Introduction to Statistical Physics

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Outline

- First law of thermodynamics (Chap. 1.1 - 1.3)

- Second law, entropy (Chap 2.1-2.5)

- Free energy and ability to work (Chap. 4.1, 4.2, 4.3.1, 4.4, 4.6-4.7)

- The classical ideal gas (Chap. 7.1-7.4)

- Systems with varying number of particles (Chap. 11)

- Quantum gases (Chap. 9.1, 11.2, 11.5, 11.5.1)

1 Introduction

1.1 Macroscopic physics

In order to describe macroscopic bodies or macroscopic quantities of fluids or gases, we need only quite few variables. In order to characterize a volume of water, for example, we need only to specify the total amount amount (given as the mole number, the number of molecules, or the total mass), the volume, and the temperature. The volume contains an enormous number of molecules, but a detailed description of how all these particles move is not required in the macroscopic description.

If we attempt a microscopic description, we are confronted with an *enormous* number of quantum eigenstates ($\sim 10^{10^{23}}$ for a mole of matter). There is no way neither in practice nor in theory to exactly specify the precise quantum state of such macroscopic bodies. Instead, one can try to use statistical arguments to deal with this microscopic chaos, and this is the approach of statistical physics.

Statistical physics was founded around 1870 by Boltzmann, Maxwell, and Gibbs (using classical physics). When quantum mechanics appeared, the general ideas of statistical mechanics could be adopted with no major difficulty. Statistical physics applied to macroscopic bodies is closely related to thermodynamics, which was also developed during the 19th century. In thermodynamics, our experience on how macroscopic amounts of matter behave is condensed into a few empirical postulates, the so-called laws of thermodynamics. There is no reference whatsoever to the atomistic nature of matter. Thermodynamics gives interrelations between macroscopic variables such as temperature, pressure, or internal energy. As opposed to statistical mechanics, it does not contain means to calculate them from underlying *microscopic* dynamics.

For a large system with $N \sim 10^{23}$ particles, there are 3N degrees of freedom. Of all there variables, only the few will be macroscopically observable. Typical examples are the total energy (E), the pressure resulting of particle collisions with boundary walls, etc. Most of the variables cannot be observed directly. **On a microscopic scale, a macroscopic measurement is extremely slow and extremely crude.** This is the main reason why so few variables remain macroscopically visible. Typically, the remaining variables are related to conservation laws of the underlying microscopic description. Thus, energy, mass, and electric charge are conserved in the microscopic dynamics and these quantities remain macroscopically visible.

I shall in what follows often use a one-component fluid (a gas or liquid) as a typical example of a macroscopic system. The one-component fluid is

made up of only one kind of atoms or molecules and is fully characterized by 3 independent state variables, such as the internal energy (E), the volume (V), and the number N of atoms or molecules. These variables are all additive or **extensive**, *i.e.* they are proportional to the *size* of the system. There are also *intensive* variables such as temperature (T) and pressure which are size-independent. If we add a fourth variable there exists a dependence between them. For a dilute gas, for example, we have the relation $pV = NkT$, *i.e,* p depends on the remaining 3 variables.

If we disturb the system in question, the the state variables will change, and the system is said to be out of equilibrium. If it is left undisturbed, the state variables will eventually no longer change, and the system has established a possibly different equilibrium state.

Thermodynamic equilibrium has been reached if (a) no macroscopic variables changes in time, and (b) the macroscopic properties are fully characterized by an independent set of thermodynamic state variables.

The existence of equilibrium states is of course an idealization that cannot be fully reached in practice. Usually, at least local equilibrium is well reached during a very short time. However, some systems exhibit metastable (non-equilibrium) states with long lifetime. Thus, very pure water which is gently cooled may reach temperatures below 0^0C. Another example is ordinary glass which is in a meta-stable non-crystalline state with frozen-in disorder. After some centuries, it will eventually reach a crystalline equilibrium state.

The material in these notes has been compiled using primarily Mandl's text[1]. A modern but somewhat more highbrow text is *Introduction to Modern Statistical Mechanics* by Chandler[2]. For a thorough but yet readable account of classical thermodynamics I recommend Callen's book[3].

2   The first law of thermodynamics

The microscopic equations of motion (the Schödinger equation in quantum physics, or Newton's equations in classical physics) conserve energy: $T + V = const$ independent of time. This constant value remains unchanged during any averaging. This conservation of the total internal energy is the contents of the first law of thermodynamics. However, because we cannot observe each individual molecule, the energy transfer is divided into two parts: One part is connected to **changes in macroscopic constraints and parameters** and constitutes the **mechanical work** W done on the system. For a one-component fluid this can be written $-pdV$. The other part is **energy transfer to internal degrees of freedom** (molecular vibrations

etc.) which we cannot observe directly but which contributes to the overall energy balance. This part of the energy transfer is **transfer of heat**. The total energy change can thus be written

$$dE = \mathrm{d}W + \mathrm{d}Q \tag{1}$$

Neither work nor heat are state variables, only changes along specific reaction paths make sense. The first law of thermodynamics states that the **energy is conserved for any closed system**, $dE = 0$.

3 Entropy and the second law

Real processes are always irreversible and proceed in a given direction. Thus heat always flows from hotter to colder parts when a constraint removed (removing e.g. an insulating walls). In 1865, Claussius introduced a new state function in classical thermodynamics, the entropy S, with the property that

$$\Delta S \geq 0$$

for any spontaneous process in an isolated system. In the idealized limit of a fully reversible process, $\Delta S = 0$, and for irreversible processes $\Delta S > 0$. The entropy to be additive, *i.e*,

$$S_{12} = S_1 + S_2$$

for a system made up of two weakly interacting subsystems "1" and "2".

If internal constraints are removed, the system seeks a new equilibrium. It is postulated that the new equilibrium state is the state which maximizes S.

The second law is today usually stated as the existence of an additive entropy function with the above properties. Originally, Claussius stated the second law differently by postulating that no spontaneous process from an initial to a final equilibrium state can have as it only net effect that heat has been transferred from a colder to a warmer part of the system. From this postulate, Claussius could then show that an entropy could be defined and that it had the properties stated here.

3.1 Intensive parameters in terms of S

For a one-component fluid, internal energy (E), volume (V), and molar (n) or particle (N) number constitute a maximal independent set av thermodynamic variables, and they are all additive or extensive. When we add a

fourth variable S there must be a dependence,

$$S = S(E, V, N). \tag{2}$$

The above relation is called a *fundamental relation*, and all remaining thermodynamical quantities can be derived from it. The intensive variables temperature (T), pressure (p), and chemical potential (μ) are *defined* as derivatives of the entropy with respect to its extensive variables,

$$
\begin{aligned}
\frac{1}{T} &= \frac{\partial S}{\partial E} \\
\frac{p}{T} &= \frac{\partial S}{\partial V} \\
\frac{\mu}{T} &= -\frac{\partial S}{\partial N},
\end{aligned}
$$

or,

$$dS = \frac{1}{T}\left[dE + pdV - \mu dN\right]. \tag{3}$$

In addition, the system may depend on internal parameters such as for example the position x of an internal wall. If the wall is let free, the system seeks a new equilibrium that maximizes the entropy (E, V, N, x) for fixed E, V, N.

In general, a system may be described by the extensive parameters E, X_1, X_2, ... A fundamental relation $S(E, X_1, X_2, ...)$ is postulated to exist. For each extensive parameter $(E, X_1, X_2, ...$. there corresponds an intensive parameter $(1/T, p_1, p_2, ...)$ defined by the partial derivatives of S,

$$dS = \frac{1}{T}\left[dE - p_1 dX_1 - p_2 dX_2 - ...\right]. \tag{4}$$

3.2   Example: Energy and pressure equilibrium

To illustrate the general principles let us consider temperature equalization of two subsystems isolated from the environment (see Fig. (2)). Initially, the subsystems are separated by an insulating wall. The amount of energy E_1 in subsystem "1" plays the role of internal parameter. If the wall is removed, the two parts can exchange energy until a new equilibrium is reached, but the total energy $E = E_1 + E_2$ remains fixed. The new equilibrium is the state which maximizes S. A small energy exchange gives the entropy change

$$
\begin{aligned}
S(E, E_1) &= S_1(E_1) + S_2(E - E_1). \\
\frac{\partial S}{\partial E_1} &= \frac{1}{T_1} - \frac{1}{T_2}; \quad \text{and} \quad dS = dE_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right)
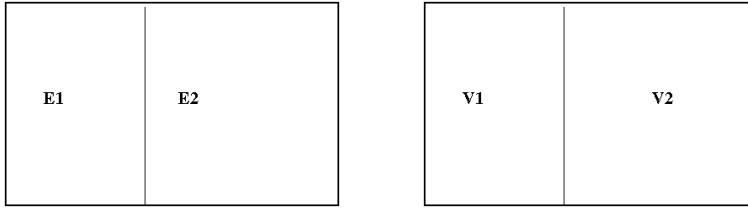\end{aligned}
$$

Figure 1: Two subsystems in energy - (left) and pressure (right) equilibrium with each other

We see that the temperature is constant at equilibrium, $T_1 = T_2$. When $T_1 \neq T_2$, energy transfer from the hotter to the colder part gives $dS > 0$ which is thus the direction of the irreversible spontaneous energy transfer when the insulating wall is removed.

Equilibrium of a system divided by a mobile wall can be treated in a similar fashion. The pressure defined as $p = T \frac{\partial S}{\partial V}$. When the wall is moved, the entropy undergoes a change

$$dS = dV_1 \, T \, (p_1 - p_2)$$

Thus, both parts have the same pressure at equilibrium, and off equilibrium the part with the higher pressure will expand.

Let us finally discuss equilibrium under particles exchange. Defining the chemical potential by $\mu = -T \frac{\partial S}{\partial N}$, we obtain

$$dS = dN_1 \, T \, (\mu_2 - \mu_1)$$

Thus, particles flow from the part of highest μ until the chemical potentials are equal.

4 Microscopic definition of entropy

Our basic goal is to define an entropy starting from the microscopic dynamics which has the correct maximal and additive properties. To this end, we will need some very basic results from quantum mechanics, and some postulate of statistical nature. The statistical postulates will lead to an entropy with exactly the same properties as the entropy function of classical thermodynamics. In addition, we will obtain means of calculating the entropy function and thereby also any other thermodynamic quantity from the microscopic dynamics, at least in principle.

4.1   Some basic results from quantum mechanics

- The energy (of a confined system) can only take discrete values E_0, E_1, E_2, ...

- Every system has a lowest energy state, the ground state ψ_0. (Otherwise, stable atoms, molecules and solids would not exist.)

- In order to measure the energy with precision ΔE, a time $t \geq \hbar/\Delta E$ is required.

In small systems (atoms, molecules), individual energy levels can be resolved. In macroscopic systems with level spacing $\sim 10^{-10^{23}}$ eV this is not possible, even in principle.

4.2   Basic postulates of statistical mechanics

- Microstates (individual quantum states) corresponding to the same macroscopic state variables (E, V, p, etc) cannot be distinguished

- **Ensembles** (Gibbs) Set set of all systems with the same given macroscopic state variables constitutes an *ensemble*. The observed result of a macroscopic measurement is the average over the corresponding ensemble.

- **Equal *a priory* probabilities**: Every reachable quantum state in a closed system is equally probable.

- Equilibrium in a macroscopic system corresponds to the most probable macrostate consistent with the given constraints.

4.3   The entropy of an isolated system

Consider an isolated, closed system with a specified energy E,

$$E < E_i < E + \Delta E.$$

The quantum states are symbolized by dots in Figure. Of course, only some of the quantum states have energies in the required energy window. If we now add some addition requirement, for instance by specifying some addition parameter α, the number of allowed states is further reduced. Thus, the number of allowed states has already the required property that it can only increase when constraints are released. Let $\omega(E, \alpha, \beta, ..)$ be the allowed
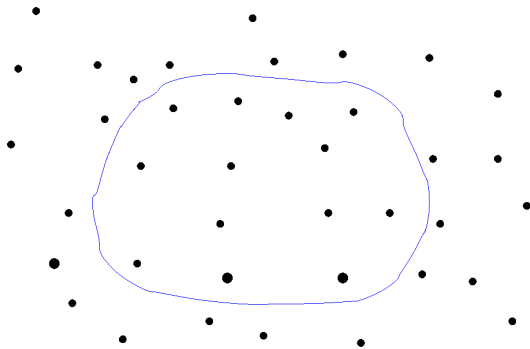
Figure 2: Allowed states of specified energy with an without additional constrains

number of states. For a system made up of two weakly interacting parts "1" and "2", $\omega = \omega_1 \omega_2$. In order to have an *additive* entropy we define

$$S(E, \alpha, \beta, ..) = k \ln \omega(E, \alpha, \beta, ..),$$

where k is a parameter to our disposal. We recall that the (intensive) temperature parameter as

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

Thus our chosen value of k will determine the temperature unit. By choosing k as the Boltzmann constant, T will be given in Kelvin.

In principle, the entropy would depend also on the size of the energy window ΔE, but this dependence is extremely weak and negligible for systems of macroscopic size. One extreme could be to choose it to be 1 eV, another extreme one Joule $\sim 10^{19}$ eV. The entropy would only change by $k \ln 19 \sim 10^{-34}$ J K^{-1}. The reason is the S is proportional to the size of the system, *i.e.*, the number of available states are of order $\exp 10^{23}$ for a macroscopic body. Changing the number of states with factors of order say Avogadro's number has therefore only a very small effect of the resulting entropy.

4.4 Microcanonical ensemble

Ensembles describing isolated systems with specified energy as above are termed **microcanonical ensembles**. In one-component gases or liquids, the energy, volume, and particle number furnish a complete description. Each energy level E_i depends on V and N, and in this way S will be a function of E, V, and N, and possibly also some internal parameters $\alpha, \beta, ...$. Thus we have

obtained the fundamental relation $S = S(E, V, N, \alpha, \beta, ...)$ which determines the equilibrium thermodynamics. We recall that the basic intensive variables are given by the differential

$$dS = \frac{1}{T}\left(dE + pdV - \mu dN\right)$$

The remaining thermodynamic variables may be expressed in higher-order derivatives. The specific heat, for example, is given by

$$C_V = \left(\frac{\partial E}{\partial T}\right) = 1/\frac{\partial T}{\partial E} = -\frac{1}{T^2}\frac{\partial(1/T)}{\partial E} = -\frac{(\partial S/\partial E)^2}{\partial^2 S/\partial E^2}$$

More complicated systems may need more variables (magnetic field, etc) for a complete description, *i.e.*, a fundamental relation involving more independent thermodynamic variables.

It is a thermodynamic stability condition that $\partial S/\partial E = 1/T \geq 0$. Thus, we can invert the function $S(E, V, N, \alpha_1, \alpha_2...)$ to obtain E as a function of the remaining variables, $E(S, V, N, \alpha_1, \alpha_2...)$. E has the differential

$$dE = TdS - pdV + \mu dN + \frac{\partial E}{\partial \alpha_1}d\alpha_1 + ...$$

The functions $S(E, V, N, \alpha_1, \alpha_2...)$ and $E(S, V, N, \alpha_1, \alpha_2...)$ contain precisely the same information. When a constraint is removed at constant energy, S can only increase. Because E is increasing with increasing S, this means that the energy can only be lowered if a constraint is removed at constant S. Thus, E behaves a a potential at constant entropy, a "thermodynamic potential".

4.5   Example: Lattice vacancies in a solid

Let the energy cost for moving an atom to the surface be ϵ. n vacancies can be distributed among $N + n$ lattice sites in $\omega(n) = \frac{(N+n)!}{n!N!}$ different ways. This gives

$$S(n) = k\ln\frac{(N+n)!}{n!N!} \approx k\left[(N+n)\ln(N+n) - n\ln n - N\ln N\right]$$

where we in the last step used Stirling's approximation $\ln x! \approx x(\ln x - 1)$. Further,

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{1}{\epsilon}\frac{\partial S}{\partial n} = \frac{k}{\epsilon}\left[\ln(N+n) - \ln n\right] \approx \frac{k}{\epsilon}\ln\frac{N}{n}$$
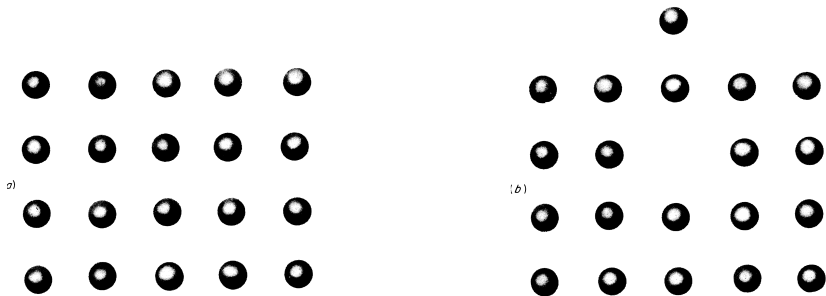$$\text{which gives}\quad n = Ne^{-\frac{\epsilon}{kT}}$$

Figure 3: A lattice with and without vacancies

5 Systems in contact with heat bath of temperature T

The description of closed systems as above by means of the microcanonical ensemble give in principle a complete description, but it is often not well suited for tackling practical problems. In the statistical description, the large number of constraints is often difficult to handle. The the thermodynamic description, the fundamental relation $E(S, V, N, ...)$ with entropy as one of the independent variables is often an unpractical starting point for describing experiments performed at given temperature and/or pressure. It is, however, possible to obtain equivalent representations in which one or more extensive variables have been replaced by their intensive counterparts. The most commonly used is the so-called free energy representation which describes systems at a given temperatures and where the temperature enters in place of the entropy as independent parameter. There is an associated ensemble, the canonical ensemble, which we will now derive.

Consider a subsystem in contact with a much larger heat bath. The system + bath is isolated from the environment. We want to obtain the conditional probability p_i that the system is in state "i" of energy E_i. The bath energy is then $E - E_i$, and the probability is proportional to number of bath states,
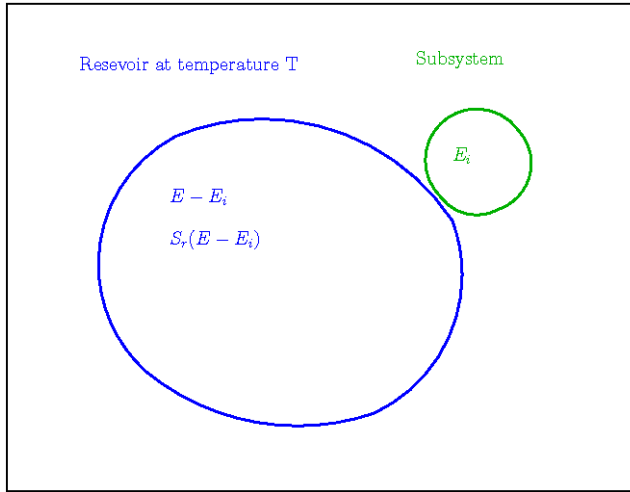
$$p_i = \text{Const} \times e^{S_r(E-E_i)/k}$$

The reservoir is very large, $E \gg E_i$, *i.e.*

$$S_r(E - E_i) \approx S_r(E) - E_i \partial S i_r / \partial E = S_r(E) - E_i / T \tag{5}$$

Thus, $p_i = Ce^{-\frac{E_i}{kT}}$

where C is another constant, which is determined by $\sum_i p_i = C \sum e^{-\frac{E_i}{kT}} = 1$

In the expansion in Eq. (5) we have tactically stopped after the first-order term involving $\partial S i_r / \partial E$. The bath entropy is of order of the bath size N_r. Each time we differentiate with respect the extensive parameter E the order of magnitude goes down one order with respect to size. Thus, the the first derivative is of order 1 (the intensive $1/T$). The next, second term would be of order (1 / bath size) and can be dropped for very large reservoirs.

5.1 The Canonical Ensemble

In summary we have found that the probability for state "i" is given by

$$p_i = Ce^{-\frac{E_i}{kT}} \equiv Ce^{-\beta E_i} \quad (\beta = \frac{1}{kT})$$

where

$$\frac{1}{C} = Z(T, V, N, \alpha_1, ...) = \sum_i e^{-\beta E_i}$$

Z, the inverse of the normalization constant, depends explicitly on T. Via the energy levels E_i it also depends on V and N, and, where applicable, on additional parameters $\alpha_1, \alpha_2, ...$ The probabilities gives another ensemble which describes systems in contact with large energy reservoirs of a given temperature T, the **canonical ensemble**.

5.2 Mean energy in the canonical ensemble

$$\langle E \rangle = \sum p_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

We show later that the entropy of the ensemble is

$$S = -k \sum_i p_i \ln p_i \quad \text{(Boltzmann's entropy definition)},$$

and this gives

$$E_i = -kT \left(\ln p_i + \ln \sum_i e^{-\beta E_i} \right) = -kT \left(\ln p_i + \ln Z \right),$$

$$\langle E \rangle = \sum p_i E_i = -kT \sum_i p_i \ln p_i - kT \ln Z \sum_i p_i = TS - kT \ln Z$$

The function $F(T, V, N, \alpha_1, ...) = -kT \ln Z(T, V, N, \alpha_1, ...) = \langle E \rangle - TS$ has been termed **free energy**. The inverse normalization Z is usually called the **partition function**.

5.3   Thermodynamics expressed in the free energy

We saw above that $F = -kT \ln Z = E - TS$. From the known differential of E we obtain

$$
\begin{aligned}
dF &= dE - TdS - SdT = TdS - TdS - SdT - pdV + \mu dN \text{ or} \\
dF &= -SdT - pdV + \mu dN
\end{aligned}
$$

Thus the entropy is obtained from $(\partial F/\partial T)_{VN}$, the pressure from the volume derivative, and chemical potential from $(\partial F/\partial N)_{TV}$ Remaining quantities can be obtained from higher derivatives. Consider *e.g.* the specific heat C_V. We have
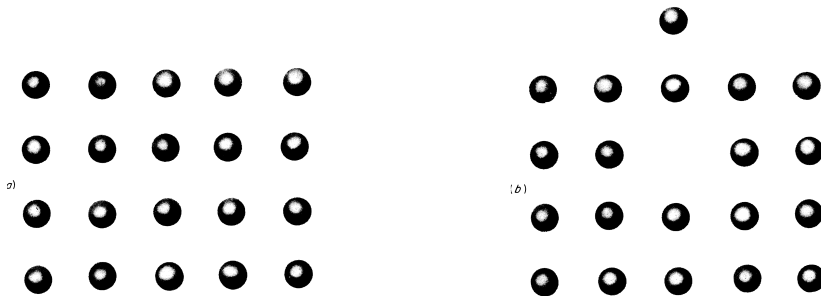
$$
\begin{aligned}
E &= -\frac{\partial \ln Z}{\partial \beta} \\
C_V &= \frac{\partial E}{\partial T} = -\frac{1}{kT^2} \frac{\partial E}{\partial \beta} = \frac{1}{kT^2} \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{1}{kT^2} \frac{\partial^2 (\beta F)}{\partial \beta^2}
\end{aligned}
$$

5.4   Example: Lattice vacancies in a solid (Canonical ensemble)

Let as before the energy cost for moving an atom to the surface be ϵ. A lattice site can be either filled (energy 0) or empty (energy ϵ), with probabilities C and $C \exp(-\epsilon/kT)$. Further, $C = 1 + \exp(-\epsilon/kT) \approx 1$ when $kT \ll \epsilon$. Thus,

$$n = Ne^{-\epsilon/kT}$$

i.e. the same result that we obtained earlier by considering the lattice as an isolated system in the microcanonical ensemble. Generally, it can be shown that the different ensembles give the same averages in the thermodynamic limit $N \to \infty$ (*cf.* Mandl, problem 2.8).

5.5 Energy fluctuations in the canonical ensemble

The microcanonical and canonical ensembles cannot of course be fully equivalent. For small systems, there is a distinct difference when the system is isolated and within a given energy window and when it can exchange energy with heat bath. In the latter case, the energy can fluctuate. However, in the thermodynamic limit of large systems, the relative size of these fluctuations goes down as $1/\sqrt{N}$, and it this limit the two ensembles do give the same result for the average thermodynamic functions. This point is further illustrated by Problem 2.8 in Mandl[1].

As a measure of energy fluctuation we choose the root mean square fluctuation defined by

$$
\begin{aligned}
(\Delta E)^2 &= \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2, \\
\langle E \rangle &= \sum_i p_i E_i = -\frac{\partial Z/\partial \beta}{Z}, \quad \langle E^2 \rangle = \sum_i p_i E_i^2 = -\frac{\partial^2 Z/\partial \beta^2}{Z}, \\
(\Delta E)^2 &= \frac{\partial^2 Z/\partial \beta^2}{Z} - \left(\frac{\partial Z/\partial \beta}{Z} \right)^2 = \frac{\partial}{\partial \beta} \left[\frac{\partial Z/\partial \beta}{Z} \right] = -\frac{\partial \langle E \rangle}{\partial \beta}
\end{aligned}
$$

The derivative $\partial \langle E / \partial \beta$ is extensive and thus of order N. Consequently, the fluctuation are of order $\sqrt{N}$, and negligible compared to $\langle E \rangle (\sim N)$ in the thermodynamic limit. The derivative in question can be related to the specific heat as follows:

$$
(\Delta E)^2 = \frac{\partial \langle E \rangle}{\partial \beta} = kT^2 C_V = O(N), \quad (\frac{\partial}{\partial \beta} = -kT^2 \frac{\partial}{\partial T})
$$

$$\frac{\Delta E}{\langle E \rangle} = O\left(\frac{1}{\sqrt{N}}\right).$$

5.6 Heat and work

Consider a system at constant T with energy $E = \sum_i p E_i$.
Make a slow volume change,

$$E_i(V) \to E_i(V) + \frac{\partial E_i}{\partial V} dV, \quad p_i \to p_i + dp_i,$$

which gives

$$dE = \sum_i dp_i E_i + \sum_i p_i dE_i = dE_1 + dE_2$$

Interpretation of $dE_1 = \sum dp_i E_i$

For transitions between two equilibrium states:

$$
\begin{aligned}
\ln p_i &= \beta(F - E_i) \\
\sum_i dp_i E_i &= F \sum_i dp_i - kT \sum_i dp_i \ln p_i \\
\sum_i dp_i &= 0 \\
-k \sum_i p_i \ln dp_i &= -k\, d\left[\sum_i p_i \ln p_i\right] = dS
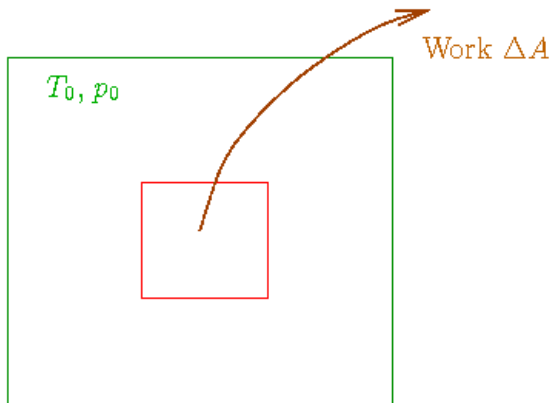\end{aligned}
$$

Thus,

$$dE_1 = \sum_i dp_i E_i = TdS$$

Interpretation of $dE_2 = \sum p_i dE_i$

Do a very slow volume change of an isolated system. According to Ehrenfest's adiabatic theorem of quantum mechanics, no quantum transitions will occur, *i.e.* a system initially in state E_i will end up in state $E_i + E_i$. This means that $dp_i = 0$. The change in energy is

$$dE_2 = \sum_i p_i dE_i = \sum_i p_i \frac{\partial E_i}{\partial V} dV.$$

Under the specified conditions, the heat transfer dQ is zero, and the entire energy change is an adiabatic work $dW = -pdV$. Thus,

$$dE_2 = dW = -pdV$$

and

$$\sum_i p_i \frac{\partial E_i}{\partial V} = -p$$

The foregoing analysis shows that

$$dE = TdS - pdV,$$

and because only state functions are involved, the above result is valid for both reversible and irreversible changes. Under reversible changes, we have also shown that $dW = -pdV$ and $dQ = TdS$. Under irreversible changes, $TdS > dQ$, and because

$$dE = TdS - pdV = dQ + dW,$$

this means that

$$-dW = \text{work obtained } \textit{from} \text{ system} < pdV.$$

This means that the maximal work that one can obtain from a system is the *reversible* work.

5.7 Claussius' inequality

In order to obtain useful work of a composite system, there must be some differences in intensive variables between its different parts, differences that

can be equalized when constraints are removed. If there is, say, a temperature difference between a subsystem and its surroundings, work can be obtained when energy (heat) is allowed to be exchanged. Let us consider a subsystem enclosed in a surrounding at temperature T_0 and pressure p_0. Constraints are released such that energy can flow between subsystem and surroundings, and some work ΔA is delivered to the outside world.

The reservoir receives reversibly the heat ΔQ from the system. If the system also expands ΔV, the surrounding changes its entropy by

$$\Delta S_0 = -\frac{1}{T_0}[\Delta Q + p_0 \Delta V].$$

Total entropy change:

$$
\begin{aligned}
\Delta S_{tot} &= \Delta S + \Delta S_0 = \Delta S - \frac{\Delta Q + p_0 \Delta V}{T_0} \geq 0 \\
\text{The system: } \Delta Q &= \Delta E - \Delta W \\
\text{Work obtained: } -\Delta W &\leq -[\Delta E - T_0 \Delta S + p_0 \Delta V] \equiv -\Delta A
\end{aligned}
$$

Thus the function

$$A = E - T_0 S + p_0 V$$

gives the maximum work that can be extracted from the system plus its surrounding.

Special cases:

- Processes at constant $T_0 = T$, and V: Maximum work given by $F(T, V) = E - TS$ (Helmholtz free energy)

- Processes at constant $T_0 = T$, and $p_0 = p$: Maximum work given by $G(T, p) = E + pV - TS$, the Gibbs' free energy.
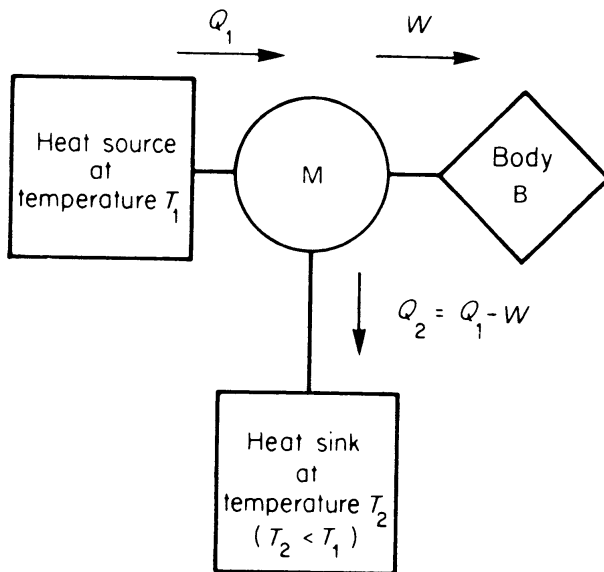
5.8   Heat engines

Heat engine: A machine is each cycle receiving heat (Q_1) from one reservoir at temperature T_1, delivering heat (Q_2) to another reservoir T_2 $(T_2 < T_1)$, and delivering work $W = Q_1 - Q_2$. Total entropy change

$$\Delta S = -\frac{Q_1}{T_1} + \frac{Q_1 - W}{T_2} \geq 0$$

The efficiency $\eta = W/Q_1$ fulfills

$$\eta \leq \frac{T_1 - T_2}{T_1}$$

5.9   Change of variables in thermodynamic equations

We have so far expressed the complete thermodynamic information on a system in two different ways:

Energy representation
$$E = E(S, V, N) \qquad dE = TdS - pdV + \mu dN$$

Free energy representation
$$F = F(T, V, N) \qquad dF = -SdT - pdV + \mu dN$$

When going from S to $T = \partial E/\partial S$ as independent variable, we also changed the *dependent* variable from E to $F = E - S\frac{\partial E}{\partial S}$. The change in dependent variable is needed in order not to loose information. In the mono-atomic ideal gas, for example, we have $E(T) = 3NkT/2$ which contains no information at all about the pressure.

Legendre transforms - simple example

Consider two simple functional relations

$$y = f(x) = x^2, \qquad \bar{y} = (x - a)^2.$$

We want to take $p = dy/dx$ $(d\bar{y}/dx)$ as new independent variable (compare $S \Rightarrow T = \partial E/\partial S$).

$$
\begin{aligned}
p &= f'(x) = g(x) = 2x \\
x &= g^{-1}(p) = \frac{p}{2} \\
y(p) &= y(g^{-1}(p)) = \frac{p^2}{4}
\end{aligned}
\qquad
\begin{aligned}
p &= f'(x-a) = g(x-a) = 2(x-a) \\
x &= g^{-1}(p) + a = \frac{p}{2} + a \\
\bar{y}(p) &= \bar{y}(g^{-1}(p) + a) \\
&= y(p) = \frac{p^2}{4}
\end{aligned}
$$

All information about a has been lost when taking $p = dy/dx$ as independent variable!

The functional relation $y = y(p) = F(p)$ constitutes actually a differential equation

$$
y = F(y'); \quad y' = F^{-1}(y)
$$

which can be solved to obtain

$$
\frac{dy}{F^{-1}(y)} = dx; \quad \int \frac{dy}{F^{-1}(y)} = x + C.
$$

The relation $y = F(y')$ contains no information of the integration constant C.

Going back to the functional relationship $E = f(T, V, N)$, we find in a similar manner

$$
\int \frac{dE}{f^{-1}(E)} = S + C(V, N)
$$

with an unknown $C(V, N)$, and the fundamental relation $E(S, V, N)$ cannot be constructed.
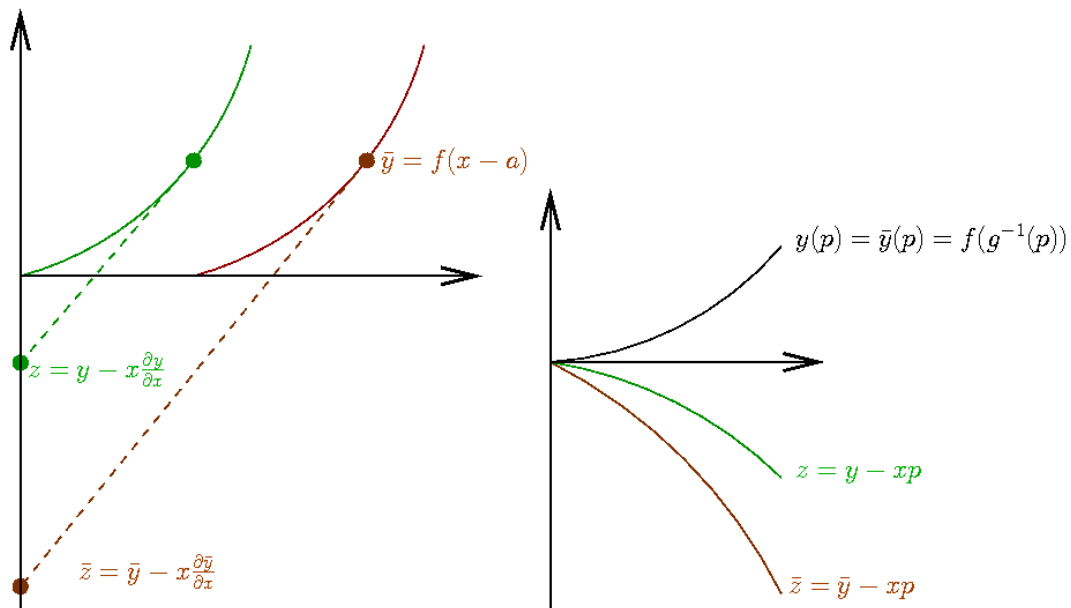
Resolution: Change dependent variable

Define a new dependent variable via a so-called **Legendre transformation**

$$
z(p) = y(x) - x\frac{\partial y}{\partial x} = y - px; \quad dz = pdx - pdx - xdp = -xdp.
$$

A new Legendre transformation takes us back!

$$
z - p\frac{\partial z}{\partial p} = z + xp = y(x)
$$

Application to thermodynamics

Let us start from the fundamental relation in the energy representation,

$$E = E(S, V, N) \quad dE = TdS - pdV + \mu dN.$$

By making Legendre transformations with respect to S, V, and N we obtain fundamental equations in new variables:

$$
\begin{array}{ll}
F(T, V, N) & \text{(Helmholtz' free energy)} \\
H(S, p, N) & \text{(Enthalpy)} \\
G(T, p, N) & \text{(Gibbs' free energy)} \\
\Omega(T, V, \mu) & \text{(The Grand potential)}
\end{array}
$$

Each "thermodynamic potential" above ($F(T, V, N)$, $H(S, p, N)$, or $G(T, p, N)$) contains precisely the same information about the thermodynamics and provide fundamental relations when expressed in their natural independent variables. The explicit expressions are

$$
\begin{aligned}
F(T, V, N) &= E - S\frac{\partial E}{\partial S} = E - TS \\
H(S, p, N) &= E - V\frac{\partial E}{\partial V} = E + pV
\end{aligned}
$$

$$
\begin{aligned}
G(T, p, N) &= E - S\frac{\partial E}{\partial S} - V\frac{\partial E}{\partial V} = E - TS + pV \\
\Omega(T, V, \mu) &= E - S\frac{\partial E}{\partial S} - N\frac{\partial N}{\partial \mu} = E - TS - \mu N
\end{aligned}
$$

In the corresponding differentials, the extensive variable "X" ($X = S, V$, or N) is replaced by the corresponding intensive variable "q" ($q = T, -p$, or μ. For instance, we find

$$
\begin{aligned}
dG &= dE - d(TS) + d(pV) = TdS - pdV + \mu dN - TdS - SdT + pdV + Vdp \\
&= -SdT + Vdp + \mu dN
\end{aligned}
$$

In this way we find

$$
\begin{aligned}
dF &= -SdT - pdV + \mu dN \\
dH &= TdS + Vdp - \mu dN
\end{aligned}
$$

$$
dG = -SdT + Vdp + \mu dN
$$

$$
d\Omega = -SdT - pdV - Nd\mu
$$

Minimal properties of the thermodynamic potentials

We have already shown that the energy tends to a minimum for processes at constant S, V, N and that the free energy F has the same property at constant T, V, N. The remaining potentials behave in an analogous way. Let α be some internal parameter of the system. For the energy $E(S, V, N, \alpha)$ we have

$$
dE = TdS - pdV + \mu dN + \beta_1 d\alpha + \beta_2 d\alpha^2
$$

where $\beta_1 = 0$ and $\beta_2 > 0$ at equilibrium. When we make Legendre transformations to obtain, say, $G(T, p, N)$ we obtain

$$
dG = d(E - TS + pV) = -SdT + Vdp + \beta_1 d\alpha + \beta_2 d\alpha^2
$$

which shows that G has a minimum at constant T, V, μ.

5.10 The Euler equation and the Gibbs-Duhem relation

Let us consider a simple one-component fluid with the fundamental relation $E(S, V, N)$. Only extensive parameters are involved, and they are all

proportional to the size of the system,

$$\lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N).$$

Differentiation with respect to λ yields

$$E = TS - pV + \mu N \quad \text{(Euler's equation)} \tag{6}$$

and since we also know $dE = TdS - pdV + \mu dN$ we have

$$SdT - Vdp + Nd\mu = 0 \quad \text{(Gibbs-Duhem relation)} \tag{7}$$

According to Eq. (6) we obtain zero result when all independent extensive parameters are converted to intensive parameters (the is no longer information about the size of the system).

Consider *e.g.* $G(T, p, N)$ with only one extensive parameter. We must have $G(T, p, N) = g(T, p)N$, N being the Gibbs free energy per particle, and as $\partial G/\partial N = \mu$, we have

$$G(T, p, N) = N\mu(T, p)$$

for a one-component fluid. For a fluid with several components,

$$G(T, p, N_1, N_2, ...) = N_1\mu_1(T, p, N_1/N, N_2/N...)$$
$$+ N_2\mu_1(T, p, N_1/N, N_2/N, ...) + ...$$

For the grand potential $\Omega(T, V, \mu)$ we find in a similar manner $\Omega(T, V, \mu) = V\omega(T, \mu)$ where ω is the potential per unit volume. Because $\partial\Omega/\partial V = -p$, we have $\omega = -p$, and

$$\Omega(T, V, \mu) = -p(T, \mu)V.$$

6   The third law of thermodynamics

The history of the third law goes back to Nernst in the 19th century and states that the entropy of pure crystalline materials goes to zero when $T \to 0$. The third law is basically inconsistent with classical physics but has a natural explanation in quantum statistics. In quantum statistics, we have $S(E) = k\ln\omega(E)$, and thus as the energy tends to the lowest possible state E_0, the ground state, the number of accessible states must tend to 1. In the idealized case the ground state would be non-degenerate, $\omega(E_0) = 1$, but it is sufficient that the the degeneracy is small compared to $exp(N)$ in order to have a macroscopically negligible entropy at zero temperature.

Some consequences are:
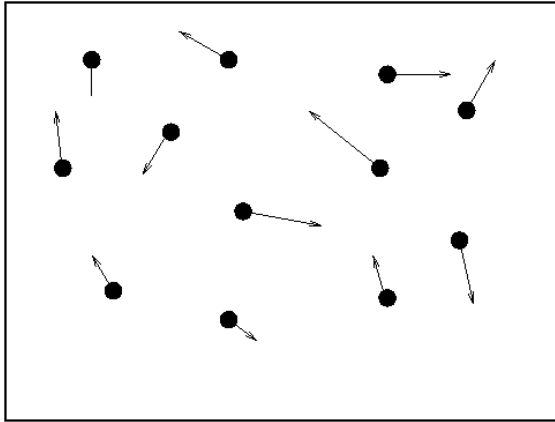
a) $c_V \to 0$ This follows from the fact that

$$S(T) - S(0) = \int_0^T \frac{c_V dT}{T}$$

is finite.

b) The volume expansion coefficient tends to zero, because

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{\partial^2 G}{\partial p \partial T} = -\left(\frac{\partial S}{\partial p}\right)_T \to 0$$

c) The pressure increase with T tends to zero,

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial V \partial T} = \left(\frac{\partial S}{\partial V}\right)_T \to 0$$

7 The classical ideal gas

The "ideal gas approximation" means that

- The gas is sufficiently dilute so that the differences between Bose and Fermi statistics can be neglected

- The interaction between the gas molecules is sufficiently weak

Let us first consider N point particles moving inside a container of volume V

$$H = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m}.$$

Let n_i be the number of particles in quantum state "i". We have $N = \sum_i n_i$. The gas is classic in the above sense if $n_i \ll 1$.

7.1 Calculating the partition sum

a) $N = 1$ We obtain $Z(T, V, 1) = \sum_i e^{-\beta \epsilon_i(V)}$

b) $N = 2$ Already now in principle bosons (integer spin) and fermions (half-integer spin) give different results. There can be at most one particle in each state for fermion, whereas in case of bosons a one-particle state can be doubly occupied:

$$Z(T, V, 2) = \frac{1}{2} \sum_{i \neq j} e^{-\beta(\epsilon_i + \epsilon_j)} \left[+ \sum_i e^{-2\beta \epsilon_i} \right],$$

The last term above involving double occupancy only occurs for bosons. The factor $1/2$ in the first term account for the fact that the gas particles are identical, the state "i,j" is the same as "j,i". **When the gas is sufficiently dilute, the probability for multiple occupancies is negligible** The occupation numbers $\sim N/V$, a double occupancy $\sim (N/V)^2$, and so on.

For N particles:

$$
\begin{aligned}
Z(T, V, N) &= \frac{1}{N!} \sum_{\text{all } i \text{ unequal}} e^{-\beta(\epsilon_{i_1} + \epsilon_{i_2} + \ldots + \epsilon_{i_N})} \\
&\quad [+ \text{ terms where two or more states coincides (bosons only)}] \\
&\approx \frac{1}{N!} \sum_{i_1, i_2, \ldots i_N} e^{-\beta(\epsilon_{i_1} + \epsilon_{i_2} + \ldots + \epsilon_{i_N})}
\end{aligned}
$$

where the last approximations holds only for sufficiently dilute gases. Thus, in the dilute limit

$$Z(T, V, N) \approx \frac{1}{N!} \sum_{i_1, i_2, \ldots i_N} e^{-\beta(\epsilon_{i_1} + \epsilon_{i_2} + \ldots + \epsilon_{i_N})} = \frac{1}{N!} Z^N(T, V, N = 1)$$

The problem has been reduced to the calculation of Z for one particle.

7.2 Calculating one-particle states

In 1D we have

$$\frac{\hat{p}^2}{2m} \psi(x) = \epsilon \psi(x)$$

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}$$

With periodic boundary conditions over a distance L, we find $\psi(x) = e^{ipxi/\hbar}$ where $pL/\hbar = 2\pi n$. Thus, only momenta $p_n = 2\pi \hbar n/L = nh/L$ are allowed,

and they are a distance h/L from one another. This corresponds to a uniform density $D_p = 1/(p_n - p_{n-1}) = L/h$.

In three dimensions we have

$$\frac{\hat{\mathbf{p}}^2}{2m}\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial x^2}\right]\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r})$$

We again use periodic boundary conditions over a box $V = L \times L \times L$, $\psi(x, y, z) = \psi(x + L, y, z)$ etc, which gives

$$\psi(\mathbf{r}) = e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \quad \text{and} \quad \epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m}.$$

The periodic boundary conditions in x, y, z gives

$$p_x L = n_x h, \ \ p_y L = n_y h, \ \ p_z L = n_z h$$

and each allowed $\mathbf{p}$ points occupies a cube of volume $h^3/(L \times L \times L) = h^3/V$. Thus, the allowed $\mathbf{p}$ points are evenly spaced with a density $D_p = V/h^3$ in momentum space.

7.3 Partition sum

$$
\begin{aligned}
Z(T, V, 1) &= \sum_{\mathbf{p}_n} e^{-\beta\frac{\mathbf{p}_n^2}{2m}} = \frac{V}{h^3}\int d^3p \, e^{-\beta\frac{\mathbf{p}^2}{2m}} \\
&= \frac{V}{h^3}\left(\int_{-\infty}^{\infty} dp_x e^{-\beta\frac{p_x^2}{2m}}\right)^3 = V\left(\frac{2\pi mkT}{\hbar^2}\right)^{3/2}
\end{aligned}
$$

where we have used that $\int_{-\infty}^{\infty}\exp(-x^2) = \sqrt{\pi}$. We next use the approximation $Z(T, V, N) \approx Z(T, V, 1)^N/N!$ and Stirling's approximation $N! \approx (N/e)^N$ to obtain

$$F(T, V, N) = -kT\ln Z(T, V, N) = -NkT\ln\left[\frac{eV}{N}\left(\frac{2\pi mkT}{\hbar^2}\right)^{3/2}\right].$$

7.4 Gas particles with internal degrees of freedom

If the gas is composed of polyatomic molecules, each particle in addition to the translational energy $(\mathbf{p}^2/2m)$ has internal excitations "i" (rotations, vibrations, etc.),

$$\epsilon_{\mathbf{p},i} = \frac{\mathbf{p}^2}{2m} + \epsilon_i.$$

The partition sum for one particle now becomes

$$Z(T, V, N = 1) = Z_{transl}(T, V, 1) \sum_i e^{-\beta \epsilon_i} = Z_{transl}(T, V, 1) \times Z_{int}(T, 1)$$

and

$$F(T, V, N) = -kT \ln \frac{(Z(T, V, 1))^N}{N!} = F_{transl}(T, V, N) + F_{int}(T, N),$$

where $F_{transl}(T, V, N)$ is the free energy for point particles, and

$$F_{int}(T, N) = -NkT \ln \sum_i e^{-\beta \epsilon_i} \quad \text{(independent of V)}.$$

7.5   Thermodynamics, equations of state

The internal excitations give a volume-independent contribution to F, which means that they do not contribute to the pressure. A simple calculation yields

$$p = -\frac{\partial F_{transl}}{\partial V} = \frac{\partial}{\partial V} NkT(\ln V + \text{const}) = \frac{NkT}{V}, \quad pV = NkT.$$

The energy is $E = F - T\partial F/\partial T = -\partial \ln(Z_{transl} \, Z_{int})/\partial \beta$, and $Z_{transl} = \text{const} \times T^{3N/2}$. This gives

$$E = \frac{3}{2}NkT + E_{int}(T)$$

For most diatomic gases, the vibrations are frozen out at 300K and do not contribute to C_V, whereas the rotations contribute $\sim NkT$ (*cf.* problem 7.1 - 7.2).

7.6   Entropy

We have $S = -\partial F/\partial T$ which gives

$$S = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{5}{2} + \frac{3}{2} \ln \frac{2\pi mk}{\hbar^2} \right] + S_{int}(T, N),$$

where the first part comes from the translation motion. This is evidently not valid when $T \to 0$.

7.7 Range of validity of the classical approximation

In the classical approximation, multiply occupied states are not treated correctly which allows us to approximate $Z(N) = Z^N(1)/N!$. This in turn requires that the mean number n_i of particles in state "i" is small, $n_i \ll 1$. Now,

$$n_i = N \frac{e^{-\beta \epsilon_i}}{\sum_j e^{-\beta \epsilon_j}} = N \frac{e^{-\beta \epsilon_i}}{Z(1)} \ll 1$$

for all ϵ_i, and in particular for the zero-momentum state $\epsilon_0 = 0$. Thus,

$$\frac{N}{Z(1)} = \frac{N}{V} \left(\frac{\hbar^2}{2\pi m k T} \right)^{3/2} \ll 1.$$

The quantity $\lambda = (\hbar^2/2\pi m k T)^{1/2}$ is the de Broglie wavelength of a particle of energy $\pi k T$, and thus $\lambda << (V/N)^{1/3}$ in order for the classical approximation to hold.

7.8 Notes on real gases

In a real gas the molecules interact,

$$U = \sum_{i<j} v(|\mathbf{r}_i - \mathbf{r}_j|),$$

which gives corrections at higher densities. This leads to modifications of the equation of state of the form ("virial expansion")

$$p = \frac{NkT}{V} \left[1 + \frac{N}{V} B(T) + \left(\frac{N}{V} \right)^2 C(T) + ... \right]$$

where the leading correction has the form (*cf.* problem 7.7)

$$B(T) = \frac{1}{2} \int d^3r (1 - e^{-\beta v(r)}).$$

A well-known semi-empirical equation of state is due to van der Waals,

$$\left[p + \left(\frac{N}{V} \right)^2 a \right] \left[1 - \frac{N}{V} b \right] = \frac{NkT}{V}$$

Here, the parameter b represents the "volume" of the molecule (the hard-core repulsion at short distances). At far distances, closed-shell molecules will experience a weak attraction ("van der Waals attraction") $\sim 1/R^6$, which will lower the pressure. This attraction is modeled by the parameter a. The van der Waals equation usually gives a good qualitative or even semi-quantitative description of condensation phenomena.

7.9 Classical statistical mechanics

Quantum statistics:

- Classical Hamiltonian $H(\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{r}_1, \mathbf{r}_2, ...)$, substitute $\mathbf{p}_\nu \rightarrow -i\hbar\nabla_\nu$

- Solve Schrödinger Eq. $H\Psi_i = E_i\Psi$

- Form the partition sum $Z = \sum_i e^{-\beta E_i}$

Classical approx: When $\hbar \rightarrow 0$, $\mathbf{r}_\nu, \mathbf{p}_\nu$ can be measured simultaneously, and the levels become more and more densely spaced. If V is slowly varying, and the particles non-interacting, we can approximately regard it constant over many de Broglie wavelength, and is seems plausible that we can treat the problem like the ideal gas. This means that the number of one-particle levels can be approximated as $d\gamma = (1/h^3)d^3r\ d^3p$, The argument can be extended to many particles which also interact, and thus in the classical limit we replace sum over states with integrals over a 6N-dimensional phase space made of of the 3N coordinates and 3N momenta, $d\Gamma = (1/h^{3N}d^3r_1\ d^3r_2...d^3p_1\ d^3p_2...$. This was exactly how statistical mechanics was handled before the quantum era. Thus, the classical entropy is

$$S_{class}(E, V, N) = k\ln[\Delta\Gamma/h^{3N}],$$

where $\Delta\Gamma$ is the volume of the accessible part of phase space (accessible when the various constraints are applied). Today we know that the proper unit for volumes in phase space is h^{3N}. Different units of phase space volume give different additive constants to the entropy, and thus entropy could not be defined on an absolute scale before quantum mechanics was discovered. In a similar fashion the classical partition function becomes

$$Z_{class} = \frac{1}{h^{3N}} \int e^{-\beta H(\mathbf{p}1, \mathbf{p}2,...,\mathbf{r}_1, \mathbf{r}_2,...)}\ d\Gamma$$

A well-known result in the classical limit is the so-called equipartition theorem. Assume that H only consists of quadratic terms, $H = a_1 q_1^2 + a_2 q_2^2 + ...$ (q_i is a coordinate or momentum).

$$
\begin{aligned}
E &= \frac{\int dq_1 dq_2 ...e^{-\beta(a_1 q_1 + a_2 q_2 + ...)}(a_1 q_1 + a_2 q_2 + ...)}{\int dq_1 dq_2 ...e^{=\beta(a_1 q_1^2 + a_2 q_2^2 + ...)}} \\
&= \sum_i \frac{\int dq_i e^{-\beta a_1 q_i^2} a_i q_i^2}{\int dq_i e^{-\beta a_1 q_i^2}} = \sum_i \frac{kT}{2}
\end{aligned}
$$

Thus, every quadratic term in H contributes $kT/2$ to E and $k/2$ to C_V in the classical limit. In a classical gas of monatomic molecules we have N

quadratic terms and $C_V = \frac{3}{2}Nk$. For vibrating atoms in a solid we have $3N$ oscillators and $6N$ quadratic terms, giving $C_V = 3Nk$ in the classical (high-T) limit (the Dulong-Petit law).

8 Thermodynamics of the harmonic oscillator and applications

The description of the quantized electromagnetic field leads naturally to a problem involving harmonic oscillators. The same is true for vibrations in molecules and solids. In both cases, the energy levels are of the form

$$E = \sum_\nu \hbar\omega_\nu [n_\nu + 1/2]$$

where $\{\omega_n u\}$ are the eigenfrequencies, and $n_\nu = 0, 1, 2, ...$ is the oscillator quantum number for mode "ν". If we measure the energy relative the the ground-state energy $E_0 = (1/2)\sum_\nu \hbar\omega_\nu$ we can regard the system as a system of bosons which occupies the energy levels $\{\omega_\nu\}$. These bosons are termed photons in the case of electromagnetic radiation, and phonons in the case of atomic vibrations in solids.

8.1 Thermodynamics of a single oscillator

For a single oscillator we have $E_n = \hbar\omega[n + 1/2]$ which gives ($x = \beta\hbar\omega$)

$$\begin{aligned}
Z &= \sum_n^\infty e^{-\beta E_n} = e^{-x/2} \sum_n^\infty e^{-nx} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \\
\langle E \rangle &= -\frac{\partial Z}{\partial \beta} = \hbar\omega \left[\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right]
\end{aligned}$$

Introducing

$$\bar{n} = \frac{1}{e^{\beta\hbar\omega} - 1}$$

we have $E - E_0 = \hbar\bar{n}$. We can thus consider the oscillator as an energy level $\hbar\omega$ occupied with 0, 1, 2, ... bosons. The quantity $\bar{n}$ is the mean occupation number.

In the limit $kT \ll \hbar\omega$, the excitation energy is exponentially small, $E = E_0 = O(e^{-\beta\hbar\omega})$, which implies that the specific heat is exponentially small as well, $C_V = O(e^{-\beta\hbar\omega})$.

In the opposite limit $kT \gg \hbar\omega$, we have

$$E - E_0 = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \approx \frac{\hbar\omega}{1 + \beta\hbar\omega - 1} = kT$$

which is the classical result ($E = kT$, $C_V = k$). For oscillations in molecules or solids, there is an upper limit ω_{max}, and thus the specific heat is classical (Nk) when $kT \gg \omega_{max}$. In the case of the electromagnetic field, there is no upper limit of photon energies, but only photons with $\hbar\omega < kT$ contributes appreciably to the energy density.

8.2   Black-body radiation

Consider a photon gas in a cavity of volume V. The photons (oscillator eigenmode) may be labeled by its momentum $\hbar\mathbf{q}$ and polarization λ, and there are two independent polarizations for each $\mathbf{q}$. In a finite cavity, the momentum becomes discretized. As in the case of the ideal gas, we find uniform density of $\mathbf{q}$ points $D_q = V/(8\pi^3)$. We count the energy relative the the ground state and use $\omega_{\mathbf{q}\lambda} = cq$ to obtain

$$E = \sum_{\mathbf{q}\lambda} \frac{\hbar\omega_q}{e^{\beta\hbar\omega_q} - 1} = \frac{2V}{8\pi^3} \int_0^\infty \frac{\hbar cq}{e^{\beta\hbar cq} - 1} 4\pi q^2 dq = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega.$$

The energy density per unit volume and frequency is thus

$$u(T, \omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1},$$

the black-body radiation law discovered by Planck. In the classical limit, $u_{cl}(T, \omega) \to \omega^2/(\pi^2 c^3)$, and the energy would diverge.

The integrated energy density per unit volume, or the radiation pressure is

$$u(T) = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\frac{\hbar\omega}{kT}} - 1} d\omega = T^4 \frac{\hbar k^4}{\pi^2 c^3 \hbar^4} \int_0^\infty \frac{x^3}{e^x - 1} = KT^4$$

where the constant has the value $K = 5.67 \times 10^{-8}$ J m^{-2} s^{-1} K^{-4}. The T^4 law is an immediate consequence of the linear dispersion $\omega_q = \text{const} \times q$. Low energy lattice vibrations behave in a similar way, and consequently the lattice vibrations in solids contributes $\sim \text{const} \times T^4$ to the internal energy and $\sim \text{const} \times T^3$ to the specific heat at low temperatures.

8.3 Lattice vibrations in solids

Lattice vibrations in solids leads to coupled harmonic oscillators. For periodic solids, the oscillator eigenmodes are traveling waves with energies $\hbar\omega_{\mathbf{q}\lambda}$. Thus, the excitation energy of the lattice is

$$E - E_0 = \sum_{\mathbf{q}\in Bz,\lambda} \frac{\hbar\omega_q}{e^{\beta\hbar\omega_q} - 1}$$

The number of $\mathbf{q}$ points in the Brillouin zone is the number of unit cell N, and there are 3 modes per atom in the unit cell for each $\mathbf{q}$. At high temperature, each oscillator becomes classical, and each atom contributes $3k$ to the specific heat. As the temperature is lowered, more and more modes are frozen out, and the specific heat tends to 0.

8.4 Einstein model

The simplest model of lattice vibrations is to approximate $\omega_{\mathbf{q}\lambda}$ by a constant ω_0:

$$E - E_0 \approx \frac{\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1} \sum_{\mathbf{q}\in Bz,\lambda} = 3N_{at}\frac{\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1}$$

The high-temperature limit $3N_{at}kT$ is correctly reproduced. At low temperatures, however, the Einstein approximation gives an exponentially small contribution to $E - E_0$ and C_V. The correct behavior, however, is that $C_V \sim T^3$ at low T, and the reason is that there are always long-wavelength phonons with $\hbar\omega < kT$ for any T.

8.5 Lattice specific heat at low temperatures

At low T, modes $\omega_{\mathbf{q}\lambda} > kT/\hbar$ are frozen out and give an exponentially small contribution. Thus only long wavelength acoustic modes $\omega_{\mathbf{q}\lambda} \approx v_\lambda|\mathbf{q}|$ need to be considered, and each such mode contribute $\sim k$ to C_V. The contributing longitudinal modes, for example, fall within a sphere $|\mathbf{q}| < kT/(\hbar v_L)$, and as the mode density in $\mathbf{q}$-space is $V/(8\pi^3)$ we find a contribution

$$\frac{V}{8\pi^3} \frac{4\pi}{3} \left(\frac{kT}{\hbar v_L}\right)^3 k$$

to C_V. Adding the contribution from the remaining two acoustic modes we find

$$C_V \sim \frac{Vk^4}{6\pi^2\hbar^3} \left(\frac{1}{v_1^3} + \frac{1}{v_2^3} + \frac{1}{v_3^3}\right) T^3, \quad T \to 0.$$

For low ω, the foregoing analysis shows that the density of modes $D(\omega)d\omega = (V/(8\pi^3)4\pi^3 q^2 dq$ is

$$D(\omega) \sim \frac{V}{2\pi^2}\left(\frac{1}{v_1^3} + \frac{1}{v_2^3} + \frac{1}{v_3^3}\right)\omega^2 \tag{8}$$

Debye approximated $D(\omega)$ by Eq. (8) all the way up to a cut-off ω_D chosen so as to have the correct total number of modes. In this way both the high and low T behavior is correct.

$$\frac{V}{2\pi^2}\left(\frac{1}{v_1^3} + \frac{1}{v_2^3} + \frac{1}{v_3^3}\right)\frac{\omega_D^3}{3} = 3N_{at}$$

This gives $D(\omega) = 9N_{at}\omega^2/\omega_D^3$, $\omega < \omega_D$, and ($\Theta_D = \hbar\omega_D/k$)

$$
\begin{aligned}
C_V &= \frac{9N_{at}k}{\omega_D^3}\int_0^{\omega_D}\frac{(\beta\hbar\omega)^2 e^{\beta\omega}}{(e^{\beta\omega}-1)^2}\omega^2 d\omega \\
&= 9N_{at}k\left(\frac{T}{\Theta_D}\right)^3\int_0^{\Theta_D/T}\frac{x^4 e^x\, dx}{(e^x-1)^2}
\end{aligned}
$$

9 Systems with varying particle number

When solving problems in statistical mechanics it often complicates the calculations to strictly maintain constraints like keeping the energy or the particle number fixed. The canonical ensemble was obtained from the microcanonical one by relaxing the constraint of a fixed total energy. We now want to relax the constraint of keeping the particle number fixed. This will lead to the so-called grand canonical ensemble, which describes a system in contact with a heat and particle reservoir.

Relaxing the constraint of a fixed particle number greatly simplifies the treatment of, for example, the Bose and Fermi quantum gases.

The system + bath is isolated from the environment. We want to obtain the conditional probability $p_i(N)$ that the system has N particles and is in state "i" of energy $E_i(N)$. The bath energy is then $E - E_i$, and the bath has $N_0 - N$ particles. The probability $p_i(N)$ is proportional to number of bath states,

$$p_i = \text{const}\ \times e^{S_r(E-E_i, N_0-N)/k}$$

The reservoir is very large, $E \gg E_i$, i.e. $S_r(E - E_i, N_0 - N) \approx S_r(E) - E_i\partial S/\partial E - N\partial S/\partial N = S_r(E) - E_i/T + \mu N/T$ Thus, $p_i(N) = Ce^{-\frac{(E_i - \mu N)}{kT}}$
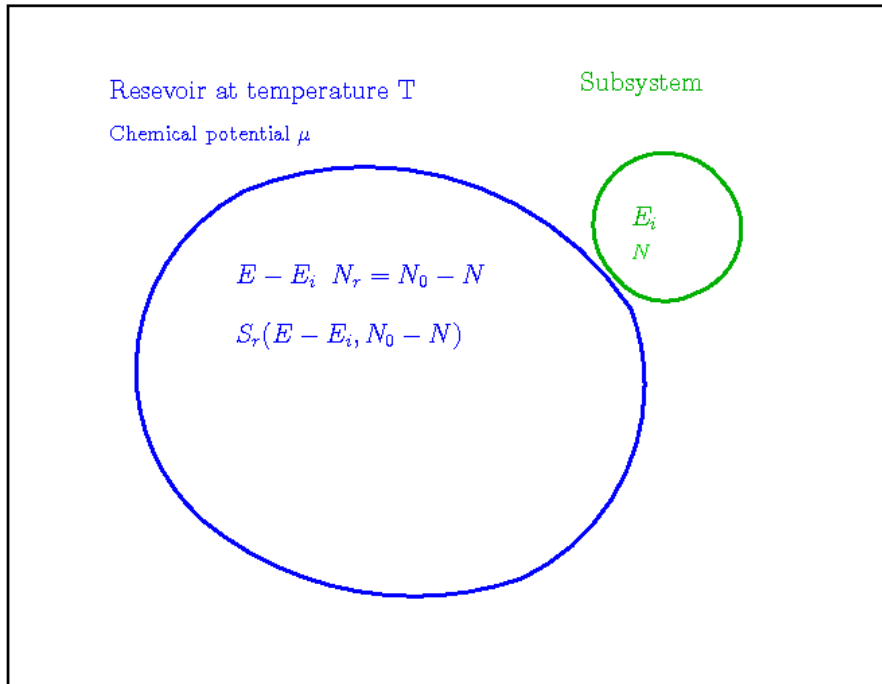
where C is another constant, which is determined by $\sum_{i,N} p_i(N) = C \sum e^{-\frac{E_i - \mu N}{kT}} = 1$

In summary we have found that the probabilities $p_i(N)$ is given by

$$p_i(N) = Ce^{-\beta(E_i(N) - \mu N)}$$

where

$$\frac{1}{C} \equiv \mathcal{Z}(T, V, \mu, \alpha_1, ...) = \sum_{i,N} e^{-\beta(E_i(N) - \mu N)} = \sum_N Z(T, V, N, \alpha_1, ...)e^{\mu N}.$$

As we shall see, the so-called grand partition sum $\mathcal{Z}(T, V, \mu, \alpha_1, ...)$, contains a complete description of the thermodynamics of systems in contact with a heat and particle reservoir. As seen above, it can also be expressed in the canonical partition sum $Z(N)$ The partition sum $\mathcal{Z}$ depends explicitly on T and μ, and via the energy levels is also depends on V and possibly other external parameters $\alpha_1, \alpha_2....$

9.1 Thermodynamics in the Grand Ensemble

We start by computing the mean energy and particle number:

$$\langle N \rangle = \sum_{i,N} N p_i(N) = \frac{\sum_{i,N} N e^{-\beta(E_i - \mu N)}}{\sum_{i,N} e^{-\beta(E_i - \mu N)}} = kT \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = kT \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

$$\langle E - \mu N \rangle = \sum_{i,N} (E_i - \mu N) p_i E_i = \frac{\sum_{i,N} (E_i - \mu N) e^{-\beta(E_i - \mu N)}}{\sum_{i,N} e^{-\beta(E_i - \mu N)}} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

$$\langle E \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - \mu kT \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

In a similar way all equilibrium thermodynamic variables can be expressed in partial derivatives of $\ln \mathcal{Z}$.

9.2   The Grand Potential

We saw above that all thermodynamic quantities could be expressed in $\ln \mathcal{Z}$ it its partial derivatives. Let us define the grand potential by

$$\Omega(T, V, \mu) = -kt \ln \mathcal{Z}.$$

The foregoing result for $\langle E \rangle$ can then be rewritten as

$$\langle E \rangle = \Omega - T \frac{\partial \Omega}{\partial T} - \mu \frac{\partial \Omega}{\partial \mu},$$

i.e., $\langle E \rangle$ is a Legendre transform of $\Omega(T, V, \mu)$. The backward transform then yields (E and N are understood to be the averaged quantities)

$$\Omega(T, V, \mu) = E - S \frac{\partial E}{\partial S} - N \frac{\partial E}{\partial N} = E - TS - \mu N$$

$$d\Omega = TdS - pdV + \mu dN - TdS - SdT - \mu dN - Nd\mu$$

$$= -SdT - pdV - Nd\mu$$

9.3   Particle fluctuations

Knowing the statistical weights $p_i(N)$ the fluctuations in N can also be obtained. We have $(\Delta N)^2 = \langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$, and

$$\langle N \rangle = kT \frac{\partial \ln \mathcal{Z}}{\partial \mu}, \quad \langle N^2 \rangle = \frac{\sum_{i,N} N^2 e^{-\beta(E_i - \mu N)}}{\sum_{i,N} e^{-\beta(E_i - \mu N)}} = (kT)^2 \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} / \mathcal{Z}$$

$$(\Delta N)^2 = \frac{(kT)^2}{\mathcal{Z}^2} \left[\mathcal{Z} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \right] = (kT)^2 \frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} = kT \frac{\partial \langle N \rangle}{\partial \mu}$$

Thus, $\Delta N / \langle N \rangle \propto 1/\sqrt{\langle N \rangle}$ and are negligible in the thermodynamic limit.

9.4   Bose and Fermi quantum gases

Consider a system of non-interacting identical particles with one-particle levels $\epsilon_1, \epsilon_2, \epsilon_3, ...$ The energy and particle number can be written

$$E = \sum_k n_k \, \epsilon_k, \quad N = \sum_k n_k,$$

where $n_k = 0, 1$ in the case of Fermions (half-integer spin), and $n_k = 0, 1, 2, 3, ...$ in the case of Bosons (integral spin). In the grand ensemble with no constraint on N we can sum the occupation numbers independently, which greatly simplifies the analysis:

$$\mathcal{Z} = \sum_{n_1} e^{-\beta(\epsilon_1-\mu)n_1} \sum_{n_2} e^{-\beta(\epsilon_2-\mu)n_2} \sum_{n_3} e^{-\beta(\epsilon_3-\mu)n_3}... = \mathcal{Z}_1 \mathcal{Z}_2 \mathcal{Z}_3....$$

$$\mathcal{Z}_k = \sum_{n_k} e^{-\beta(\epsilon_k-\mu)n_k}, \quad \Omega = -kT \ln \mathcal{Z} = -kT \sum_k \ln \mathcal{Z}_k \equiv \sum_k \Omega_k$$

$$\langle n_k \rangle = -\frac{\partial \Omega_k}{\partial \mu}$$

$$\textbf{Fermions: } \mathcal{Z}_k = \sum_{n_k=0}^{1} e^{-\beta(\epsilon_k-\mu)n_k} = 1 + e^{-\beta(\epsilon_k-\mu)}$$

$$\langle n_k \rangle \equiv f_{FD}(\epsilon_k) = \frac{1}{1 + e^{\beta(\epsilon_k-\mu)}}$$

$$\textbf{Bosons: } \mathcal{Z}_k = \sum_{n_k=0}^{\infty} e^{-\beta(\epsilon_k-\mu)n_k} = \frac{1}{1 - e^{-\beta(\epsilon_k-\mu)}}$$

$$\langle n_k \rangle \equiv f_{BE}(\epsilon_k) = \frac{1}{e^{\beta(\epsilon_k-\mu)} - 1}$$

$$\textbf{Classical gas: } \langle n_k \rangle \equiv f_{MB}(\epsilon_k) = A e^{-\beta\epsilon_k} = e^{\beta(\mu-\epsilon_k)}$$

The classical approximation is valid when all $n_k \ll 1$ and is the limiting case of both statistics. We notice $f_{BE}(\epsilon) > f_{MB}(\epsilon) > f_{FD}(\epsilon)$.

9.5   The degenerate electron gas

The electron-gas is an often used model for those properties which are not sensitive the the lattice structure. At $T = 0$, all states are occupied up to a certain energy ϵ_F, and all states above are empty. At finite T, there is a transition region of width $\sim kT$ in which $f_{FD}(\epsilon)$ differs appreciably from its $T = 0$ limit. The Fermi energy ϵ_F is typically of the order 5-10 eV and is

Fermi surface,
at energy
ϵ_F
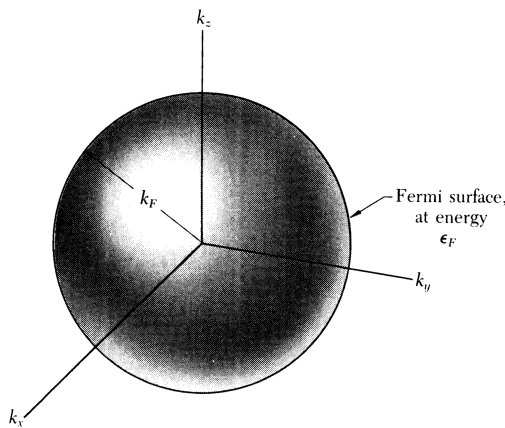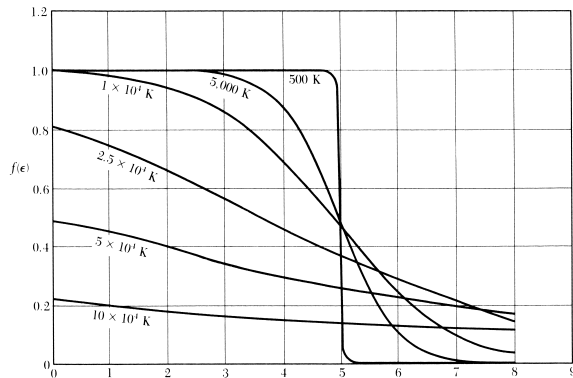
thus much larger than kT ($\sim$ 25 meV at room temperature); the Fermi gas is said to be degenerate. Only electrons within $\sim kT$ from the Fermi energy are affected by thermal excitations. This leads to a dramatic reduction of the specific heat compared to the classical Boltzmann gas.

9.6   The Fermi gas at zero temperature

We consider a gas of non-interacting Fermions enclosed in a box $V = L \times L \times L$. With periodic boundary conditions, the one-particle orbitals are plane waves, $\phi_{\mathbf{k}}(\mathbf{r}) = (1/\sqrt{V} \exp(i\mathbf{k} \cdot \mathbf{r})$ of energies $\epsilon_{\mathbf{k}} = \hbar^2 k^2/(2m)$. The periodic boundary conditions make $\mathbf{k}$ discrete, $\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$, which means that they are uniformly distributed with density $D_k = V/(8\pi^3)$. At $T = 0$, all states with $|\mathbf{k}| < k_F$ are filled, and all other empty ($\hbar^2 k_F^2/(2m) = \epsilon_F$).

$$n \equiv \frac{N}{V} = 2\frac{1}{8\pi^3}\frac{4\pi}{3}k_F^3 = \frac{k_F^3}{3\pi^2}$$
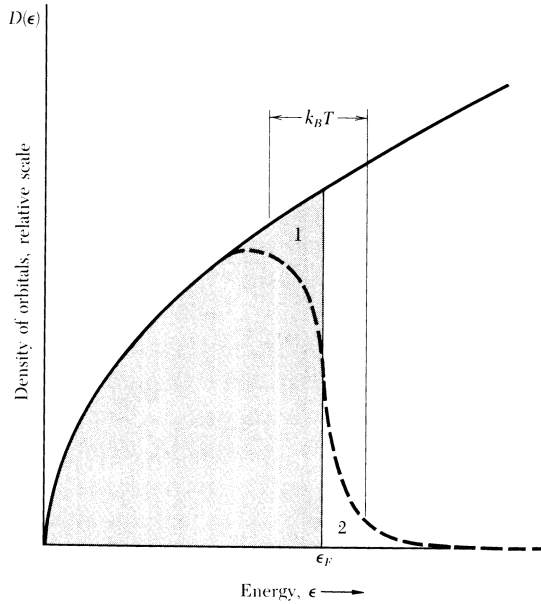
The Fermi wave-vector thus only depends on the density, $k_F = (3\pi^2 n)^{1/3}$. We also notice that $\epsilon_F \propto k_F^2 \propto n^{2/3}$, and that $E/V \propto n\epsilon_F \propto n^{5/3}$. The degenerate Fermi gas is thus quite incompressible, and E/V increases rapidly with density.
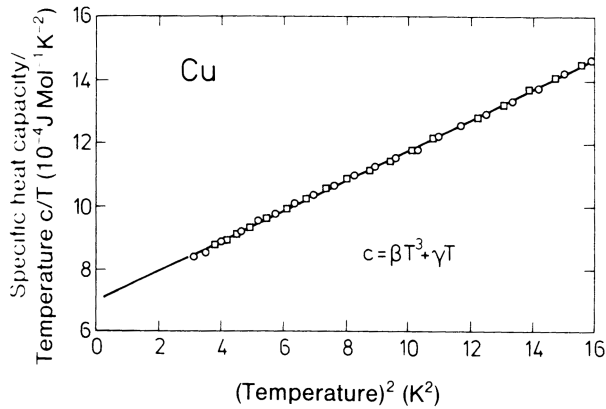
9.7 Density of states per unit energy

In what follows it proves convenient to introduce a density of states $D(\epsilon)$ and $N(\epsilon) = \int_0^\epsilon D(\epsilon')d\epsilon'$. $N(\epsilon)$ equals the number of states within the sphere $k < \sqrt{2m\epsilon}/\hbar$ in **k**-space, which gives

$$N(\epsilon) = \frac{2}{8\pi^3}\frac{4\pi}{3}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2} = \frac{1}{3\pi^2\hbar^3}(2m\epsilon)^{3/2} \propto \epsilon^{3/2}$$

$$D(\epsilon) = \frac{dN}{d\epsilon} = \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\sqrt{\epsilon} \propto \sqrt{\epsilon}.$$

In 1D the the density of k-points is $1/(2\pi)$ per unit length, and in 2D it is $1/(4\pi^2)$ per unit area (systems which can be realized today as nanoscopic micro structures). In 1D, the "sphere" volume $\propto k \propto \sqrt{\epsilon}$, and in 2D it is $\propto k^2 \propto \epsilon$. Thus, $D_{1D}(\epsilon) \propto 1/\sqrt{\epsilon}$, and $D_{2D}(\epsilon) \propto d\epsilon/d\epsilon = 1$.

The figure shows a plot with y-axis labeled "Specific heat capacity/ Temperature c/T (10^{-4} J Mol^{-1} K^{-2})" ranging from 6 to 16, and x-axis labeled "(Temperature)^2 (K^2)" ranging from 0 to 16. Labeled "Cu" with equation $c = \beta T^3 + \gamma T$.

9.8 The Fermi-gas specific heat

In the dilute classical Boltzmann gas, every particle is affected by a temperature change. The specific heat per particle is here $\frac{3}{2}k$. In the degenerate Fermi gas, on the other hand, only electrons near the Fermi surface can be excited thermally. This leads to a dramatic reduction of the specific heat. Assuming that only electrons within $\sim kT$ contribute, and that each particle in this thin shell each contributes $\sim k$ per particle, we find

$$\frac{C_V}{V} \sim n\frac{kT}{\epsilon_F}k = nk\frac{T}{T_F} \quad (kT_F = \epsilon_F).$$

A more accurate analysis shows (*cf.* Ibach-Lüth chapter 6.4, Mandl problem 11.3)

$$\frac{C_V}{V} = \frac{\pi^2}{3}D(\epsilon_F)k^2T = \frac{\pi^2}{2}nk\frac{T}{T_F}.$$

9.9 Specific heat from phonons and electrons at low temperatures

At room temperature, the lattice gives a contribution $\sim N_{at}k$ to C_V, and because the number of electrons is of the same order as N_{at}, the contribution from the electrons is completely overshadowed. At low temperatures, however, the lattice contribution tends to zero at T^3, and the electronic contribution becomes visible:

$$C_V = \gamma T + \beta T^3$$

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