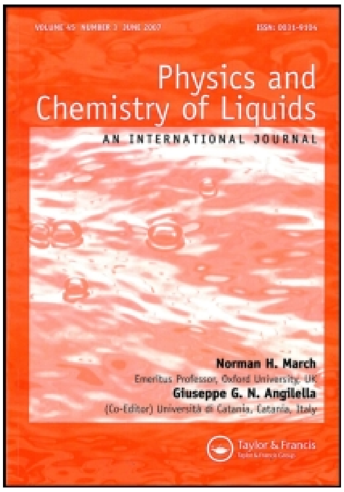
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Dieterici's Equation of State: An Almost Quantitative Modelling of some Critical Point Properties of Heavy Rare Gases

N. H. March[a]; M. P. Tosi[a]
[a] Istituto Nazionale di Fisica della Materia and Classe di Scienze, Pisa, Italy

To cite this Article March, N. H. and Tosi, M. P.(1999) 'Dieterici's Equation of State: An Almost Quantitative Modelling of some Critical Point Properties of Heavy Rare Gases', Physics and Chemistry of Liquids, 37: 4, 463 — 467
To link to this Article: DOI: 10.1080/00319109908031450
URL: http://dx.doi.org/10.1080/00319109908031450

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phys. Chem. Liq., 1999, Vol. 37, pp. 463–467
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Letter

DIETERICI'S EQUATION OF STATE: AN ALMOST QUANTITATIVE MODELLING OF SOME CRITICAL POINT PROPERTIES OF HEAVY RARE GASES

N. H. MARCH and M. P. TOSI*

Istituto Nazionale di Fisica della Materia and Classe di Scienze,
Scuola Normale Superiore, I-56126 Pisa, Italy

(Received 24 January 1998)

In recent work March, Perrot and Tosi have pointed out that the virial equation for the pressure, together with its first and second density derivatives, are constrained at the liquid–gas critical point of the heavier rare gases. Here it is demonstrated that Dieterici's equation of state allows an almost quantitative modelling of these constraints. Some related comments on structural theories are added.

Keywords: Equation of state at critical point

In recent work, March, Perrot and Tosi [1] have demonstrated an integral relationship at the critical point c in their study of the heavier condensed rare gases, Ar, Kr and Xe. This reads

$$2I_0 + 4I_1 + I_2 = \frac{\rho_c}{6k_B T_c}\int \left[2g(r)|_c + 4\rho_c \frac{\partial g(r)}{\partial \rho}\bigg|_c + \rho_c^2 \frac{\partial^2 g(r)}{\partial \rho^2}\bigg|_c \right] r\frac{d\phi(r)}{dr}\,d\mathbf{r} = 0, \tag{1}$$

with $g(r)$ the pair distribution function and $\phi(r)$ the (assumed) density-independent pair potential. They also stress that the compressibility

---

*Corresponding author.

ratio Z_c defined by

$$Z_c = \left.\frac{p}{\rho k_{\mathrm{B}} T}\right|_c \tag{2}$$

with p the pressure, ρ the number density and $k_{\mathrm{B}}T$ the thermal energy, has a value close to 0.29 for these three rare gases Ar, Kr and Xe.

We have subsequently noticed that, while we referred in [1] to the van der Waals equation of state, the Dieterici equation of state is much more realistic for the above problem near the critical point. Though Dieterici's equation of state is given some prominence in standard textbooks [2, 3], for completeness let us first outline its derivation and the consequences that flow from it.

Following, for example, Blinder [3], consider rare gas atoms in their container. Atoms near one of the walls will experience an asymmetric distribution of attractive forces, resulting in a reduction of the boundary-layer density ρ_{b} relative to the bulk density ρ. To estimate the influence of such interatomic forces on the equation of state, let us use the Boltzmann law

$$\rho(\mathbf{r}) \propto \exp[-V(\mathbf{r})/k_{\mathrm{B}}T] \tag{3}$$

where $V(\mathbf{r})$ denotes the potential energy of an atom at position $\mathbf{r}$. Let ε represent the average potential energy of an atom in the interior of the fluid, while ε_{b} is the corresponding quantity near the container walls. Neglecting other possible effects, the ratio ρ_{b} to ρ is

$$\frac{\rho_{\mathrm{b}}}{\rho} = \exp(-\Delta\varepsilon/k_{\mathrm{B}}T) \tag{4}$$

where $\Delta\varepsilon = \varepsilon_{\mathrm{b}} - \varepsilon > 0$, the inequality following from the fact that atoms tend to be pulled away from the walls. Introducing excluded volume effects as in the van der Waals equation of state, one is led rather directly from Eq. (4) to the Dieterici equation of state [4]:

$$p(\Omega - b)\exp\left(\frac{a}{k_{\mathrm{B}}T\Omega}\right) = k_{\mathrm{B}}T, \tag{5}$$

where $\Omega = 1/\rho$ is the atomic volume and $a \propto \Delta\varepsilon$. If it is valid to expand the exponential to first-order only, then the van der Waals equation can be recovered by only inessential approximations. However, we stress below that, to model the heavier rare gases, it is very important to retain the exponential form in the equation of state (5).

Then, by standard calculation, the critical constants can be derived from Eq. (5) as [2, 3]

$$\Omega_c = 1/\rho_c = 2b, \tag{6}$$

$$k_{\rm B}T_c = a/4b \tag{7}$$

and

$$p_c = a/4e^2b^2. \tag{8}$$

Returning to Eq. (2) one finds

$$Z_c = 2/e^2 \cong 0.27 \tag{9}$$

whereas the van der Waals value is $Z_c = 3/8 = 0.375$. Equation (9) is indeed remarkably close to the experimental value $Z_c \cong 0.29$ for the heavier condensed rare gases.

Using the results of Ref. [1], where three structural integrals were defined at the critical point, namely I_n, $n = 0$, 1 and 2,

$$I_0 = 1 - Z_c = 0.73, \tag{10}$$

$$I_1 = 2Z_c - 1 = -0.46 \tag{11}$$

and

$$I_2 = 2 - 6Z_c = 0.38. \tag{12}$$

Evidently, the error in Z_c is most magnified in estimating I_2.

Using the value in Eq. (10) the virial structural integral can thus be modelled as

$$\int g(r) r \frac{d\phi(r)}{dr} d\mathbf{r} = \frac{k_{\rm B}T_c}{\rho_c} I_0 = \frac{a}{2} I_0, \tag{13}$$

showing that the excluded-volume parameter b goes out. This is physically satisfactory because, as was already known to Ornstein and

Zernike, the total pair correlation function $h(r) = [g(r) - 1]$ becomes very long-range as the critical point is approached. Indeed, modern critical point theory shows that $h(r)|_c \propto r^{-(1+\eta)}$ where the critical exponent $\eta \ll 1$ [4, 5]. Similar expressions can be written for the structural integrals involved in I_1 and I_2 as defined in Ref. [1].

To conclude this Letter, we wish to add some related comments on structural theories of liquids. Equation (1) makes it tempting to write, as the critical point is approached:

$$2g(r) + 4\rho\frac{\partial g(r)}{\partial \rho} + \rho^2\frac{\partial^2 g(r)}{\partial \rho^2} = \Delta \tag{14}$$

where Δ tends to zero at the critical point itself. The motivation for modelling the density dependence of $g(r)$ according to Eq. (14) is that, for reasons given above, we expect the attractive part of the force law $-d\phi(r)/dr$ to dominate the physics at or near the critical point.

While Eq. (14) may seem surprising in its shape, let us conclude by mentioning two of the available structural theories of fluids: (i) the hypernetted-chain (HNC) approximation and (ii) the Born-Green equation. As to (i), the unmodified HNC equation (*i.e.*, with the so-called bridge function put equal to zero [6]) reads

$$\ln g(r) = -\frac{\phi(r)}{k_B T} + h(r) - c(r) \tag{15}$$

and hence, for the case of a density-independent pair potential as treated in Ref. [1] we have

$$\frac{g(r) - 1}{g(r)}\frac{\partial g(r)}{\partial \rho} = \frac{\partial c(r)}{\partial \rho}. \tag{16}$$

Equation (16) is more complicated than Eq. (14) as $\Delta \to 0$, because it involves the Ornstein-Zernike convolution relating $h(r)$ and $c(r)$. But we stress that there is some similarity of shape.

Turning finally to the Born-Green equation for liquid structure, this has some aspects of a theory valid at the critical point [7]. However, the compressibility ratio $Z_c = 1/2$ [8], and this is so far from our main interest, the heavier rare gases, that we shall not pursue the detail.

Acknowledgements

One of us (N.H.M.) wishes to thank the Scuola Normale Superiore for its generous hospitality during his visit, in which his contribution to this work was brought to fruition.

References

[1] March, N. H., Perrot, F. and Tosi, M. P. (1998). *Molec. Phys.*, **93**, 355.
[2] Guggenheim, E. A. (1949). Thermodynamics (North-Holland: Amsterdam).
[3] Blinder, S. M. (1969). Advanced Physical Chemistry (Macmillan: Toronto).
[4] Fisher, M. E. (1964). *J. Math. Phys.*, **5**, 944.
[5] Fisher, M. E. (1967). *Repts Progr. Phys.*, **30**, 615.
[6] See, for example, March, N. H. (1990). Chemical Physics of Liquids (Gordon and Breach: New York).
[7] Green, K. A., Luks, K. D. and Kozak, J. J. (1979). *Phys. Rev. Lett.*, **42**, 985.
[8] See, for instance, Kumar, N., March, N. H. and Wasserman, A. (1982). *Phys. Chem. Liquids*, **11**, 271.