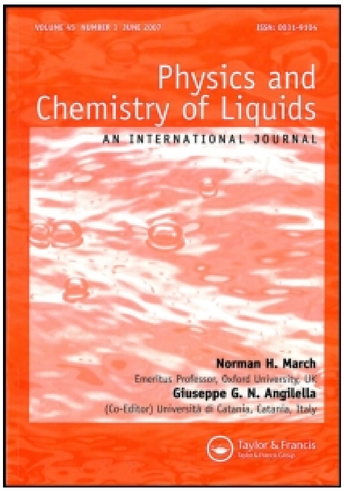

Physics and Chemistry of Liquids

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

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To cite this Article Kumar, N. , March, N. H. and Wasserman, A.(1982) 'Critical-point Properties of Liquids and the Born-Green Theory', Physics and Chemistry of Liquids, 11: 3, 271 — 275
To link to this Article: DOI: 10.1080/00319108208080749
URL: http://dx.doi.org/10.1080/00319108208080749

Phys. Chem. Liq., 1982, Vol. 11, pp. 271–275
0031-9104/82/1103-0271$06.50/0

Printed in the U.S.A.

Letter

Critical-point Properties of Liquids and the Born–Green Theory

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(*Received August 11, 1981*)

Recent work of Jones *et al.* giving the long-range behaviour of the pair correlation function is used to confirm that the critical ratio $P_c/n_c k_B T_c = \frac{1}{2}$ in the Born–Green theory. This deviates from experimental results on simple insulating liquids by more than the predictions of the van der Waals equation of state. A brief discussion of conditions for thermodynamic consistency, which the Born–Green theory violates, is then given. Finally, the approach of the Ornstein–Zernike correlation function to its critical point behaviour is discussed within the Born–Green theory.

Recent work on the Born–Green equation for fluids at or near the critical point[1–3] prompts us to record the P–V–T relation at $T = T_c$, the critical temperature, from this approximate theory, together with results on the approach of the pair correlation function and the Ornstein–Zernike function to their critical point forms.

Our argument starts from the Rushbrooke form of the Born–Green equation[4]

$$\frac{1}{k_B T}(\phi(r) - U(r)) = n \int d\mathbf{s} h(s) E(|\mathbf{s} - \mathbf{r}|). \tag{1}$$

Here $\phi(r)$ is the pair potential, $U(r, T)$ is the potential of mean force related to the pair function $g(r)$ by

$$g(r) = \exp\left(-\frac{U}{k_B T}\right) \tag{2}$$

while $h(r)$ is the total correlation function $g(r) - 1$. As Gaskell[5] has shown, Eq. (1) can be solved in Fourier transform to read, with $\tilde{v}(k)$ the Fourier transform of $1/k_B T(\phi(r) - U(r))$

$$\tilde{v}(k) = \tilde{h}(k)\tilde{E}(k) \tag{3}$$

where

$$\tilde{E}(k) = \frac{n}{k_B T}\int d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) \int_r^\infty ds\, g(s) \frac{d}{ds}\phi(s) \tag{4}$$

is the Fourier transform of $E(r)$ in Eq. (1). Gaskell[5] has then proved that if P is the fluid pressure as given by the virial theorem, namely

$$\frac{P}{nk_B T} = 1 - \frac{n}{6k_B T}\int d\mathbf{r}\, rg(r)\frac{d}{dr}\phi(r) \equiv 1 - nI, \tag{5}$$

n being the mean density, then

$$\hat{E}(0) = 2\left(1 - \frac{P}{nk_B T}\right). \tag{6}$$

We now combine the above results with the work of Jones *et al.*[3] actually at the critical point characterized by P_c, n_c and T_c. These workers show from the Born–Green theory that $h(r)$ has the long-range behaviour

$$h(r) = \frac{D_0}{r^2}. \tag{7}$$

Substituted into Eq. (2), this leads, for $U(r)/k_B T_c \ll 1$, to

$$g(r) = 1 - \frac{U}{k_B T_c} = 1 + \frac{D_0}{r^2}. \tag{8}$$

Taking the Fourier transform of $U(r)$ in Eq. (8) evidently leads to the small k form of $U(k)$ as

$$\tilde{U}(k) = \text{const}/k + \cdots \tag{9}$$

and hence, provided $\phi(r)$ falls off more rapidly than $1/r^2$

$$\tilde{v}(k) = \text{const}/k + \cdots. \tag{10}$$

But evidently, from Eq. (8), $h(r) \simeq -U/k_B T_c$ and therefore

$$\tilde{h}(k) = \tilde{v}(k) \text{ at } T_c \text{ as } k \text{ tends to zero.} \tag{11}$$

It follows from Eqs. (3) and (11) that

$$\tilde{E}_{T_c}(0) = 1 \tag{12}$$

and hence from Eq. (6) that

$$P_c/n_c k_B T_c \equiv R = \tfrac{1}{2}, \tag{13}$$

a result noted also by Fisher.[6]

The above critical ratio R is to be compared with the well-known results for the same ratio of $\frac{3}{8}$ and $2e^{-2}$ from van der Waals and Dieterici's equations of state respectively. As discussed, for example, by Guggenheim,[7] even $\frac{3}{8}$ is too large for simple insulating fluids, Dieterici's value being in distinctly better accord with experiment.

To understand further the reasons for the above limitation of the Born–Green theory, based on the Kirkwood factorization of the three-particle correlation function into the product of pair terms, it will be useful to place it in the context of an exact expansion on the critical isotherm T_c for a fluid with a density independent pair potential. In terms of $I(n, T_c)$ defined through Eq. (5), it is straightforward to show that I has the explicit expansion

$$n_c I(n, T_c) = (1 - R) + \frac{(n - n_c)}{n_c}\left[2R - 1 - \frac{1}{k_B T_c}\left(\frac{\partial P}{\partial n}\right)_{n_c, T_c}\right] + \frac{(n - n_c)^2}{n_c^2}\left[1 - 3R + \frac{2}{k_B T_c}\left(\frac{\partial P}{\partial n}\right)_{n_c, T_c} - \frac{n_c}{2k_B T_c}\left(\frac{\partial^2 P}{\partial n^2}\right)_{n_c, T_c}\right] + \cdots . \tag{14}$$

Evidently in an exact theory $(\partial P/\partial n)_{n_c, T_c} = (\partial^2 P/\partial n^2)_{n_c, T_c} = 0$ and these derivatives drop out from Eq. (14). But as discussed in Eq. (15) below, thermodynamic inconsistency means that these derivatives do not vanish in the Born–Green theory. Thus although in the term $\propto (n - n_c)$ in Eq. (14) $2R - 1 = 0$ from Eq. (13) in the Born–Green theory, the term does not go to zero because of the non-zero contribution from $(\partial P/\partial n)_{n_c, T_c}$. To develop the above point, we note next the exact relations for the compressibility, namely

$$n\frac{\partial P}{\partial n} = nk_B T\left(1 - n\int c(r)\, d\mathbf{r}\right) = 2P - nk_B T - k_B T n^3 \frac{\partial I}{\partial n}, \tag{15}$$

the last part of Eq. (15) following by differentiation of Eq. (5) with respect to n. In the first part of Eq. (15), $c(r)$ is the Ornstein–Zernike direct correlation function. In the Born–Green theory, the critical point corresponds to

$$\left(1 - n\int c(r)\, d\mathbf{r}\right) = 0,$$

but thermodynamic inconsistency leads to the violation of Eq. (15), with $(\partial P/\partial n)_{n_c, T_c} \neq 0$, as discussed above. In this context, it is of interest to note at this point that a sufficient condition for thermodynamic consistency can be obtained by substituting P in Eq. (15) from Eq. (5) to obtain

$$-n\int c(r)\,d\mathbf{r} = -\frac{\partial}{\partial n}\left[\int d\mathbf{r}\, rg\frac{d\phi}{dr}\frac{n^2}{6k_BT}\right] \tag{16}$$

or

$$-r^2c(r)n = \phi(r)\frac{\partial^2}{\partial n\,\partial r}\left[\frac{gr^3n^2}{6k_BT}\right] + F(r, n, T) \tag{17}$$

where the function F must satisfy

$$\int_0^\infty F\,dr = 0. \tag{18}$$

Returning to the necessary condition for thermodynamic consistency in Eq. (16) we use the definition of $E(r)$ in Eq. (4) to find

$$\frac{dE(r)}{dr} = -\frac{1}{k_BT}g(r)\frac{d\phi(r)}{dr} \tag{19}$$

and hence

$$n\int c(r)\,d\mathbf{r} = -\frac{\partial}{\partial n}\left[\frac{n^2}{6}\int_0^\infty 4\pi r^3\frac{dE}{dr}\,dr\right] = \frac{1}{2}\frac{\partial}{\partial n}(n\tilde{E}(0)). \tag{20}$$

The last step in Eq. (20) follows by an integration by parts plus the condition that r^3E vanishes at the limits 0 and ∞. In general, when $g(r)$ and hence $c(r)$ and $E(r)$, are calculated in the Born–Green approximation embodied in Eq. (1), Eq. (20) will not be satisfied.

In spite of the severe limitations imposed by its thermodynamic inconsistency, the current interest[1–3] in the Born–Green predictions prompts us to return finally to the critical point correlation functions. We note that the compressibility formula for the pressure in the first part of Eq. (15) leads from Eqs. (10) and (11), plus the fact that the structure factor $S(k)$ at $k = 0$ is infinite at the critical point, to the conclusion that, at long wavelengths,

$$c(k) = 1 + \text{const}\,k + \cdots \tag{21}$$

and hence in r space $c(r)$ has the large r dependence proportional to r^{-4}. This leads to a further comment. In the customary linear Ornstein–Zernike theory of the approach to the critical point, one has

$$\nabla^2 h = \frac{h}{\xi^2} \tag{22}$$

where the correlation length ξ is given by

$$\xi^2 = \frac{c_2S(0)}{6}, \tag{23}$$

c_2 being the second moment of $c(r)$, namely $c_2 = \int r^2 c(r)\, d\mathbf{r}$. Evidently, with $c(r)$ at the critical point having the asymptotic decay as r^{-4} pointed out above, in the Born–Green theory c_2 diverges as T tends to T_c. If we write therefore, in the customary notation

$$\xi \propto (T - T_c)^{-\nu}, S(0) \propto (T - T_c)^{-\gamma}, c_2 \propto (T - T_c)^{-\Gamma} \tag{24}$$

then from Eq. (23) it follows that

$$\Gamma = 2\nu - \gamma. \tag{25}$$

Thus if $2\nu > \gamma$, the second moment diverges at T_c. With $c(r) \approx \text{const}\ r^{-4}$ at $T = T_c$ then $c_2 \propto \int^{\xi} r^0\, dr \propto \xi$ and comparison with Eqs. (23) and (24) yields

$$\Gamma = \nu = \gamma. \tag{26}$$

All this is consistent with the work of Stell[8] who, by quite different arguments, obtains at small k

$$c(k) = 1 + \text{const}\ k^{\gamma/\nu} + \cdots . \tag{27}$$

We note that the value $\gamma = 1.23 \pm 0.02$ has been found from numerical solution of the Born–Green equation for the square well fluid by Green *et al.*[2]

Acknowledgements

One of us (NHM) acknowledges valuable discussions with Professor J. W. Essam at an early stage of this work. Two of us (NK and NHM) wish to thank the International Centre for Theoretical Physics, Miramare, Italy, for providing facilities for this work to be carried out during a research workshop in condensed matter theory.

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