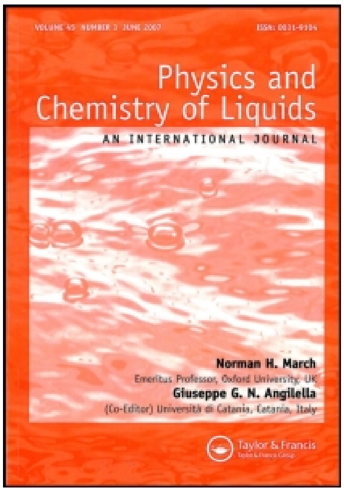

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Structural Theory of The Liquid-Gas Critical Point

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To cite this Article March, N. H.(1993) 'Structural Theory of The Liquid-Gas Critical Point', Physics and Chemistry of Liquids, 25: 4, 269 — 272
To link to this Article: DOI: 10.1080/00319109308030366
URL: http://dx.doi.org/10.1080/00319109308030366

Phys. Chem. Liq., 1993, Vol. 25, pp. 269–272
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LETTER

Structural Theory of The Liquid-Gas Critical Point

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(Received 9 July 1992)

Recent work on the liquid-gas critical point by Zhang and Badiali invokes the Callan-Symanzik equation from renormalisation group theory. The relation of this approach to structural theory, based on a form of the three-atom correlation function near the critical point is discussed. Some further knowledge of this function can be gained by invoking the $\varepsilon = 4 - D$ expansion, where D is the dimensionality.

KEY WORDS: Force equation, direct correlation function

Though the renormalization group technique has considerably aided our understanding of critical behaviour, a major problem which remains for the liquid-gas critical point is to relate critical behaviour to liquid structure theories.

An early important step in the latter context was taken by Choy and Mayer[1], who proposed to used the BBGKY hierarchy of equations of liquid-state structural theory. Though their work was certainly illuminating, the approximations to which they ultimately had recourse led them back to what was, essentially, the original Ornstein-Zernike (OZ) theory[2]. Experiment amply demonstrates the need to transcend this treatment[3].

Further work with related aims is that of Reatto and his co-workers[4,5]. These workers took the next step towards a final solution by attempting to combine the liquid-state hierarchical equations with the ideas of renormalization group theory. Very recently, Zhang and Badiali[6] have extended this work considerably, but their explicit results beyond OZ theory were obtained by working only to lowest order in the $\varepsilon(=4-D$, with D the dimensionality) expansion.

In Ref 6, a formal separation of the OZ direct correlation function (DCF) into a short plus a long range part was invoked; the first point in this Letter is to propose a completely defined separation of this kind, using the earlier work of Kumar *et al.*[7–9]. Defining the OZ DCF from the pair function $g(r) = 1 + h(r)$ by

$$h(r) = c(r) + \rho \int h(r')c|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}' \tag{1}$$

then in Ref 7 one starts from the relation

$$\left(\frac{\partial p}{\partial \rho}\right)_T = k_B T(1 - \tilde{c}(0)): \tilde{c}(0) = \rho \int c(r) d\mathbf{r}. \tag{2}$$

Kumar *et al.* then compared this with the result obtained by differentiating the virial expression for the pressure p, namely

$$p = \rho k_B T - \frac{\rho^2}{6} \int g(r) r \frac{\partial \phi(r)}{\partial r} d\mathbf{r}, \tag{3}$$

where $\phi(r)$ is the (assumed) pair potential, with respect to the fluid number density. These workers were then led, rather directly, to the result that the OZ DCF $c(r)$ can be written as the sum of two contributions:

$$c(r) = c_{\text{potential}}(r) + c_{\text{cooperative}}(r) = c_p(r) + c_c(r). \tag{4}$$

Most significant in the present context is the explicit expression they gave for $c_p(r)$:

$$c_p(r) = -\frac{\phi(r)}{k_B T}\left[\frac{A(r)}{2} + \frac{1}{6} r \frac{\partial A}{\partial r}\right]. \tag{5}$$

In this Eq. (5), we have now introduced the function $A(r)$, defined by

$$A(r) = 2g(r) + \rho \frac{\partial g(r)}{\partial \rho} \tag{6}$$

as this function will also play a key role in determining three-particle correlations as the critical point is approached. What is additionally interesting about the explicit separation above is that

$$\int c_p(r) d\mathbf{r} = \int c(r) d\mathbf{r}; \quad \text{i.e.} \int c_c(r) d\mathbf{r} = 0. \tag{7}$$

Having referred already to three-particle correlations above, it is natural to turn next to the so-called "force equation" which is the second member of the BBGKY hierarchy. This is the place where closure is normally applied, via an ansatz for the triplet correlation function $g^{(3)}$, which is related to $\phi(r)$ and $g(r)$ via this force equation.

At the critical point itself, Fisher[10] has given the form of the first two "partial wave" terms $g_l^{(3)}(r, R)$, as[11]

$$g_0^{(3)}(\mathbf{r}, R) = g(r) + A(r)(g(R) - 1) + \text{higher order terms} \tag{8}$$

and

$$g_1^{(3)}(\mathbf{r}, R) = \frac{1}{2}\, rA(r)\, \frac{dg(R)}{dR} + \cdots \tag{9}$$

The second result (9) is the only part of $g^{(3)}$ which enters the force equation in practice.

Whereas Eqs. (8) and (9) are valid at the critical point itself, Senatore and March[11] have considered the approach to the critical point by relating Eqs. (8) and (9) to the later ansatz of Jones[12]. However, his Eq. (5) for $g^{(3)}$ contained an undetermined function $a(r)$ and an unspecified constant b (related by Jones though to the critical exponent η; see below). Utilizing Eqs. (8) and (9), Senatore and March[11] have partially specified the function $a(r)$ as

$$a(r) = A(r) + \frac{R(r)}{S(0)} + \text{higher order terms} \tag{10}$$

where $R(r)$ is a regular function of r. Evidently $a(r)$ becomes equal to $A(r)$ actually at the critical point since the long wavelength limit $S(0)$ of the fluid structure factor $S(k)$ diverges there.

With regard to the constant b in Jones' work, it is highly relevant to note that in the recent work of Zhang and Badiali[6] the Callan–Symanzik equation is invoked. If we consider this as an equation for the "long-range" component, $\Gamma^L(k)$ say, of the two-point vertex function, then the long-range part of the total correlation function $h(r)$, but now in k space, say $h^L(k)$, is related to the vertex function by

$$h^L(k)\Gamma^L(k) = 1. \tag{11}$$

Then the Callan–Symanzik equation leads to

$$\Gamma^L(k) \sim k^{2-\eta}; \qquad k \to 0 \tag{12}$$

with η the usual critical exponent characterizing the critical point behaviour of the pair function. To lowest order in the ε expansion, $\eta = \varepsilon^2/54$, and this result can be utilized directly, in conjunction with the ansatz of Jones[12], to get

$$b = -\frac{\varepsilon^2}{324} + \text{higher order terms} \tag{13}$$

In summary, the present Letter, motivated by Ref. 6, has in addition to making the separation of $c(r)$ into two parts quite precise, three other aims:

(i) To note that, whereas customary liquid-state procedures make an ansatz on $g^{(3)}$ in the force equation to close the BBGKY hierarchy, Zhang and Badiali do this by invoking the Callan-Symanzik equation.

(ii) To get b in Jones' ansatz for $g^{(3)}$, using point (i) above with η given by $\varepsilon^2/54$ to find b as in Eq. (13).

(iii) To emphasize, following Senatore and March[11], that Jones' ansatz, with unspecified function $a(r)$ as well as b above has the structural shape exhibited in Eq. (10).

This leads into the final, and now speculative, comment. As noted again by Senatore and March[11], the form (10) leads to a connection between the correlation length ξ and the compressibility, of the form

$$\frac{1}{\xi^2} = \frac{1}{k_B T}\frac{\partial p}{\partial \rho}\frac{(1-e)}{C_2}; \qquad C_2 = \frac{\pi}{15}\frac{\rho}{k_B T}\int_0^{r_0} \frac{\partial \phi(r)}{\partial r}\, a(r) r^5 dr \tag{14}$$

where r_0 is the (assumed) finite range of $\phi(r)$. Here the presence of e in Eq. (14) arises from the regular function $R(r)$ in Eq. (10). But Zhang and Badiali[6] have shown that (a) the three-body direct correlation function $c^{(3)}$ is important in characterizing critical behaviour and (b) that the fully integrated $c^{(3)}$ tends, in their normalization, to -1 at the critical point. As Senatore and March note, if $(1-e)$ tends to zero as the critical point is approached, then the modification introduced by $R(r)$ in Eq. (10) leads to a compressibility diverging less rapidly than the square of ξ, which is the qualitatively correct behaviour. Therefore, our conjecture is that $R(r)$, and hence e, are intimately related to integrals on $c^{(3)}$, or equivalently to the density derivative of $c(r)$, since

$$\frac{\partial c(r)}{\partial \rho} = \int c^{(3)}(\mathbf{r}, \mathbf{r}')d\mathbf{r}'. \tag{15}$$

Already, this relation (15) has been employed in liquid structural theory by Barrat *et al.*[13], as an alternative approximate closure by decoupling $c^{(3)}$; a procedure which they have utilized successfully, however, near the triple rather than the critical point.

Acknowledgements

It is a pleasure to acknowledge that this work was done during a period spent at the Research Workshop in Condensed Matter at ICTP Trieste in 1992.

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