Note

Baxter Solution to the O-Z Equation
near the Critical Point

The pair distribution function, $g(r)$, and the interparticle pair potential, $u(r)$, permit the equilibrium properties of homogeneous classic liquids to be described. To obtain $g(r)$ some different procedures can be used and one of them, the most frequently used, is to solve the Ornstein–Zernike, O-Z, equation

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

where $h(r) = g(r) - 1$ is the total correlation function, $c(r)$ is the direct correlation function, and ρ is the density number.

To solve Eq. (1) a second equation is needed which relates $h(r)$, $g(r)$, and $c(r)$ to the potential $u(r)$ and temperature $\beta = (k_B T)^{-1}$, where k_B is the Boltzmann constant. This second equation can be obtained in several ways using different approximations to the density expansion of $g(r)$ such as:

$$c(r) = g(r)[1 - \exp(\beta u(r)] \tag{2a}$$

$$g(r) = \exp[-\beta u(r) + h(r) - c(r)] \tag{2b}$$

$$g(r) = \exp[-\beta u(r) + h(r) - c(r) + E(r)], \tag{2c}$$

where (2a) is the Percus–Yevic equation, P-Y, (2b) is the hypernetted-chain equation, HNC, and (2c) is the modified hypernetted-chain equation, MHNC, when a model form for the bridge function $E(r)$ is used and a constrain of thermodynamic consistency is enforced. $E(r)$ is the so-called bridge function because it takes into account the sum of the elemental diagrams, or bridges, in the diagrammatic analysis of the two-point function [1].

For realistic potentials, an iterative numerical procedure is used to solve the O-Z equation with Eqs. (2a), (2b), or (2c). In those cases one usually uses $c(r)$ and $H(r) = h(r) - c(r)$, and Eq. (1) becomes (with the tilde denoting Fourier transform)

$$\tilde{H}(k) = \rho \tilde{c}^2(k)/(1 - \rho \tilde{c}(k)) \tag{3a}$$

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and the iterative cycle used is

$$H_{i-1}(r) \rightarrow c_i(r) \rightarrow \tilde{c}_i(r) \rightarrow \tilde{H}_i(k) \rightarrow H_i(r). \tag{3b}$$

For the correlation functions in liquid, an algorithm [2] has been proposed to obtain the direct and inverse Fourier transform:

$$\tilde{f}(k_j) = \frac{4\pi}{k_j} \sum_{i=1}^{N-1} \Delta r \, r_i \sin(k_j r_i) f(r_i) \tag{4a}$$

$$f(r_i) = (2\pi^2 r_i)^{-1} \sum_{j=1}^{N-1} \Delta k \, k_j \sin(k_j r_i) \tilde{f}(k_j), \tag{4b}$$

where $\Delta r = R/N$, $\Delta k = \pi/R$, $r_i = i \, \Delta r$, $k_j = j \, \Delta k$, R is a distance which makes $f(r) \simeq 0$ for $r > R$, and N is the number of points considered in the interval $(0, R)$.

This procedure has been used in the calculation of simple liquid properties in the neighbourhood of the critical point, since the critical density ρ_c and critical temperature T_c can be obtained by minimization of the inverse isothermal compressibility, defined as

$$\chi^{-1} = \frac{1}{k_B T}\left(\frac{\partial p}{\partial \rho}\right)_T = 1 - 4\pi\rho \int_0^\infty dr \, r^2 c(r) \tag{5}$$

and from the numerical point of view, χ^{-1} can be calculated as

$$\chi^{-1} = 1 - 4\pi\rho \left[\sum_{j=1}^N \Delta r \, r_j^2 c(r_j) - \int_R^\infty dr \, r^2 c(r) \right], \tag{6}$$

where the integral in (r, ∞) is calculated using either some approximations [3] about the asymptotic behaviour of $c(r)$, or taking $c(r) = 0$ for relatively large values of R[4].

To carry out the Fourier transform, the step size in the k space is $\Delta k = \pi/R$ and the values used until now [3, 4] have been from $\Delta k = \pi/5\sigma = 0.63\sigma^{-1}$ up to $\Delta k = \pi/160\sigma = 0.02\sigma^{-1}$. From the numerical point of view it means that the algorithm does not depend on what $\tilde{H}(k)$ is for $k < \Delta k$. The basic O-Z contribution to the criticality appears in the integrand $k\tilde{H}(k)$ for $k \leqslant \zeta^{-1}$, where ζ is the correlation length, so that, if $\zeta > R$ the algorithm does not take account of the increase of the correlation in a self-consistent manner. This implies that the calculation, in the neighbourhood of the critical point, is limited by $\zeta \simeq R$, so the accuracy in obtaining ρ_c and T_c will decrease and the calculations of the critical exponents will be difficult to do. This could be the explanation of the non-physical abrupt decay of $\mathrm{Ln}[rh(r)]$ near R, shown in Fig. 1 in Ref. [5], and consequently one cannot be sure of good asymptotic behaviour of the net correlation function if it is obtained by means of the O-Z expression in the critical zone, i.e., $h(r) \sim \exp(-r/\zeta)/r$.
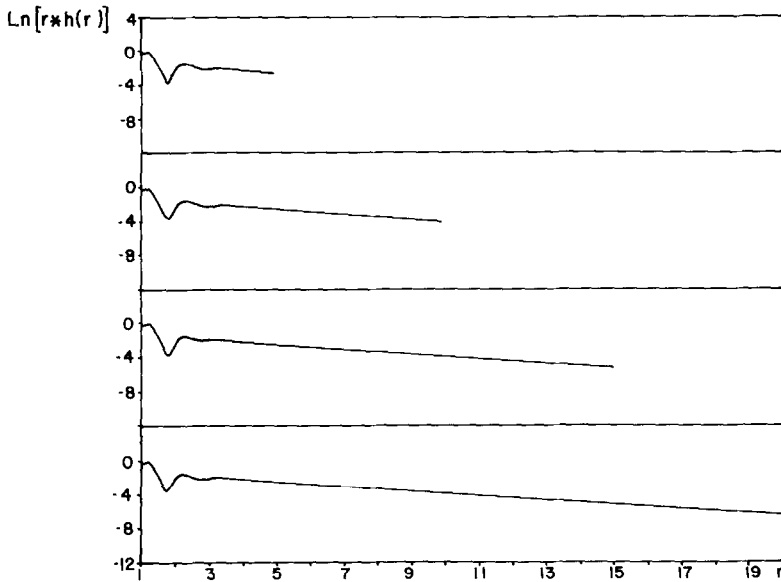
FIG. 1. Plot of $Ln[rh(r)]$ obtained using the numerical method described in Ref. [6]. The thermodynamic conditions are $kT/\varepsilon = 1.3195$ and $\rho\sigma^{-3} = 0.225$, where ε and δ are the parameters of the Lennard–Jones potential. The distances are measured in units of σ.

An alternative solution to the O-Z equation, when $c(r) = 0$ for $r > R$, has been proposed by Baxter [6], who found

$$rc(r) = -Q'(r) + 2\pi\rho \int_r^R dt\, Q'(b)\, Q(t-r) \qquad (7a)$$

$$rh(r) = -Q'(r) + 2\pi\rho \int_0^R dt(r-t)\, h(|r-t|)\, Q(t), \qquad (7b)$$

where $Q(r)$ is a real function and $Q'(r)$ its derivative. These equations, using any of the approximate equations (2a)–(2c), allow one to find $h(r)$ values without using the approximation of the Fourier transforms.

We have solved Eqs. (7a) and (7b), with the P-Y equation (Eq. (2a)), by an iterative numerical procedure which uses the Simpson rule and a weight factor to give adequate mixing of the input function of the iteration i, Q_i^{in}, with the output function, Q_i^{out}. The iteration process is continued until the value [7]

$$\int (Q'^{out}(r) - Q'^{in}(r))\, dr < 10^{-3} \qquad (8)$$

is reached, which satisfies the convergence condition on the thermodynamic properties, used in the Fourier transform procedure [3].

As Eqs. (7a) and (7b) require $c(r) = 0$, for $r > R$, we have used the Lennard–Jones (12-6) potential, $u_{LJ}(r)$, modified according to the suggestions of Nicolas *et al.* [8], giving the so-called shifted-force potential defined as

$$u(r) = u_{LJ}(r) + 48(R^{-13} - 0.5R^{-7})\, r + 28R^{-6} - 52R^{-12} \qquad (9a)$$

with the properties

$$u(R) = 0 \qquad (9b)$$

$$\left.\frac{du(r)}{dr}\right|_{r=R} = 0. \qquad (9c)$$

We have taken different values of R ($R = 5\sigma$, 10σ, 15σ, and 20σ) with the same increment interval of $\Delta r = 0.0125$ for all the calculations.

This numerical approach is similar to that employed by Watts [9] using another of Baxter's equations, obtainable by eliminating the auxiliary function $Q(r)$ from Eqs. (7a) and (7b). He used a truncated Lennard–Jones potential and three values of the range parameter ($R = 3.5\sigma$, 5σ, and 6σ) and found a strong sensitivity to R in the critical temperature computed, but a relative insensitivity to the critical density.

In order to test the behaviour in the critical zone we have repeated the same thermodynamic conditions as in Ref. [5]; i.e., $k_B T/\varepsilon = 1.3195$ and $\rho \sigma^3 = 0.225$, which is a state point very close to the critical points shown in Table I, corresponding to Ref. [10].

In Fig. 1, $\mathrm{Ln}[rh(r)]$ is plotted versus r and one can see in the figure how the linear behaviour is maintained from distances of $r > 3\sigma$ up to the range of the potential R, independently of the R value. The non-physical decay for $r \simeq R$ is not found in any of the cases.

From these results we can conclude that at points neighbouring the critical point, the behaviour of the O-Z equation is obtained independently of the interparticle pair potential and its range. Thus the procedure described above seems to give the most suitable results for calculating the equilibrium properties in liquids in the critical region, since there are no limitations in determining the critical point and, consequently, the critical exponents.

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