.2 Fokker-Planck equation

Starting from the Master equation, make the following assumptions:

(i) Jumps are small: $R(x,x') \approx 0$ for large $(x-x')$; large peak at $x = x'$

$\rightsquigarrow$ Moment expansion: Define $R(x,x') =: \tilde{R}(x-x',x')$

$$\cdot \int \mathrm{d}x'\, p(x',t)\, R(x,x') = \int \mathrm{d}x'\, p(x',t)\, \tilde{R}(x-x',x')$$
$$= \int \mathrm{d}\xi\, p(x-\xi,t)\, \tilde{R}(\xi,x-\xi)$$
$$\overset{\text{Taylor}}{\approx} \int \mathrm{d}\xi\, \sum_k \tfrac{(-1)^k}{k!} \tfrac{\partial^k}{\partial x^k} \big[p(x,t)\, \tilde{R}(\xi,x)\big]\, \xi^k$$
$$= \sum_k \tfrac{(-1)^k}{k!} \tfrac{\partial^k}{\partial x^k} \big[p(x,t) \underbrace{\int \mathrm{d}\xi\, \xi^k \tilde{R}(\xi,x)}_{\alpha_k(x)} \big]$$

$$\cdot \int \mathrm{d}x'\, p(x,t)\, R(x',x) = p(x,t) \int \mathrm{d}x'\, \tilde{R}(x'-x,x) = p(x,t)\, \alpha_0(x)$$

$\rightsquigarrow$ Kramers Moyal expansion of the master equation

$$\boxed{\frac{\partial}{\partial t} p(x,t) = \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \frac{\partial^k}{\partial x^k} \big[\, \alpha_k(x)\, p(x,t)\, \big]}$$

with $\boxed{\alpha_k(x) = \int \mathrm{d}\xi\, \xi^k\, \tilde{R}(\xi,x)}$

(ii) $R(x,x')$ varies only slowly as a function of $x (\approx x')$

$\rightsquigarrow$ $p(x,t)$ also varies only slowly

$\rightsquigarrow$ Cut off the expansion after the second moment

$$\Rightarrow \boxed{\frac{\partial}{\partial t} p(x,t) = -\frac{\partial}{\partial x}\big(\alpha_1(x)\, p(x,t)\big) + \frac{1}{2}\frac{\partial^2}{\partial x^2}\big(\alpha_2(x)\, p(x,t)\big)}$$

9.2.2.3 Evolution of single paths and Langevin equation

Now consider evolution of single paths (X_t)

Assume $p(x,0) = \delta(x)$ (initial condition) and τ small $\Rightarrow$ $p(x,\tau) = \delta(x) + \frac{\partial p}{\partial t}\, \tau$

$$\langle X_\tau^n \rangle = \int \mathrm{d}x\, x^n p(x,\tau) = \tau \int \mathrm{d}x\, x^n\, \tfrac{\partial p}{\partial t} = \tau \big[\sum_k \tfrac{(-1)^k}{k!} \int \mathrm{d}x\, x^n \tfrac{\partial^k}{\partial x^k} \big(\alpha_k(x) \delta(x)\big)\big]$$
$$= \tau \Big[\sum_k \tfrac{(-1)^k}{k!} \alpha_k(0) \tfrac{\partial^k}{\partial x^k}\, x^n \Big|_{x=0} \Big] = \tau\, \alpha_n(0)$$

Generalization: $\langle (X_\tau - X_0)^n \rangle \equiv \big\langle \big(x(\tau) - x(0)\big)^n \big\rangle = \tau\, \langle \alpha_n(x(0)) \rangle + \mathscr{O}(\tau^2)$

Specifically: Cutoff at $n = 2$ (Fokker-Planck equation)

$\Rightarrow$ Formal notation as "Langevin equation"

$$\boxed{\mathrm{d}x = a(x)\, \mathrm{d}t + b(x) \cdot \mathrm{d}W} \quad \text{with} \quad \langle \mathrm{d}W \rangle = 0,\ \langle \mathrm{d}W^2 \rangle = \mathrm{d}t$$

Idea: $a(x)$ takes care of α_1, $b(x)^2$ takes care of α_2

However, at this point, it is not yet clear what is meant by this notation.

How to integrate over $\mathrm{d}x$?

How to calculate $\langle (x(\tau) - x(0))^2 \rangle$ given "$x(\tau) - x(0) = \int_0^\tau \mathrm{d}x$" ?

$\rightsquigarrow$ What is the relation between $a(x)$, $b(x)$ and $\alpha_1(x)$, $\alpha_2(x)$?

→ Next section!

9.2.3 Stochastic differentials and stochastic integration

Question: Given a differential such as that quoted in the last section (9.2.2.3), $\mathrm{d}x = v(x)\,\mathrm{d}t + b(x)\cdot\mathrm{d}W$. How does it have to be integrated?
$\rightsquigarrow$ Requires some more definitions!

9.2.3.1 Wiener process

Special stochastic process $W(t)$ with

- $W(0) = 0$
- Increments $(W(t+\tau) - W(t))$ are Gaussian distributed with mean zero and variance τ
- For $0 \leqslant t_0 < t_1 < t_2 \cdots$, the $(W(t_{n+1} - W(t_n))$ are stochastically independent.

Consequence: $\langle W(\tau_1)\,W(\tau_2)\rangle = \min(\tau_1,\tau_2)$ for $\tau_1,\tau_2 > 0$

(Increment $\mathrm{d}W$ is the mathematical version of a δ-correlated noise $\mathrm{d}W = \mathrm{d}t\,\xi(t)$
with $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\,\xi(t')\rangle = \delta(t-t')$, i.e., $\mathrm{d}W = \xi(t)\,\mathrm{d}t$
$\Rightarrow \langle W(\tau_1)\,W(\tau_2)\rangle = \int_0^{\tau_1}\mathrm{d}t\int_0^{\tau_2}\mathrm{d}t'\,\langle\xi(t)\xi(t')\rangle = \int_0^{\tau_1}\mathrm{d}t\int_0^{\tau_2}\mathrm{d}t'\,\delta(t-t') = \min(\tau_1,\tau_2)$)

9.2.3.2 Stochastic integrals: Itô and Stratonovich convention

Here: Wiener process as "Integrator". Can be generalized for other Martingales.

$$\int_{t_0}^{t} G(t')\cdot\mathrm{d}W(t') = \underset{\epsilon\to 0}{\text{ms-lim}} \sum_{j=0}^{(t-t_0)/\epsilon-1} \bar{G}(\bar{t}_j)\big[W(t_{j+1}) - W(t_j)\big] \qquad (t_j = t_0 + \epsilon j)$$

where $\underset{n\to\infty}{\text{ms-lim}}\, x_n = \bar{x} \;\Leftrightarrow\; \lim_{n\to\infty}\langle(x_n-\bar{x})^2\rangle = 0$: Mean square limit
(NB: regular limit cannot be used if random variables are involved!)

To complete the definition, we must specify how to evaluate $\bar{G}(\bar{t}_j)$.

- Itô integral: $\bar{G}(\bar{t}_j) = G(t_j)$ (Notation: "$\int G(t')\,\mathrm{d}W(t')$")
- Stratonovich integral: $\bar{G}(\bar{t}_j) = \frac{1}{2}\big(G(t_j) + G(t_{j+1})\big)$ ("$\int G(t')\circ\mathrm{d}W(t')$")

Example illustrating the difference: Calculate $\langle\int_0^t W(t')\cdot\mathrm{d}W(t')\rangle$

Itô integral: $\langle\int_0^t W(t')\,\mathrm{d}W(t')\rangle = 0$

($\langle\int_0^t W(t')\,\mathrm{d}W(t')\rangle = \langle\lim_{\epsilon\to 0}\sum_j W(t_j)\,(W(t_{j+1}) - W(t_j))\rangle$
$= \lim_{\epsilon\to 0}\sum_j\,(\langle W(t_{j+1})\,W(t_j)\rangle - \langle W(t_j)^2\rangle) = \lim_{\epsilon\to 0}\sum_j\,(t_j - t_j) = 0$)

Stratonovich integral: $\langle\int_0^t W(t')\circ\mathrm{d}W(t')\rangle = \frac{t}{2} = \langle W^2(t)/2\rangle$

($\langle\int_0^t W(t')\circ\mathrm{d}W(t')\rangle = \langle\lim_{\epsilon\to 0}\sum_j \frac{1}{2}\big(W(t_{j+1}) + W(t_j)\big)\,\big(W(t_{j+1}) - W(t_j)\big)\rangle$
$= \lim_{\epsilon\to 0}\sum_j \frac{1}{2}\big(\langle W(t_{j+1})^2\rangle - \langle W(t_j)^2\rangle\big) = \lim_{\epsilon\to 0}\sum_j \frac{1}{2}\big(t_{j+1} - t_j\big) = t/2$)

(Compare regular integral: $\int_0^t W\,\mathrm{d}W = W^2/2$)

$\rightsquigarrow$ Comparison:

Itô: Simpler, stochastic integral is a Martingale process
But: New rules for differentiation and integration (Itô calculus)
Preferred convention in financial mathematics

Stratonovich: More "physical", usual calculus rules apply
Convention often adopted in physics and engineering

9.2.3.3 Implications for stochastic differential equations

Consider a stochastic differential of the type: $\mathrm{d}x = a(x)\,\mathrm{d}t + b(x)\cdot\mathrm{d}W$

$\rightsquigarrow$ Defined by the chosen convention (Itô or Stratonovich) for calculating the integral $x(t) - x(0) = \int_0^t \mathrm{d}t'\, v(x(t')) + \int_0^t b(x(t'))\cdot \mathrm{d}W(t')$

⋆ Remark on the difference between the two conventions. When is it important?

Distinguish between

(i) Additive noise: $b =$ const. independent of x
$\rightsquigarrow$ Then, the choice of convention does not matter!
(since $\int \mathrm{d}W(t')$ is the same in both cases!)

(ii) Multiplicative noise: $b(x)$ depends on x
$\rightsquigarrow$ In that case, the conventions give different results.
Background: Multiplicative noise induces drift.
This is described differently in the different conventions.

Note: By a suitable choice of variables ($\mathrm{d}y = \mathrm{d}x/b(x)$), one can turn multiplicative noise into additive noise. In one dimensional systems, the difference between Itô and Stratonovich is thus not truly fundamental.

⋆ Variable transform

Given a stochastic differential equation $\mathrm{d}x = a(x)\,\mathrm{d}t + b(x)\cdot\mathrm{d}W$

Goal: Change of variables $x \to y = f(x,t)$
$\rightsquigarrow$ Expand $\mathrm{d}f = f(x+\mathrm{d}x, t+\mathrm{d}t) - f(x,t)$ up to $\mathcal{O}(\mathrm{d}t)$,
using $(\mathrm{d}W) \sim \mathcal{O}(\sqrt{\mathrm{d}t})$ ("Itô rule": $(\mathrm{d}W)^2 \,\hat{=}\, \mathrm{d}t$)

In the Itô formalism: Itô formula

$$\boxed{\mathrm{d}f(x(t),t) = \Big[\frac{\partial}{\partial t}f + a\,\frac{\partial}{\partial x}f + \frac{1}{2}\,b^2\,\frac{\partial^2}{\partial x^2}f\Big]\mathrm{d}t + b\,\frac{\partial f}{\partial x}\,\mathrm{d}W}$$

(Quick and dirty calculation: $\mathrm{d}f = f(x+\mathrm{d}x, t+\mathrm{d}t) - f(x,t)$

$\mathrm{d}f = \frac{\partial f}{\partial x}\big|_x\,\mathrm{d}x + \frac{1}{2}\frac{\partial^2 f}{\partial x^2}\big|_x\,(\mathrm{d}x)^2 + \frac{\partial f}{\partial t}\big|_t\,\mathrm{d}t +$ higher order terms

| $\mathrm{d}x = a\,\mathrm{d}t + b\,\mathrm{d}W$,
| $(\mathrm{d}x)^2 = b^2\,(\mathrm{d}W)^2 +$ higher order $\hat{=}\; b^2\,\mathrm{d}t +$ higher order

$= \big[\frac{\partial f}{\partial x}\big|_x\,a + \frac{1}{2}\,\frac{\partial^2 f}{\partial x^2}\big|_x b^2 + \frac{\partial f}{\partial t}\big|_t\big]\mathrm{d}t + b\,\frac{\partial f}{\partial x}\big|_x\,\mathrm{d}W \quad \checkmark$)

In the Stratonovich formalism: Chain rule

$$\boxed{\mathrm{d}f(x(t),t) = \big(\frac{\partial}{\partial t}f + a\,\frac{\partial}{\partial x}f\big)\mathrm{d}t + b\,\frac{\partial f}{\partial x}\circ\mathrm{d}W}$$

(Quick and dirty: $\mathrm{d}f = \frac{\partial f}{\partial x}\,a\,\mathrm{d}x + \frac{1}{2}\frac{\partial^2 f}{\partial x^2}\,(\mathrm{d}x)^2 + \frac{\partial f}{\partial t}\,\mathrm{d}t$ as above

| $\mathrm{d}x = a(x)\,\mathrm{d}t + b(x)\circ\mathrm{d}W = a(x)\,\mathrm{d}t + \frac{1}{2}(b(x) + b(x+\mathrm{d}x))\,\mathrm{d}W$
| $= a\,\mathrm{d}t + b\,\mathrm{d}W + \frac{1}{2}(\partial_x b)\,\mathrm{d}x\,\mathrm{d}W = a\,\mathrm{d}t + b\,\mathrm{d}W + \frac{1}{2}(\partial_x b)\,b\,(\mathrm{d}W)^2$
| $(\mathrm{d}x)^2 = b^2\,(\mathrm{d}W)^2$

$\mathrm{d}f = \big(\frac{\partial f}{\partial x}\,a + \frac{\partial f}{\partial t}\big)\mathrm{d}t + \frac{1}{2}\,\big((\partial_x f)b(\partial_x b) + (\partial_{xx}f)\,b^2\big)(\mathrm{d}W)^2 + (\partial_x f)\,b\,\mathrm{d}W$
$= \big(\frac{\partial f}{\partial x}\,a + \frac{\partial f}{\partial t}\big)\,\mathrm{d}t + \frac{1}{2}\,b\,\partial_x(b\,\partial_x f)\,(\mathrm{d}W)^2 + b\,(\partial_x f)\,\mathrm{d}W$

Compare chain rule: $\mathrm{d}f = \big(\frac{\partial f}{\partial x}\,a + \frac{\partial f}{\partial t}\big)\,\mathrm{d}t + b(\partial_x f)\circ\mathrm{d}W$
with $b\,(\partial_x f)\circ\mathrm{d}W = \frac{1}{2}\big(\big[b\,(\partial_x f)\big]_x + \big[b\,(\partial_x f)\big]_{x+\mathrm{d}x}\big)\,\mathrm{d}W$
$= b\,(\partial_x f)_x\,\mathrm{d}W + \frac{1}{2}\,\partial_x(b\,(\partial_x f)\,\mathrm{d}x\,\mathrm{d}W$
$= b\,(\partial_x f)_x\,\mathrm{d}W + \frac{1}{2}\,b\,\partial_x(b\,(\partial_x f)\,(\mathrm{d}W)^2 \to$ same expression! $\checkmark$)

9.2.3.4 Implications for corresponding Fokker-Planck equations

Consider Langevin differential of the form $\boxed{\mathrm{d}x = a(x)\,\mathrm{d}t + b(x)\cdot\mathrm{d}W}$
with $b(x)\cdot\mathrm{d}W = b(x)\,\mathrm{d}W$ (Itô) or $b(x)\cdot\mathrm{d}W = b(x)\circ\mathrm{d}W$ (Stratonovich)

Question: Corresponding Fokker-Planck equations?

Solution: Use Kramer's Moyal expansion (Sec. 9.2.2.3),
i.e., calculate <u>moments</u>: $\alpha_n(x_0) = \lim\limits_{\tau\to 0}\frac{1}{\tau}\,\langle (x(\tau)-x(0))^n\rangle_{x(0)=x_0}$

Calculation:
Consider $\Delta x(t) := x(t) - x(0) = \int_0^t \mathrm{d}x$ for fixed initial value $x(0) = x_0$
Expand up to order t using $W(t) = \mathscr{O}(\sqrt{t})$
Notation: $a_0 = a(x_0),\ b_0 = b(x_0),\ b_0' = (\partial b)_{x_0}$ (numbers, not stochastic!)
Split up: $\Delta x(t) := \Delta x_1(t) + \Delta x_2(t)$
with $\Delta x_1(t) = \int_0^t a\,\mathrm{d}t = a_0 t + \mathscr{O}(t^{3/2})$
and $\Delta x_2(t) = \int_0^t b\cdot\mathrm{d}W(t) = \mathscr{O}(t^{1/2})$
Calculate $\Delta x_2(t) = \int_0^t b(x(t'))\cdot\mathrm{d}W(t') = \int_0^t \big(b_0 + b_0'\,\Delta x(t')\big)\cdot\mathrm{d}W(t') + \mathscr{O}(t^{3/2})$
$= b_0\,W(t) + b_0\,\int_0^t \Delta x_2(t')\cdot\mathrm{d}W(t') + \mathscr{O}(t^{3/2})$
Iterative solution by successive insertion: $\Delta x_2 = \Delta x_2^{(}1) + \Delta x_2^{(2)} + \cdots$
with $\Delta x_2^{(1)}(t) = b_0 W(t)$ $\quad\sim \mathscr{O}(t^{1/2})$
$\Delta x_2^{(2)}(t) = b_0'\int_0^t \Delta x_2^{(1)}(t')\cdot\mathrm{d}W(t') = b_0'\,b_0\int_0^t W(t')\cdot\mathrm{d}W(t')$ $\quad\sim \mathscr{O}(t)$
$\Delta x_2^{(n)}(t) = b_0'\int_0^t \Delta x_2^{(n-1)}(t')\cdot\mathrm{d}W(t')$ $\quad\sim \mathscr{O}(t^{n/2})$
$\Rightarrow\ \Delta x_2(t) = b_0\,W(t) + b_0'\,b_0\int_0^t W(t')\cdot\mathrm{d}W(t') + \mathscr{O}(t^{3/2})$
Insert to calculate moments up to order τ
– $\langle\Delta x(\tau)\rangle = a_0\,\tau + b_0'\,b_0\langle\int_0^t W(t')\cdot\mathrm{d}W(t')\rangle = (a_0 + \theta\,\frac{1}{2}\,b_0'\,b_0)\,\tau$
with $\theta = 0$ (Itô) or $\theta = 1$ (Stratonovich) (see Sec. 9.2.3.2)
– $\langle(\Delta x(\tau))^2\rangle = b_0^2\,\langle W(\tau)^2\rangle = b_0^2\,\tau$
– $\langle(\Delta x(\tau))^n\rangle \sim \mathscr{O}(\tau^{3/2})$ for $n > 2$

Result: $\alpha_1(x) = a(x)$ (Itô) or $a(x) + \frac{1}{2}(\partial_x b(x))\,b(x)$ (Stratonovich)
$\alpha_2(x) = b(x)^2$
$\alpha_n(x) = 0$ for $n > 2 \rightsquigarrow$ Expansion stops as expected ✓

⇒ Fokker-Planck equations corresponding to the above stochastic differential

<u>Itô case</u>:

$$\boxed{\frac{\partial}{\partial t}p(x,t) = -\frac{\partial}{\partial x}\big(a(x)\,p(x,t)\big) + \frac{1}{2}\frac{\partial^2}{\partial x^2}\big(b(x)^2\,p(x,t)\big)}$$

<u>Stratonovich case</u>:

$$\boxed{\frac{\partial}{\partial t}p(x,t) = -\frac{\partial}{\partial x}\big(a(x)\,p(x,t)\big) + \frac{1}{2}\frac{\partial}{\partial x}\,\Big(b(x)\,\frac{\partial}{\partial x}\,b(x)\,p(x,t)\Big)}$$

$$\Big(\partial_t p(x,t) = -\partial_x\big(a(x)\,p(x,t) + \tfrac{1}{2}b(x)\,(\partial_x b)\,p(x,t)\big) + \tfrac{1}{2}\partial_{xx}\,\big(b(x)^2\,p(x,t)\big)$$
$$\text{Use } \partial_{xx}\big(b(x)^2 p(x,t)\big) = \partial_x\,\big(b(x)\partial_x\,b(x)\,p(x,t)\big)\big) + \partial_x\,\big((\partial_x b(x))\,b(x)p(x,t)\big)\ \Big)$$

<u>Remark</u>: The <u>physical dynamics</u> of a system is actually defined by the the Fokker-Planck equation, not the Langevin equation.

→ Depending on the convention, different Langevin equations must be used to represent the same system ("Itô / Stratonovich" dilemma)

⋆ <u>Physical theories</u> are often based on the Stratonovich convention.
<u>Simulation schemes</u> often tacidly use the Itô convention.

⋆ Luckily, the difference only matters if $b(x)$ depends on x, i.e., in cases of multiplicative noise.

9.3 Applications: Brownian particles revisited

With the mathematical formalism at hand, we will now turn back to the problem of Brownian motion and discuss a few simple applications.

9.3.1 General description

We consider a Brownian particle of mass m with velocity $\vec{v}$ and position $\vec{r}$ in an external field $\vec{F}(\vec{r})$ with fixed friction constant $\mu = m\,\gamma$.

⋆ Stochastic differential equation (two coupled differentials)

$$\begin{array}{lll} (1) & \mathrm{d}\vec{r} & = \vec{v}\,\mathrm{d}t \\ (2a) & m\,\mathrm{d}\vec{v} & = (\vec{F}(\vec{r}) - \mu\,\vec{v})\,\mathrm{d}t + \Gamma\,\mathrm{d}W \\ & \text{or, alternatively} & \\ (2b) & \mathrm{d}\vec{v} & = (\frac{\vec{F}(\vec{r})}{m} - \gamma\,\vec{v})\,\mathrm{d}t + \frac{\Gamma}{m}\,\mathrm{d}W \end{array}$$

NB: Here, W stands for a three dimensional Wiener process

⋆ Corresponding Fokker-Planck equation for $\boxed{p(\vec{r},\vec{v},t)}$

Klein-Kramers equation

$$\boxed{\frac{\partial p}{\partial t} = -\nabla_{\vec{r}}\cdot(\vec{v}\,p) + \nabla_{\vec{v}}\cdot\big[\big(\gamma\vec{v} - \frac{\vec{F}}{m}\big)\,p\big] + \frac{1}{2}\big(\frac{\Gamma}{m}\big)^2\,\Delta_{\vec{v}}\,p}$$

(Kramers 1940: Description of chemical reactions)

Determination of the constant Γ

Assume $\vec{F}(\vec{r}) = -\nabla_{\vec{r}}U(\vec{r})$ can be derived from a potential

At thermal equilibrium, the Fokker-Planck equation should have the stationary solution $p_{\mathrm{eq}}(\vec{r}) \sim \exp(-\frac{1}{k_BT}\big(U + \frac{1}{2}m\vec{v}^2\big))$

Insert this in the r.h.s. of the Klein-Kramers equation (exercise)

$$\Rightarrow \partial_t p_{\mathrm{eq}}(\vec{r}) = \cdots = \nabla_{\vec{v}}\cdot\big(\gamma\vec{v} - \frac{1}{2}\frac{\Gamma^2}{k_BT\,m}\vec{v}\big)\,p_{\mathrm{eq}}(\vec{r}) \overset{!}{\equiv} 0$$

$\Rightarrow$ $\boxed{\Gamma^2 = 2\,m\gamma\,k_BT = 2\,\mu\,k_BT}$: "Fluctuation-dissipation relation"

⋆ Overdamped limit

Assume that the time scale $1/\gamma$ of velocity relaxation (the inertial time scale) is very small compared to the time scales of interest. Then the stochastic differential equation can be simplified:

$$\mathrm{d}\vec{r} = \frac{\vec{F}(\vec{r})}{\mu}\,\mathrm{d}t + \frac{\Gamma}{\mu}\,\mathrm{d}W$$

(Sloppy reasoning: Neglect inertia → set $m = 0$ and insert $\mathrm{d}\vec{r} = \vec{v}\,\mathrm{d}t$ above in Eqn. (2a). However, in fact, one makes an expansion $1/\gamma \to 0$ and keeps the leading term. below for a cleaner calculation.)

Corresponding Fokker-Planck equation: Smoluchowski equation

$$\boxed{\frac{\partial p(\vec{r},t)}{\partial t} = -\frac{1}{\mu}\nabla_{\vec{r}}\,\vec{F}(\vec{r})\,p(\vec{r},t) + \frac{1}{2}\big(\frac{\Gamma}{\mu}\big)^2\,\Delta_{\vec{r}}\,p(\vec{r},t)}$$

⋆ Addendum (Side calculation):

Derivation of Smoluchowski equation from Klein-Kramers equation in one dimension. For the sake of generality allow the parameters γ etc. to depend on x.

Starting point: Klein-Kramers equation for $p(x,v,t)$

$$\boxed{\partial_t p = -\partial_x (v\, p) + \partial_v (\gamma v - \frac{F}{m})\, p + \frac{\gamma k_B T}{m} \partial_{vv} p}$$

Define velocity moments: $p^{(n)}(x,t) = \int \mathrm{d}v\, v^n\, p(x,v,t)$ for $n \geqslant 0$

$\Rightarrow \partial_t p^{(n)} = -\partial_x p^{(n+1)} + \gamma\big(- n\, p^{(n)} + n\, \frac{F}{m\,\gamma}\, p^{(n-1)} + \frac{k_B T}{m} n\,(n-1)\, p^{(n-2)}\big)$

where we formally set $p^{(n)}(x,t) \equiv 0$ for $n < 0$

Laplace transform in time domain: $P^{(n)}(s) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st}\, p^{(n)}(t), \quad p^{(n)}(0) = p_{n0}$

$\Rightarrow sP^{(n)} = p_{n0} - \partial_x P^{(n+1)} + \gamma\big(- nP^{(n)} + n\frac{F}{m\,\gamma} P^{(n-1)} + \frac{k_B T}{m}\, n\,(n-1)\, P^{(n-2)}\big)$

Expand in powers of $1/\gamma$ in the limit $\gamma \to \infty$

Starting point:

$n = 0 :\ sP^{(0)} = p_{00} - \partial_x\, P^{(1)}$

$n \neq 0 :\ P^{(n)} = \big[1 + \frac{s}{\gamma\, n}\big]^{-1} \big[\frac{k_B T\,(n-1)}{m}\, P^{(n-2)} + \frac{F}{m\gamma}\, P^{(n-1)} - \frac{1}{\gamma n}\, \partial_x\, P^{(n+1)} + \frac{1}{\gamma n}\, p_{n0}\, \big]$

Expansion for $n \neq 0$

Zeroth order: $P^{(n)} = \frac{k_B T}{m}(n-1)\, P^{(n-2)} \quad (\rightsquigarrow\ P^{(n+1)} = \frac{k_B T}{m}\, n\, P^{(n-1)})$

First order: $P^{(n)} = (1 - \frac{s}{\gamma n})\frac{k_B T}{m}(n-1)\, P^{(n-2)} + \frac{1}{\gamma}\, \big[\big(\frac{F}{m} - \frac{1}{n}\partial_x \frac{k_B T}{m}\big)\, P^{(n-1)} + \frac{1}{n} p_{n0}\big]$

Specifically $n = 1$: $P^{(1)} = \frac{1}{\gamma}\, \big[\big(\frac{F}{m} - \partial_x \frac{k_B T}{m}\big)\, P^{(0)} + p_{10}\big]$

Insert in equation for $n = 0$

$\Rightarrow\ sP^{(0)} = \big(p_{00} - \partial_x\, \frac{1}{\gamma}\, p_{10}\big) + \partial_x\, \frac{1}{\gamma}\, \big(- \frac{F}{m} + \partial_x \frac{k_B T}{m}\big) P^{(0)}$

Backtransformation $\rightsquigarrow$ Equation for $\boxed{p^{(0)}(x,t) = \int \mathrm{d}v\, p(x,v,t) =: \tilde{p}(x,t)}$

$$\boxed{\partial_t \tilde{p}(x,t) = \partial_x\, \big(- \frac{F}{\mu} + \partial_x \frac{k_B T}{\mu}\big)\, \tilde{p}(x,t)}$$

with effective boundary condition $\tilde{p}(x,0) = \int \mathrm{d}v\, p(x,v,0) - \frac{1}{\gamma}\, \partial_x \int \mathrm{d}v\, v\, p(x,v,0)$

9.3.2 Free diffusion

First we describe a freely diffusing Brownian particle ($F = 0$) in one spatial dimension.

9.3.2.1 Velocity process

If the position is not of interest, the stochastic process reduces to an effectively one-dimensional Ornstein-Uhlenbeck process

$$\boxed{\mathrm{d}v = -\gamma\, v\, \mathrm{d}t + \frac{\Gamma}{m}\, \mathrm{d}W} \qquad \boxed{\frac{\partial p}{\partial t} = \partial_v(\gamma\, v\, p) + \frac{1}{2}\big(\frac{\Gamma}{m}\big)^2 \frac{\partial^2}{\partial v^2}\, p}$$

Solution: Fokker-Planck equation is linear $\rightsquigarrow$ Greens functions formalism

For given initial condition $p(v_0, t_0)$, the solution has the form

$$\boxed{p(v,t) = \int \mathrm{d}v_0\, G(v,t;v_0,t_0)\, p(v_0,t_0)}$$

where $G(v,t;v_0,t_0)$: Greens function or propagator, which fulfills

$\partial_t G = \partial_v(\gamma\, v\, G) + \frac{1}{2}(\frac{\Gamma}{m})^2 \partial_{vv} G$

with initial condition: $G(v,t_0;v_0,t_0) = \delta(v - v_0)$

Ansatz for G: Inspired by discussion in Secs. 9.1: Gaussian distribution

$$\boxed{G(v,t;v_0,t_0) = \frac{1}{\sqrt{2\pi\sigma(t)^2}} \exp\big(-\frac{(v-\bar{v}(t))^2}{2\sigma(t)^2}\big)} \text{ with } \sigma(t) \xrightarrow{t\to t_0} 0$$

Determination of $\bar{v}(t)$, $\sigma(t)$: Moment equations

$$\partial_t\langle v^n(t)\rangle = \partial_t \int \mathrm{d}v^n\, v\, G = \int \mathrm{d}v\, v^n\, \partial_t G = \int \mathrm{d}v\, v^n \left[\partial_v(\gamma v G) + \tfrac{1}{2}(\tfrac{\Gamma}{m})^2 \partial_{vv} G\right]$$

$$\overset{\text{part. int.}}{=} \int \mathrm{d}v\big[-\gamma\, n\, v^n\, G + \tfrac{1}{2}(\tfrac{\Gamma}{m})^2\, n(n-1)\, v^{n-2}\, G\big]$$

$$= -\gamma\, n\, \langle v^n(t)\rangle + \tfrac{1}{2}(\tfrac{\Gamma}{m})^2\, n(n-1)\, \langle v^{n-2}\rangle$$

with initial condition $\langle v^n(t_0)\rangle = v_0^n$

$$n=1: \ \partial_t\langle v(t)\rangle = -\gamma\langle v(t)\rangle \quad \Rightarrow \ \langle v(t)\rangle = v_0\, \mathrm{e}^{-\gamma(t-t_0)}$$

$$n=2: \ \partial_t\langle v^2(t)\rangle = -2\gamma\langle v^2(t)\rangle + (\tfrac{\Gamma}{m})^2$$

$$\Rightarrow \ \langle v^2(t)\rangle = \tfrac{1}{2\gamma}(\tfrac{\Gamma}{m})^2(1-\mathrm{e}^{-2\gamma(t-t_0)}) + v_0^2\mathrm{e}^{-2\gamma(t-t_0)}$$

Compare with Gaussian distribution $\Rightarrow$ $\langle v(t)\rangle = \bar{v}(t)$, $\langle v^2(t)\rangle = \bar{v}(t)^2 + \sigma^2(t)$

$$\Rightarrow \quad \boxed{\bar{v}(t) = v_0\, \mathrm{e}^{-\gamma(t-t_0)}} \quad \boxed{\sigma^2(t) = \frac{1}{2\gamma}(\frac{\Gamma}{m})^2(1-\mathrm{e}^{-2\gamma(t-t_0)})}$$

(Check, e.g. by insertion, that this Ansatz works – exercise)

9.3.2.2 Full solution including position

In case the position is of interest, it must be treated separately $\rightsquigarrow$ $p(x,v,t)$

$$\boxed{\frac{\partial p}{\partial t} = -\partial_x(v\, p) + \partial_v(\gamma\, v\, p) + \frac{1}{2}(\frac{\Gamma}{m})^2 \frac{\partial^2}{\partial v^2}\, p}$$

Solution again via propagator formalism

$\rightsquigarrow$ Distribution $G(x,v,t;x_0,v_0,t_0)$

with initial condition $G(x,v,t_0;x_0,v_0,t_0) = \delta(x-x_0)\,\delta(v-v_0)$

Consider again moments

- $\langle v(t)\rangle$, $\langle v^2(t)\rangle$ as in 9.3.2.1

  $\Rightarrow \langle v(t)\rangle = v_0\, \mathrm{e}^{-\gamma(t-t_0)}$

  $\langle v^2(t)\rangle - \langle v(t)\rangle^2 = \frac{1}{2\gamma}(\frac{\Gamma}{m})^2(1-\mathrm{e}^{-2\gamma(t-t_0)})$
- Differential equation for $\langle x^n v^k\rangle$

  $$\partial_t\, \langle x^n v^k\rangle = \int \mathrm{d}x\, \mathrm{d}v\, x^n v^k\big[-\partial_x(vG) + \partial_v(\gamma v G) + \tfrac{1}{2\gamma}(\tfrac{\Gamma}{m})^2\, \partial_{vv} G$$

  $$\overset{\text{part. int.}}{=} n\langle x^{n-1}v^{k+1}\rangle - \gamma k\langle x^n v^k\rangle + \tfrac{1}{2\gamma}(\tfrac{\Gamma}{m})^2\, k(k-1)\langle x^n v^{k-2}\rangle$$

  $(n,k) = (1,0)$: $\partial_t\, \langle x\rangle = \langle v\rangle \quad \Rightarrow \langle x\rangle = x_0 + \frac{v_0}{\gamma}(1-\mathrm{e}^{-\gamma(t-t_0)})$

  $(n,k) = (1,1)$: $\partial_t\, \langle xv\rangle = \langle v^2\rangle - \gamma\langle xv\rangle$

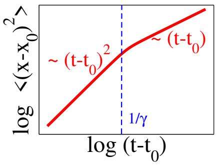
  $\Rightarrow \ \cdots \ \Rightarrow \ \langle xv\rangle - \langle x\rangle\, \langle v\rangle = \frac{1}{2\gamma^2}(\frac{\Gamma}{m})^2\, (1-\mathrm{e}^{-\gamma(t-t_0)})^2$

  $(n,k) = (2,0)$: $\partial_t\, \langle x^2\rangle = 2\, \langle xv\rangle$

  $\Rightarrow \ \langle x^2\rangle - \langle x\rangle^2 = (\frac{\Gamma}{m\gamma})^2(t-t_0) - \frac{1}{2\gamma}(\frac{\Gamma}{m\gamma})^2(3-\mathrm{e}^{-\gamma(t-t_0)})(1-\mathrm{e}^{-\gamma(t-t_0)})$

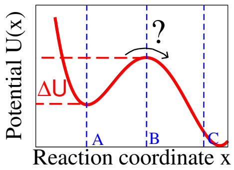
These can be used to construct Gaussians for the propagator

$$\langle(x-x_0)^2\rangle \sim \left\{\begin{array}{lll} v_0^2\,(t-t_0)^2 & \text{for } \gamma t \ll 1 & : \underline{\text{ballistic}} \text{ regime} \\ (\frac{\Gamma}{m\gamma})^2(t-t_0) & \text{for } \gamma t \gg 1 & : \underline{\text{diffusive}} \text{ regime} \end{array}\right.$$



9.3.3 Crossing potential barriers: The Kramers problem

Situation: Brownian motion in external potential $U(x)$,



i.e., external force $F(x) = -\frac{\mathrm{d}U}{\mathrm{d}x}$
(1940, Kramers – description of chemical reactions)

Time scales

τ_{bath} : Fast degrees of freedom
$1/\omega_A$: Oscillation frequency in Minimum A from Newtonian motion ($\omega \sim \sqrt{U''(x_{\min})/m}$)
$1/\omega_B$: Time scale for taking up/releasing kinetic energy at maximum B
$1/\gamma$: Relaxation time of velocity
τ_T : Equilibration time at the minimum
τ_e : Mean escape time from the minimum: Time required to escape the minimum and reach an (arbitrary) point C beyond the barrier at B!

Assumption $\tau_{\text{bath}} \ll \tau_T \ll \tau_e \quad \leftrightarrow \quad$ Energy $k_BT \ll \Delta U$

Regimes: $\gamma/\omega_B \gg 1$: Spatially diffusive (Smoluchowski) regime
$\gamma/\omega_B \ll 1$: Energy diffusive regime

Here we will study the first regime

⇝ Overdamped regime, described by Smoluchowski equation

$$\mathrm{d}x = v\,\mathrm{d}t = \frac{F(x)}{\mu}\mathrm{d}t + \sqrt{\frac{2k_BT}{\mu}}\,\mathrm{d}W$$

$$\partial_t p = -\partial_x\big(\frac{F(x)}{m\gamma}\,p\big) + \frac{1}{2}\partial_{xx}\big(\frac{2k_BT}{m\gamma}\,p\big)$$

Question: What is the mean escape time τ_e?

9.3.3.1 General "first passage time" problem

Rephrase question outlined above in more general terms: How long does it take a particle starting at $x < x_c$ to reach the point x_c for the first time?

⇝ "First passage time": Classical problem in the theory of stochastic processes

Shall be discussed at a very general level here, and then applied to the Kramers problem in the next subsection.

Given: General Fokker-Planck equation

$$\frac{\partial}{\partial t}\,p(x,t) = -\frac{\partial}{\partial x}\,\big(D^{(1)}(x)\,p(x,t)\big) + \frac{1}{2}\,\frac{\partial^2}{\partial x^2}\big(D^{(2)}(x)\,p(x,t)\big)$$

Goal: Find probability $P(x,t)$, that a particle starting at $x < x_c$ hits the point x_c for the first time at at time larger than t.

Knowing $P(x,t)$, one can calculate $\cdots$

- Probability distribution of the first passage time: $-\frac{\partial}{\partial t}P(x,t)$
- Mean first passage time: $\bar{\tau}(x) = -\int_0^\infty \mathrm{d}t\, t\, \frac{\partial}{\partial t}P(x,t) \overset{\text{part. int.}}{=} \int_0^\infty \mathrm{d}t\, P(x,t)$
- Higher moments: $\overline{\tau^n}(x) = -\int_0^\infty \mathrm{d}t\, t^n\, \frac{\partial}{\partial t}P(x,t) = n\int_0^\infty \mathrm{d}t\, t^{n-1}\, P(x,t)$

Calculation of $P(x,t)$: Must fulfill the equations

<u>Boundary conditions</u>

(i) <u>Absorbing</u> at $x = x_c$: $P(x_c, t) = 0$ for $t > 0$

(ii) <u>Reflecting</u> at $x \to -\infty$: $\partial_x P(x,t) \to 0$ at $x \to -\infty$

<u>Initial condition</u>: $P(x,0) = \begin{cases} 1 & : x \leqslant x_c \\ 0 & : x > x_c \end{cases}$

<u>Dynamical equation</u>

$$\boxed{\frac{\partial}{\partial t}P(x,t) = \big(D^{(1)}(x)\,\frac{\partial}{\partial x} + \frac{1}{2}\,D^{(2)}(x)\,\frac{\partial^2}{\partial x^2}\big)\,P(x,t)}$$

(Proof: Rewrite $P(x,t) = \int_{-\infty}^{x_c} \mathrm{d}x'\, G(x',t;x,0)$ where $G(x,t;x_0,t_0$ is the Greensfunktion of the Fokker-Planck equation with the boundary conditions (i),(ii).

First find backward equation for $G(x,t;x_0,t_0)$ (i.e., eqn. with respect to x_0, t_0)

Use $G(x,t;x_0,t_0) = \int \mathrm{d}x'\, G(x,t;x',t')\, G(x',t';x_0,t_0)$ for $t_0 \leqslant t' \leqslant t$.

and homogeneity $G(x',t';x_0,t_0) = G(x',t'-t_0;x_0,0) \;\Rightarrow\; \partial_{t_0} G = -\partial_{t'} G$

$$\begin{aligned}
\Rightarrow \frac{\partial}{\partial t_0}G(x,t;x_0,t_0) &= \int \mathrm{d}x' G(x,t;x',t')\partial_{t_0} G(x',t';x_0,t_0) \qquad \Big|\text{ Choose } t' \to t_0\\
&= -\int \mathrm{d}x'\, G(x,t;x',t_0)\, \partial_{t'} G(x',t';x_0,t_0)\big|_{t'=t_0}\\
&\underset{\substack{\text{Fokker}\\ \text{Planck}}}{=} -\int \mathrm{d}x' G(x,t;x',t_0)\big(-\partial_{x'} D^{(1)}(x') + \tfrac{1}{2}\partial_{x'x'} D^{(2)}(x')\big)\,\underbrace{G(x',t_0;x_0,t_0)}_{\delta(x'-x_0)}\\
&\overset{\text{part. int.}}{=} \int \mathrm{d}x'\, \delta(x'-x_0)\big(-D^{(1)}(x')\partial_{x'} - \tfrac{1}{2}D^{(2)}(x')\partial_{x'x'}\big)\, G(x,t;x',t_0)\\
&= -\big(D^{(1)}(x_0)\partial_{x_0} + \tfrac{1}{2}D^{(2)}(x_0)\partial_{x_0 x_0}\big)G(x,t;x_0,t_0)
\end{aligned}$$

Insert in $P(x_0,t) = \int_{-\infty}^{x_c} \mathrm{d}x'\, G(x',t;x_0,0) = \int_{-\infty}^{x_c} \mathrm{d}x'\, G(x',0;x_0,-t)$

$$\begin{aligned}
\Rightarrow\; \partial_t P(x_0,t) &= \int_{-\infty}^{x_c} \partial_t G(x',0;x_0,-t)\\
&= \int_{-\infty}^{x_c} \mathrm{d}x'\, \big(D^{(1)}(x_0)\partial_{x_0} + \tfrac{1}{2}D^{(2)}(x_0)\partial_{x_0 x_0}\big)\, G(x',0;x_0,-t)\\
&= \big(D^{(1)}(x_0)\partial_{x_0} + \tfrac{1}{2}D^{(2)}(x_0)\partial_{x_0 x_0}\big)\, P(x_0,t) \quad \checkmark\;)
\end{aligned}$$

These equations determine $P(x,t)$ uniquely.

Instead of solving directly fo $P(x,t)$, one can also derive differential equations for the <u>moments</u> (sometimes simpler!)

$$\begin{aligned}
\overline{\tau^n}(x) &= -\int_0^\infty \mathrm{d}t\, t^n\, \partial_t\, P(x,t) = -\int_0^\infty \mathrm{d}t\, t^n\, \big(D^{(1)}(x)\,\tfrac{\partial}{\partial x} + \tfrac{1}{2}\,D^{(2)}(x)\,\tfrac{\partial^2}{\partial x^2}\big)\, P(x,t)\\
&= -\big(D^{(1)}(x)\,\tfrac{\partial}{\partial x} + \tfrac{1}{2}\,D^{(2)}(x)\big)\,\tfrac{\partial^2}{\partial x^2}\,\underbrace{\int_0^\infty \mathrm{d}t\, t^n\, P(x,t)}_{\overline{\tau^{n+1}}(x)/(n+1)}
\end{aligned}$$

$$\Rightarrow\; \boxed{-(n+1)\,\overline{\tau^n}(x) = \big(D^{(1)}(x)\,\frac{\partial}{\partial x} + \frac{1}{2}\,D^{(2)}(x)\,\frac{\partial^2}{\partial x^2}\big)\,\overline{\tau^{n+1}}(x)}$$

$\rightsquigarrow$ Hierarchy of differential equations for $\overline{\tau^n}(x)$

with boundary conditions $\overline{\tau^n}(x_c) = 0$, $\partial_x \overline{\tau^n}(x_c) \overset{x\to-\infty}{\longrightarrow} 0$

and "initial condition" $\overline{\tau^0}(x_c) = -\int_0^\infty \partial_t P(x,t) = P(x,0) = 1$ for $x \leqslant x_c$

Specifically, the equation for the mean first passage time $\bar{\tau}(x)$ reads

$$\boxed{-1 = \big(D^{(1)}(x)\,\frac{\partial}{\partial x} + \frac{1}{2}\,D^{(2)}(x)\,\frac{\partial^2}{\partial x^2}\big)\,\bar{\tau}(x)}$$

Formal solution of the differential equation for $\bar{\tau}(x)$

Homogeneous equation: $0 = D^{(1)}\bar{\tau}_h' + \frac{1}{2}D^{(2)}\bar{\tau}_h''$

$\Rightarrow \frac{\mathrm{d}\bar{\tau}_h'}{\mathrm{d}x} = -2\frac{D^{(1)}}{D^{(2)}}\bar{\tau}' \Rightarrow \frac{\mathrm{d}\bar{\tau}_h'}{\mathrm{d}\bar{\tau}_h'} = \mathrm{d}(\ln\bar{\tau}_h') = -2\frac{D^{(1)}}{D^{(2)}}\,\mathrm{d}x \Rightarrow \bar{\tau}_h' = A\,\exp(-\int^x \mathrm{d}x'\,2\,\frac{D^{(1)}(x')}{D^{(2)}(x')}$

Inhomogeneous equation by variation of the constant $A \to A(x)$

$\Rightarrow\; -1 = \frac{1}{2}D^{(2)}\bar{\tau}_h'\frac{\mathrm{d}}{\mathrm{d}x}A(x) \;\Rightarrow\; A(x) = -2\int^x \mathrm{d}x'/(D^{(2)}(x')\,\bar{\tau}_h'(x'))$

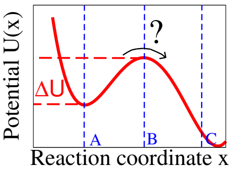
All together: $\bar{\tau}'(x) = -2\int_{-\infty}^{x}\mathrm{d}x'\,\frac{\Phi(x')}{D^{(2)}(x')}\,\frac{1}{\Phi(x)} + \bar{\tau}_h'(x)$ with $\Phi(x) := \exp\big(\int^x \mathrm{d}x'\,2\,\frac{D^{(1)}(x')}{D^{(2)}(x')}\big)$

Last term vanishes due to boundary condition $\bar{\tau}'(x) \to 0$ at $x \to -\infty$

Integration of $\bar{\tau}'(x)$ with second boundary condition $\bar{\tau}(x_c) = 0$ gives $\bar{\tau}(x) = \int_{x_c}^{x}\int \mathrm{d}x'\,\bar{\tau}'(x')$

$$\Rightarrow \boxed{\bar{\tau}(x) = 2\int_x^{x_c}\mathrm{d}x'\,\frac{1}{\Phi(x')}\,\int_{-\infty}^{x'}\mathrm{d}x''\,\frac{\Phi(x'')}{D^{(2)}(x'')}} \qquad \boxed{\Phi(x) = \exp\Big(2\int_{-\infty}^{x}\mathrm{d}x'\,\frac{D^{(1)}(x')}{D^{(2)}(x')}\Big)}$$

9.3.3.2 Application to the Kramers problem



Recall: We were looking for the mean escape time from a metastable minimum in a potential $U(x)$

⇝ First passage time $\bar{\tau}(x_c)$ in a system obeying the Fokker-Planck equation:

$$\frac{\partial}{\partial t}p(x,t) = -\frac{\partial}{\partial x}\Big(\underbrace{-\frac{U'(x)}{m\gamma}}_{D^{(1)}(x)}\;p(x,t)\Big) + \frac{1}{2}\,\frac{\partial^2}{\partial x^2}\Big(\underbrace{\frac{2k_BT}{m\gamma}}_{D^{(2)}}\;p(x,t)\Big)$$

(Ideally, the result should not depend on x_c as long as $x_c > x_B$)

Apply result from 9.3.3.1: Exact solution!

$$\bar{\tau}(x) = \frac{m\gamma}{k_BT}\int_x^{x_c}\mathrm{d}x'\int_{-\infty}^{x'}\mathrm{d}x''\;\exp\big(\frac{1}{k_BT}\big(U(x') - U(x'')\big)\big]$$

Approximation: $\Delta U \gg k_BT$

⇝ Main contribution stems from $x' \approx x_B$ and $x' \approx x_A$

⇝ Harmonic expansion (≙ saddle point approximation)

$$U(x') \approx U(x_B) - \tfrac{1}{2}m\omega_B^2\,(x' - x_B)^2$$
$$U(x'') \approx U(x_A) - \tfrac{1}{2}m\omega_A^2\,(x' - x_A)^2$$

$$\Rightarrow \bar{\tau} \approx \frac{\mu}{k_BT}\,\underbrace{\mathrm{e}^{\frac{1}{k_BT}(U(x_B - x_A))}}_{\mathrm{e}^{\Delta U/k_BT}}\;\underbrace{\int_{-\infty}^{\infty}\mathrm{d}x'\;\mathrm{e}^{-\frac{1}{2k_BT}m\omega_B^2\,x'^2}}_{\sqrt{2\pi k_BT/m\omega_B^2}}\;\underbrace{\int_{-\infty}^{\infty}\mathrm{d}x''\;\mathrm{e}^{-\frac{1}{2k_BT}m\omega_A^2\,x''^2}}_{\sqrt{2\pi k_BT/m\omega_A^2}}$$

⇒ Mean escape time: $\boxed{\bar{\tau} = \frac{2\pi\gamma}{\omega_A\omega_B}\;\exp\big(\frac{\Delta U}{k_BT}\big)}$

Interpration and remarks

- $\exp(\Delta U/k_BT)$: Energy barrier (Arrhenius behavior)
- ω_A: Frequency of attempts to escape
- Result does not depend on the specific choice of x_c as expected.

Chapter 10

Stochastic Thermodynamics and Fluctuation Theorems

TODO