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An Improved State Equation in the Vicinity of the Critical Point

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An improved state equation for the vicinity of the critical point is proposed. An analysis of the experimental data on helium and xenon has been carried out in order to investigate the influence of the number of constants in the equation and the $P\rho T$ range on the critical constants T_c and ρ_c and on the critical exponents α, β, γ, and δ. No such influence has been detected. The model for the critical point, recently proposed by Widom, has been checked regarding its consequences for the rectilinear diameter. No definite confirmation but indications for its correctness have been found.

Key words: Compressibility; critical point; equation of state; fluid; low temperature; methane; scaling law; specific heat; helium; xenon.

1. Introduction

Recently an equation of state for the vicinity of the critical point has been proposed by Verbeke et al. [1].[1] This equation was applied to the data for xenon of Habgood and Schneider [3]. In a subsequent paper the equation was applied to data for methane of Jansoone et al. [2]. It is the purpose of this paper to report improvements in the equation which have been made since then.

2. Formulation of the Modified State Equation

Several questions concerning the original equation remained to be answered.

The temperature derivative, $\frac{d^2P_s}{dT^2}$, where P_s is the vapor pressure and T is the temperature, is believed to diverge as

$$\frac{d^2P_s}{dT^2} \sim (T_c - T)^{-\alpha_2} \tag{1}$$

close to the critical point. The value of α_2 must, according to the weak inequality of Griffiths which is based on thermodynamics, be less than or equal to $\alpha+\beta$, where β is the exponent of the power law for the difference of the coexisting densities and α is the exponent of the power law for C_v. It has been proved [7] for an equation of state of the type proposed by M. S. Green et al. [4], that α must be equal to α_2. The present equation can also, but must not necessarily, imply the latter equality.

The divergence of $\frac{d\rho_m}{dT}$, where ρ_m is the rectilinear diameter, is a consequence of a model for the critical state, which has recently been proposed by Widom and Rowlinson [5]. This divergence is given by another power law,

$$\frac{d\rho_m}{dT} \sim (T_c - T)^{-\alpha_1}$$

with $\alpha_1 = \alpha$ (as derived by Widom). The same model yields a similar divergence of $\frac{d\rho_t}{dT}$, where ρ_t is the line of symmetry in the $C_v(P, T)$ surface where C_v is the specific heat at constant volume. A divergence of $\frac{d\rho_t}{dT}$ was incorporated in our original eq (1) in order to provide a similar divergence in all terms of that equation; since λ in that equation was not necessarily equal to 1, the corresponding α_1 was restricted to

$$\alpha_1 = 1 - \beta.$$

It was found, however, that a value of λ different from 1 does introduce a discontinuity across the critical isochore.

In order to test the conjectures on α_1 and α_2 made by M. S. Green et al. and Widom respectively, our original equation [1] was modified as follows:

$$P = P_s + B(\rho)(T - T_s) + A\rho(\rho - \rho_t)[(T + T_c - 2T_s)^{1+\mu} - (T_c - T_s)^{1+\mu}] \tag{2}$$

with

$$P_s = P_{s0} + P_{s1}T_s + P_{s2}(T_c - T_s)^{2-\alpha_2}, \tag{3}$$

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[1] Figures in brackets indicate the literature references at the end of this paper.

$$B(\rho) = P_{s1} + B_1(\rho - \rho_m)|\rho - \rho_m|^{\mu/\beta} + B_2 \ldots, \quad (4)$$

$$\rho_m = \rho_c + \rho_{m1}(T_c - T_s)^{1-\alpha_1}, \quad (5)$$

$$T_s = T_c - [C|\rho - \rho_m|]^{1/\beta} \quad (6)$$

and

$$\rho_t = \rho_c + \rho_{t0}(T - T_s)^{1-\alpha_1}. \quad (7)$$

It can be shown from eq (2) that the exponent, α, of the power law for C_v can be expressed in terms of μ and β as follows:

$$\alpha = 1 - (2\beta + \mu).$$

Several questions can now be formulated.

1. Is $\alpha = \alpha_1 = \alpha_2$?
2. Is ρ_{m1} equal to $-\rho_{t0}$?
3. Is there any $P\rho T$ range-dependence for the exponents β, γ, δ for the following power laws $\rho_e - \rho_g \sim (Y_c - T)^{\beta}$ (the indices l and g refer to liquid and gas),

$$\frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \sim |T_c - T|^{-\gamma}$$

(at saturation or at the critical isochore),

$$|\rho - \rho_c|_{T = T_c} \sim |P - P_c|_{\delta}.$$

4. How many terms are relevant in equation (6)?

Answers to these questions have been obtained by applying eq (2) to two substances for which excellent data is available, i.e., the data on helium by Roach [6] and the data on xenon by Habgood and Schneider [3]. As far as the latter data are concerned, a rather large difference was detected previously between the measurements on isochores and on isotherms [1]. The error (for version 2) with the isotherm data included amounted to 0.00311 atmospheres versus 0.00227 without. In the subsequent analysis only measurements on isochores have been considered.

3. Analysis and Results

Before estimating the $P\rho T$ range dependence of the critical point parameters, the ranges have to be defined. The choice of the ranges will always be more or less arbitrary. In this case the ranges are defined by confining the variables density, temperature and pressure within a selected percentage around the cirtical point parameters. The method of defining the various ranges is illustrated in figure 1. The actual ranges indicated by the cross hatching in figure 1 are given in table 1. A single significant parameter, N, the number of data points in the range, results from this limiting procedure; N will be taken as a quantitative measure of the range. In table 1 the boundaries are defined for each range and for each substance, and the corresponding number of data points in the range is given. Range No. 1 for helium extends farther than any other range, and for this range the number of coefficients, B, in eq (6) was varied in order to investigate their relevance.

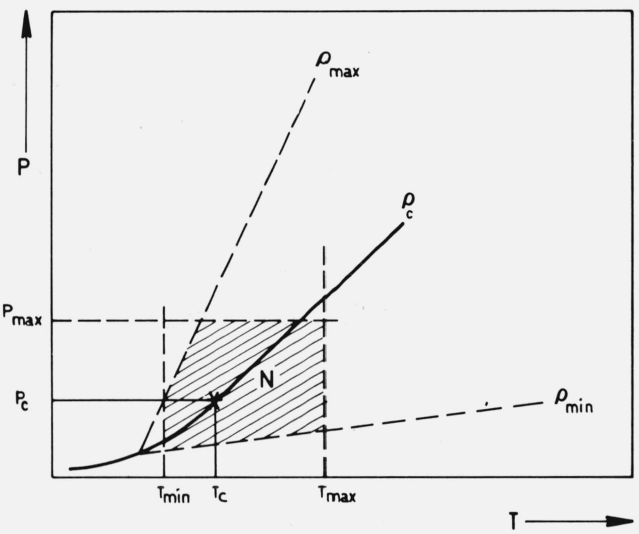

FIGURE 1. *Schematic* P–T *diagram showing boundaries of a "range" around the critical point.*

The variation of the error and the apparent values of the scaling exponents α, β, γ, and δ as a function of the number of coefficients in eq (6) is shown in figure 2. B_0 and B_1 were found to provide a satisfactory description for data of the given accuracy within the given range. Beyond these two constants, no dependence on the number of B's was found for α and γ and only a slight dependence for β and δ. Consequently in further calculations all other B-s have been assumed to be zero. Equation (2) can be applied on the data in two alternative versions; version 1 where α_1, α_2, ρ_{m1} and ρ_{t0} are independent adjustable

TABLE 1. *Boundaries of the different* PρT *ranges for xenon and helium and the number of data points left in each range*

No. of range	$\left(\frac{\lvert\rho_{max} - \rho_c\rvert}{\rho_c}\right)$	$\left(\frac{\lvert T_{max} - T_c\rvert}{T_c}\right)$	$\left(\frac{\lvert P_{max} - P_c\rvert}{P_c}\right)$	Number of data points, N	
				Xenon	Helium
1.....	0.50	0.05	0.08	173	414
2.....	.35	.035	.05		295
3.....	.30	.03	.05	142	
4.....	.10	.01	.02	114	

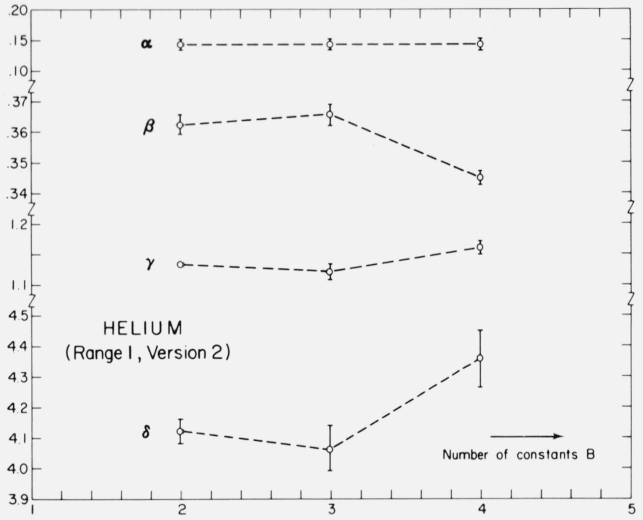

FIGURE 2. *α, β, γ and δ and their dependence on the number of B's in eq (2).*

parameters and version 2, where $\alpha_1 = \alpha_2 = 1 - (2\beta + \mu)$ and $\rho_{m1} = -\rho_{f0}$. The two versions are compared for helium and for xenon in table 2. The difference in the quality of fit between the two versions is not substantial, and therefore further speculations on the range dependence of the critical parameters have been carried out with version 2. The dependence of the critical exponents α, δ, γ and β on the range is illustrated in figure 3. The constants for range 1 and for version 2 of equation (2) are given for helium in table 3, and for xenon in table 4.

The estimation of the parameters has been carried out through an iterative procedure. Initial constants have been chosen and the equation has been linearized with respect to the deviations of the constants. These deviations were then calculated by the well known least-squares methods for the linear case.

The error analysis is carried out on the basis of the correlation matrix for the linear case. There may be some doubt whether this is entirely justified in the case of a nonlinear equation.

TABLE 2. *Comparison of the relevant parameters for the two versions of eq (2) and for helium and xenon*

Range No.	Parameter	Helium		Xenon	
		Version 1	Version 2	Version 1	Version 2
1	δ	4.28 ±0.09	4.16 ±0.06	4.45 ±0.14	4.39 ±0.101
	γ	1.128 ± .004	1.119 ± .003	1.232 ± .012	1.191 ± .006
	β	.343 ± .003	.353 ± .002	.356 ± .005	.351 ± .005
	α	.184 ± .008	.173 ± .006	.054 ± .020	.108 ± .014
	α_1	.270 ± .045	.173 ± .006	.287 ± .116	.108 ± .014
	α_2	.400 ± .026	.173 ± .006	.470 ± .045	.108 ± .014
	ρ_{f0}	−.00100 ± .00015	−.00132 ± .00015	−.0000417 ± .0000131	−.0000145 ± .000004
	ρ_{m1}	+.00208 ± .00022	$-\rho_{f0}$	+.0000453 ± .0000186	$-\rho_{f0}$
	$\sqrt{\frac{\Sigma \Delta P_i}{N-NC}}^{*}$ atm	0.00072	0.00074	0.00224	0.00227
2(He) and 3(Xe)	δ	4.24 ±0.24	4.13 ±0.08	3.73 ±0.76	4.72 ±0.39
	γ	1.137 ± .012	1.138 ± .009	1.178 ± .016	1.208 ± .012
	β	.351 ± .009	.363 ± .006	.430 ± .052	.324 ± .012
	α	.161 ± .023	.135 ± .015	−.039 ± .106	.142 ± .033
	α_1	.277 ± .286	.135 ± .015	−.149 ± .389	.142 ± .033
	α_2	.338 ± .124	.135 ± .015	.060 ±1.591	.142 ± .033
	ρ_{f0}	−.000314 ± .000439	+.00013 ± .0004	−.0000105 ± .0000070	−.0000251 ± .0000059
	ρ_{m_1}	+.00168 ± .00107	$-\rho_{f0}$	+.000228 ± .000057	$-\rho_{f0}$
	$\sqrt{\frac{\Sigma \Delta P_i}{N-NC}}^{*}$	0.00059	0.00059	0.00198	0.00203
4	δ				5.73 ±8.19
	γ				1.284 ± .074
	β				.271 ± .129
	α				.172 ± .283
	α_1				.172 ± .283
	α_2				.172 ± .283
	ρ_{f0}				+.0000171 ± .0000425
	ρ_{m1}				$-\rho_{f0}$
	$\sqrt{\frac{\Sigma \Delta P_i}{N-NC}}^{*}$				0.00209

*N is the number of data points; NC is the number of constants.

TABLE 3. *Constants for eq (2) applied to helium data* [6][a]

Constants of the equation			
Constant	Value	Error	The standard deviation is 0.00074
A	0.32043251E 04	0.10131254E 03	
P_{s1}	.17091894E 01	.19034584E−02	
B_1	.33758179E 03	.12381564 02	
P_{s2}	.72719432E 00	.34948345E−01	Maximum error in pressure is −0.0025 atm.
P_{s0}	−.66253524E 01	.98947437E 02	At $T=5.26370$ and
ρ_{t0}	−.13174329E−02	.15183463E−03	$P=2.40487$ atm.
$2-\alpha_2$	$=1+2\beta+\mu$		
C	0.74227144E 02	.45068578E 00	
ρ_c	.17232286E−01	.52370344E−05	
ρ_{m1}	$-\rho_{t0}$		
T_c	.51909878E 01	.27286947E−03	
β	.35366522E 00	.23593233E−02	
μ	.11915742E 00	.33542782E−02	
$1-\alpha_1$	$=2\beta+\mu$		
Derived Constants			
Constant	Value	Error	
α	0.17351214E 00	0.60508733E−02	
γ	.11191574E 01	.33542782E−02	
δ	.41644543E 01	.62999387E−01	

[a] The density range is 50, the temperature range is 5 and the pressure range is 8 percent around the critical point. The number of data points is 414.

TABLE 4. *Constants for eq (2) applied to xenon data* [3][a]

Constants of the equation			
Constant	Value	Error	The standard deviation is 0.00227.
A	0.94959356E 04	0.21903837E 03	
P_{s1}	.11860651E 01	.83952672E−03	
B_1	.13935997E 04	.53686691E 02	
P_{s2}	.15611421E−01	.23977382E−02	Maximum error in pressure is 0.0067 atm.
P_{s0}	−.28601355E 03	.24339522E 00	At $T=289.13990$ K and
ρ_{t0}	−.14547437E−04	.39990010E−05	$P=56.3430$ atm.
$2-\alpha_2$	$=1+2\beta+\mu$		
C	0.47872048E 03	.12869899E 01	
ρ_c	.84971537E−02	.39913666E−05	
ρ_{m1}	$-\rho_{t0}$		
T_c	.28976481E 03	.31386983E−02	
β	.350500350 00	.46079306E−02	
μ	.19110181E 00	.63731809E−02	
$1-\alpha_1$	$=2\beta+\mu$		
Derived Constants			
Constant	Value	Error	
α	0.10789750E 00	0.13966633E−01	
γ	.11911018E 01	.63731809E−02	
δ	.43982899E 01	.10541327E 00	

[a] The density range is 50, the temperature range is 5 and the pressure range is 8 percent around the critical point, the number of data points is 165.

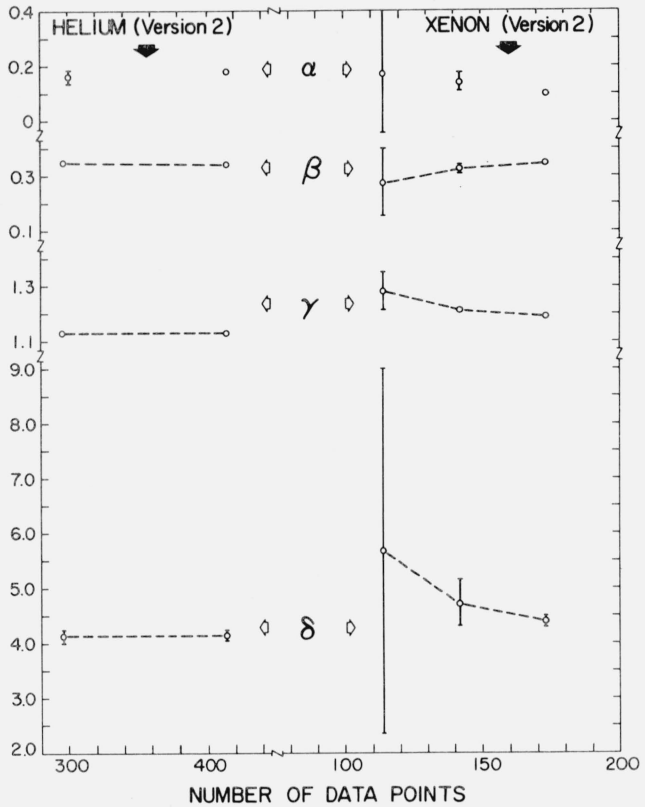

FIGURE 3. *α, β, γ and δ for helium and xenon and their dependence on the number of data points (error bars are indicated by the cross-hatched strips).*

4. Conclusions

Only qualitative conclusions can be drawn from table 2. The values obtained for α_1 and α_2, indeed, are consistent with the divergences as claimed by Widom and by Green et al. The values obtained, however, are larger than α. Furthermore the equality $\rho_{m1} = -\rho_{t0}$ seems to check out qualitatively. It should be emphasized however that the accuracy of the data, although being within the limits of the present state of the art, does not allow definite conclusions. The small differences obtained for α, β, γ, and δ in versions 1 and 2 and by other authors [7] could be explained by the fact that equations of this type can be very suggestive with respect to these values.

It should also be noted that the value for α obtained for helium is much higher than the values obtained in the past by other authors [7].

In a more recent analysis, however, higher values have been obtained [8]; other recent experiments on helium also suggest higher values for α (e.g., $\alpha = 0.14$ [9]).

It can be seen from the error bars in figure 3 that helium is the more likely candidate for interpretation of the resulting exponents:

The agreement between the exponents for the different ranges and for the different versions of the state equation for helium is almost within the error bars.

Noteworthy is the fact that α_1 tends to be higher ($\sim 0.3 \pm 0.1$) than α and that α_2 seems to be even higher (~ 0.45) for version 1 and for both helium and xenon.

We do not exclude the possibility that these values are suggested by version 1 but it is noteworthy that an α_2 equal to 0.45 is still lower than $\alpha + \beta$ ($0.15 + 0.355$). This value ($\alpha_2 = 0.45$) however, would imply a thermodynamic potential divergent at the critical point, a possibility which is doubted by many.

A weak point in eq (2) is the nonanalyticity introduced by the second term on the right side of eq (6) resulting in a divergent $\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T$ for ρ equal to ρ_m. This nonanalyticity can be avoided but we doubt that its influence on the critical parameters is important.

More difficult to avoid is the nonanalyticity introduced by the third term of eq (2). This nonanalyticity disappears when γ/β is an integer, say $\gamma/\beta \equiv 3$, for instance. This effect may have had the odd result of producing rather high values for α.

We are indebted to J. M. H. Levelt Sengers for stimulating discussions on this subject, and to V. Jansoone who suggested the error analysis. Most of of the calculations were performed on the CDC3800 computer, the use of which was granted by the Cryogenics Division of the National Bureau of Standards, Boulder, Colorado 80302. We are also indebted to the "Rekencentrum" of the University of Leuven, Belgium where part of the computations were performed.

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