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RESEARCH NOTE

Absence of criticality in the reference hypernetted chain equation for short ranged potentials

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In this note the reference hypernetted chain equation is solved for a finite ranged potential. For the model considered no solution to the integral equation is found in a certain region of the phase diagram. To determine the presence of criticality in the no-solution line, the behaviour of the total correlation function $h(r)$ at large distances is investigated. For finite ranged potentials, the decay of the function $rh(r)$ at large distances can be either exponential (at low and intermediate densities) or exponentially damped oscillatory (at high densities). For the model considered, the no-solution line falls within the region where the function $rh(r)$ shows exponential decay. The correlation length in the region where the decay of $rh(r)$ is exponential is given by the inverse of the purely imaginary pole of the structure factor. The purely imaginary pole is analysed in the proximities of the no-solution line. It is shown that the correlation length remains finite when approaching the no-solution line. Therefore for the finite ranged potential considered in this work, the reference hypernetted chain equation does not exhibit criticality.

1. Introduction

For finite ranged potentials, the long range decay of the total correlation function can be of two different types depending on the thermodynamic conditions (i.e. density and temperature) [1–3]. In one region of the phase diagram, the decay to zero of the function $rh(r)$ is exponential. In the other region, the function $rh(r)$ decays to zero in an exponentially damped oscillatory fashion. The locus of points on the phase diagram where the transition from exponential to oscillatory decay occurs is denoted as the Fisher–Widom (FW) line [1].

Recently, Evans *et al.* [2–4] have considered how to analyse the long range behaviour of $rh(r)$ for three-dimensional systems interacting through a short ranged potential. The analysis of Evans *et al.* [2–4] shows that the asymptotic form of $rh(r)$ at large r is dominated by the pole (purely imaginary or complex) of the structure factor $S(q = \alpha_1 + i\alpha_0)$ with the smallest imaginary part. In the case where this pole is purely imaginary, exponential decay occurs with a decay length of $1/\alpha_0$, whereas if this pole is complex, exponentially damped oscillatory decay occurs with a wavelength of $2\pi/\alpha_1$ and a decay length of $1/\alpha_0$. The FW line [1] is just the locus on points of the phase diagram where the purely imaginary pole ($\alpha_1 = 0$) of $S(q)$ and the complex pole of $S(q)$ with the smallest imaginary part have the same inverse decay length α_0.

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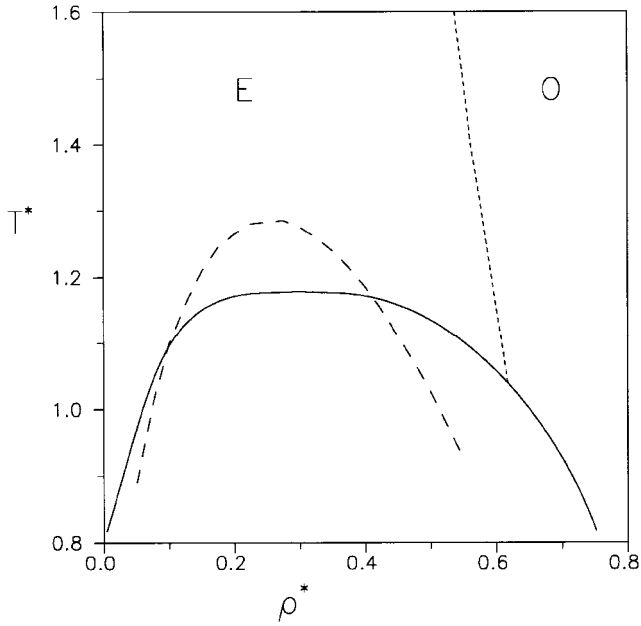

Figure 1. Location of the no-solution line (long dashed line) of the RHNC equation for the SLJ model. The vapour–liquid equilibria as obtained from Gibbs ensemble simulation (solid line) and the FW line (short dashed line) as computed from the RHNC equation [5] are also shown. The temperature is given in units of ε/k. In region E an exponential decay of $rh(r)$ occurs, whereas in region O a damped oscillatory decay occurs.

We have recently applied the methodology proposed by Evans *et al.* to determine the FW line of a finite ranged potential [5]. The reference hypernetted chain (RHNC) equation [6, 7] was solved and the poles of the structure factor were computed. By performing Gibbs ensemble simulations [8], the vapour–liquid equilibrium was computed for this model [5]. In this way the FW line was located within the phase diagram of the model. For a certain region of the phase diagram of the model considered (which includes the simulation estimate of the critical point), we were unable to find a solution of the RHNC equation. The no-solution line was found to be located in the region where the function $rh(r)$ shows exponential decay. The presence of a region of no-solution for the RHNC equation had been previously noticed by Lomba [9] for the complete Lennard-Jones (LJ) potential. Brey and Santos [10] also found a region of no-solution for the hypernetted chain equation (HNC). Brey and Santos analysed the presence or absence of criticality along this no-solution line. They concluded that, for the LJ potential, the HNC equation does not exhibit true criticality on the no-solution line. The same conclusion was obtained in a later study by Belloni [11].

However, the HNC equation is not particularly accurate for describing the structure of LJ-like potentials. During the past few years it has been shown that the RHNC equation yields quite accurate predictions of the structure of a number of spherical fluids [5, 9, 12]. An interesting possibility is the presence of true criticality in the RHNC equation. It is this problem that we shall consider in this note. We shall consider a finite ranged potential and the presence or absence of criticality will be determined by considering the correlation length of the exponential decay in the proximity of the no-solution line. Since the no-solution line is located in the region of

exponential decay of $rh(r)$, the behaviour of the purely imaginary pole of the structure factor will completely determine the correlation length of the fluid. The behaviour of the purely imaginary pole of the structure factor in the proximity of the no-solution line will be considered. It is shown that the correlation length does not diverge in the proximity of the no-solution line. Therefore, for the model considered, we conclude that the RHNC equation does not exhibit true criticality and this is in common with the simpler HNC equation.

2. Long range decay of the total correlation function

Here we will briefly outline the basic equations for the determination of the long range decay of the total correlation function and refer the reader to the original papers [1–4] for further details. The Ornstein–Zernike (OZ) equation [7] for a spherical fluid can be written as

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})\, h(r_{23})\, \mathrm{d}\mathbf{r}_3, \tag{1}$$

where ρ is the number density and $c(r)$ is the direct correlation function. The three-dimensional Fourier transform of a function $f(r)$ will be denoted as $f(q)$. By taking the Fourier transform of equation (1) and then taking the inverse Fourier transform (taking into account that $h(q)$ is an even function of q) one obtains that [3]

$$rh(r) = \frac{1}{4\pi^2 i} \int_{-\infty}^{+\infty} q \frac{c(q)}{(1 - \rho c(q))} \exp(iqr)\, \mathrm{d}q. \tag{2}$$

The real and imaginary part of the complex number q are expressed as

$$q = \alpha_1 + i\alpha_0. \tag{3}$$

By performing contour integration in equation (2) on an infinite radius semicircle in the upper half plane, one obtains that [2, 3]

$$rh(r) = \frac{1}{2\pi} \sum_{\mathrm{n}} \exp(iq_{\mathrm{n}} r)\, R_{\mathrm{n}} \tag{4}$$

where q_{n} is the nth pole and R_{n} the residue of $qc(q)/(1 - \rho c(q))$ at $q = q_{\mathrm{n}}$. Poles of the function $qc(q)/(1 - \rho c(q))$ are obtained by setting both the real and imaginary part of the function $1 - \rho c(q)$ to zero. Therefore poles are obtained by solving the following equations:

$$\alpha_0 = 4\pi\rho \int rc(r) \sinh(\alpha_0 r) \cos(\alpha_1 r)\, \mathrm{d}r, \tag{5}$$

$$\alpha_1 = 4\pi\rho \int rc(r) \cosh(\alpha_0 r) \sin(\alpha_1 r)\, \mathrm{d}r. \tag{6}$$

Two types of solutions to equations (5) and (6) can be found [2, 3]. The first type of solution has $\alpha_1 = 0$, $\alpha_0 \neq 0$, and yields an exponential decay contribution to $rh(r)$ (see equation (4)). A second type of solution is obtained with $\alpha_1 \neq 0$ and $\alpha_0 \neq 0$. In this case poles occur in conjugate pairs $q = \pm\alpha_1 + i\alpha_0$. The contribution of a conjugate pair to $rh(r)$ is that of an exponentially damped (with inverse decay length α_0) oscillatory (sinusoidal) function. The behaviour of $rh(r)$ at large values of r is dominated by the solution of equations (5) and (6) with the smallest value of α_0. In this work we consider

a finite-ranged potential denoted as SLJ. The pair potential u for the SLJ model is given by [13]

$$u_{SLJ}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]\,\theta(r - r_c), \tag{7}$$

$$\theta(x) = \frac{1}{(1 + \exp(-x/(x^2 - \Delta^2)))} \quad |x| < \Delta, \tag{8}$$

$$\theta(x) = 1 \quad x < -\Delta; \qquad \theta(x) = 0 \quad x > \Delta. \tag{9}$$

The value of Δ is set to $0{\cdot}5\sigma$ and r_c was set to $2{\cdot}5\sigma$. The potential given by equations (7)–(9) and its derivatives vanish at $r_c + \Delta$. Therefore, in this work the pair potential vanishes for $r > 3\sigma$. One of the advantages of using the potential given by equations (7)–(9) is that the potential and all its derivatives are continuous functions of r. Therefore, the functions $g(r)$ and $c(r)$ are also continuous functions of r so that equations (5) and (6) can be easily solved without the numerical difficulties arising from discontinuities in the potential. The structure of the SLJ potential will be obtained by solving the OZ equation with the RHNC closure which is given by [6]

$$c(r) = h(r) - \ln((h(r) + 1)\exp(u(r)/(kT))) + B_{HS}(r, d_{HS}) \tag{10}$$

where B_{HS} is the bridge function [7] of the hard sphere (HS) system with the same number density as the fluid under consideration. The diameter of the equivalent hard sphere, d_{HS}, is obtained by solving the equation [6]

$$\rho \int (g(r, \rho, T) - g_{HS}(r, \rho; d_{HS}))\frac{\mathrm{d}B_{HS}(r)}{\mathrm{d}(d_{HS})}\mathrm{d}\mathbf{r} = 0. \tag{11}$$

If the diameter d_{HS} of the hard sphere is obtained from the solution of equation (11) then pressures obtained from the virial theorem and from the derivative of the free energy are identical [6]. This fact will turn out to be of a certain importance as we shall discuss later. The bridge function of hard spheres required in equations (10) and (11) is taken from the parametric form proposed by Labik and Malijevsky [14, 15]. The RHNC integral equation is solved by using the algorithm proposed by Labik *et al.* [16], and the computational details are similar to those described in [5]. For a given temperature and density, the poles of the structure factor are obtained by solving equations (5) and (6).

3. Results

In figure 1 the region of no-solution of the RHNC equation for the SLJ model is shown. The FW line as obtained from our previous work is also shown. Since the RHNC provides very good results for $g(r)$, we believe that the FW line computed from the RHNC theory to be quite accurate. Although the vapour–liquid equilibria can be obtained from the RHNC theory at low temperatures, it is not possible to compute either the vapour–liquid equilibria at high temperatures or the critical point. Because of that and in order to locate the position of the FW line and of the no-solution line within the true phase diagram of the system, the vapour–liquid equilibria as computed from Gibbs ensemble data has also been included in figure 1. The FW line seems to cut the no-solution line when $T/T_c = 0{\cdot}60$; the same was found by Evans *et al.* (see figure 2 of [2]).

Let us now analyse the behaviour of the system when the no-solution line is approached. If the no-solution line exhibits true critical behaviour, then the correlation length diverges when one gets close to it. As it can be seen, the no-solution line falls in the region where the decay of the function $rh(r)$, at large values of r, is exponential. Therefore the critical character of the no-solution line can be analysed by studying the

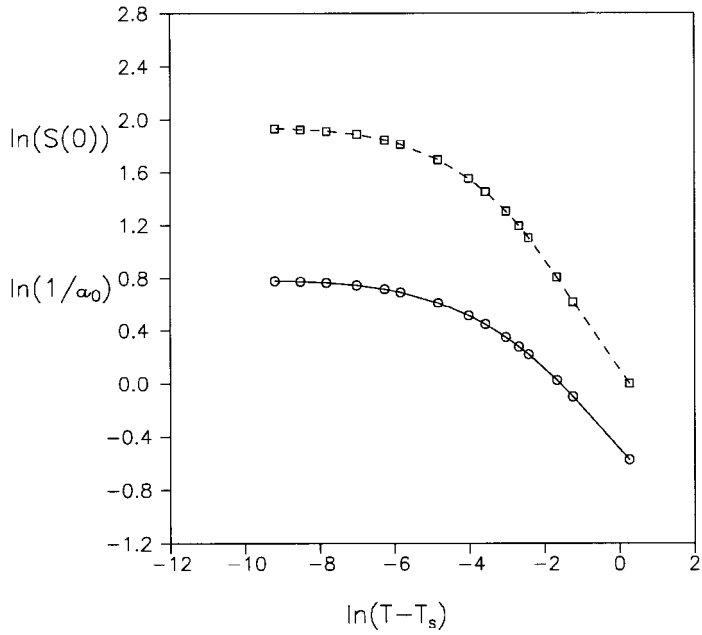

Figure 2. The logarithm of the correlation length $(1/\alpha_0)$ and of $S(0)$ as a function of $\ln(T - T_s)$ where T_s is the temperature of no-solution of the RHNC equation. Results correspond to the isochore $\rho^* = (N/V)\,\sigma^3 = 0{\cdot}15$. Temperatures are given in units of ε/k. Results for $(1/\alpha_0)$: circles and solid line. Results for $S(0)$: squares and dashed line. The lines are shown to guide the eye.

behaviour of the purely imaginary pole $q = i\alpha_0$ when the no-solution line is approached. Since in the region of exponential decay the correlation length is given by $1/\alpha_0$, the divergence of the correlation length is equivalent to the fact that the purely imaginary pole tends to zero (i.e. $\alpha_0 = 0$) close to the no-solution line.

In figure 2 the behaviour of the correlation length (i.e. the inverse of α_0 for the purely imaginary pole) is plotted as a function of $\ln(T - T_s)$, where T_s is the no-solution temperature for the density considered. Results presented in figure 2 correspond to the isochore $\rho^* = (N/V)\,\sigma^3 = 0{\cdot}15$. This isochore cuts the coexistence curve in the vapour branch. As can be seen, the correlation length does not diverge when T approaches T_s. Hence, the no-solution line does not present a critical character (divergence of the correlation length).

As a cross-check of our calculations we plotted $\ln(rh(r))$ versus r for several temperatures along the isochore $\rho^* = 0{\cdot}15$. In all cases a linear behaviour was found for large values of r and the slope was in excellent agreement with the value of α_0 of the purely imaginary pole computed from the solution of equation (5) with $\alpha_1 = 0$.

The spinodal line of a fluid is the locus of points where

$$\left(\frac{\mathrm{d}p}{\mathrm{d}\rho}\right)_T = 0. \tag{12}$$

By using the compressibility route, the spinodal line can also be obtained from the equation

$$\rho k T \kappa_T = S(0) = 1 + \rho h(q = 0) = \frac{1}{(1 - \rho c(q = 0))} = \infty, \tag{13}$$

Table 1. The correlation length $1/\alpha_0$ and $S(0)$ as obtained from the solution of the RHNC equation for the SLJ model. The results correspond to the isochore $\rho^* = 0{\cdot}15$. The temperature is given in units of ε/k.

T	$1/\alpha_0$	$S(0)$
2·5	0·564 3	0·998 9
1·5	0·905 8	1·859 1
1·4	1·024 7	2·238 6
1·3	1·244 1	3·019 3
1·28	1·318 2	3·302 5
1·26	1·416 0	3·684 6
1·24	1·561 0	4·269 8
1·23	1·670 0	4·719 2
1·22	1·844 3	5·455 5
1·215	2·001 6	6·127 4
1·214	2·050 0	6·333 1
1·213	2·112 8	6·600 6
1·212 5	2·152 8	6·770 5
1·212 3	2·171 5	6·849 3
1·212 2	2·182 0	6·896 6

where κ_T stands for the isothermal compressibility and $S(0)$ is the structure factor $S(q)$ computed at $q = 0$. If the exact function $g(r)$ is known, then equations (12) and (13) are equivalent definitions of the spinodal line. However, when using an approximate $g(r)$, then equations (12) and (13) provide different spinodal lines.

In figure 2 results for the structure factor $S(0)$ are shown. According to equation (13), $S(0)$ diverges on a spinodal line due to the divergence of the isothermal compressibility κ_T. As shown in figure 2, $S(0)$ does not diverge when the no-solution temperature is approached. We conclude that the RHNC closure does not yield a spinodal line, at least when the compressibility route is used to define the spinodal line. However, when the pressure is computed from the virial route, then equation (12) is satisfied for certain densities. In other words, the RHNC yields a virial spinodal line, but not a compressibility spinodal line for the potential described by equations (7)–(9). This problem is not new and has been discussed in detail before [17, 18]. According to Schlijper *et al.* [17] and Ferreira *et al.* [18], the way to avoid this difficulty is to compute the pressure from the functional which upon minimization yields the integral equation of interest. They showed that the HNC equation can be obtained by minimizing a certain functional for the grand potential $\Omega = U - TS - \mu N$ [17]. For the RHNC equation, Lado *et al.* [6] showed that the RHNC can be obtained by minimizing a certain functional for the free energy, and that the pressure computed from the virial route is identical to that obtained from the derivative of the free energy (provided that d_{HS} is obtained from equation (11)). Therefore, if the criterion proposed in [17, 18] is used to define the spinodal line, then the virial route should be used when dealing with the RHNC equation. The main purpose of this work however is not to establish the presence or absence of a spinodal line within the RHNC theory. Our main aim here is to establish the presence or absence of criticality within the RHNC theory. In this respect, the results presented in figure 1 are conclusive. Neither the correlation length nor the isothermal compressibility diverge when the no-solution line is approached, and therefore the RHNC equation does not present criticality. In Table 1, the correlation lengths and values of $S(0)$ plotted in figure 1 for states along the isochore $\rho^* = 0{\cdot}15$ are presented. In figure 3, $S(0)$ and $1/\alpha_0$ are plotted for the isochore

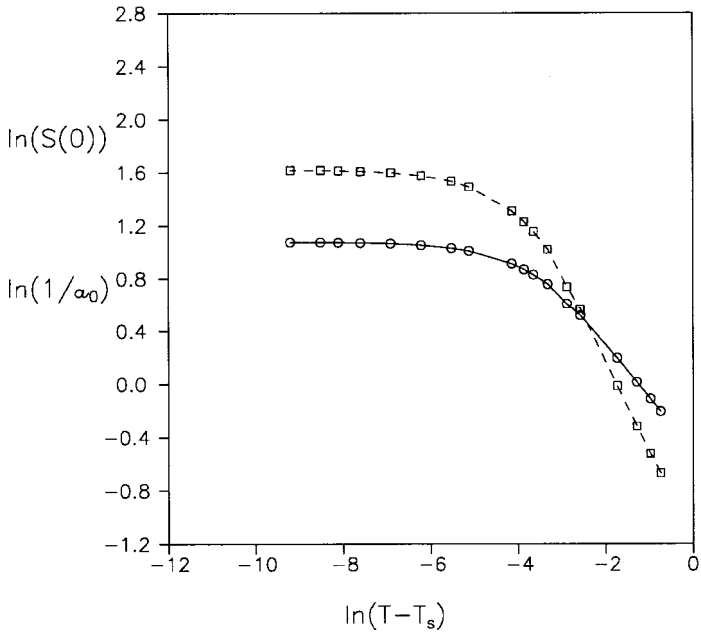

Figure 3. As in figure 2 for the isochore $\rho^* = 0{\cdot}50$.

$\rho^* = 0{\cdot}50$. This isochore cuts the liquid branch of the coexistence curve. Results presented for this density are similar to those presented for the smaller density and figure 3 shows that no criticality is exhibit by the liquid-like isochore. We conclude that the RHNC equation does not exhibit criticality, which is in accordance with similar studies carried out using the HNC equation.

For the HNC equation, Telo da Gama and coworkers [17, 18] were able to describe the origin of the no-solution line. The HNC equation was derived by minimizing an approximate functional for Ω [17]. They found [18] that the no-solution line appears when the solution of the HNC equation corresponds to a saddle point of the grand potential. The important conclusion arising from the work of Telo da Gama *et al.* [17, 18] is that the no-solution line is a consequence of the loss of convexity of the grand potential functional with respect to changes in $h(r)$ at a given density, whereas spinodal behaviour is related to loss of convexity of the grand potential with respect to changes in density along the line of solution (for $h(r)$) of the integral equation. Therefore, for the HNC equation, it has been shown that the no-solution line and the spinodal line are two different concepts, and there is no reason why these two lines should be coincident. For the RHNC equation, the situation will be similar since the RHNC equation can be obtained from the minimization of a certain functional of the free energy [6]. Note that the use of equation (11) is crucial in our discussion of the RHNC theory, since it guarantees that virial pressure and the pressure obtained from the derivative of the free energy are the same (which is not true in other applications of the RHNC theory where the condition given by equation (11) is not imposed [19]).

In this note we have shown that when the RHNC equation is used with the bridge function obtained from a hard sphere system the no-solution line does not present a critical character. For the HNC and RHNC equations the explanation of that is now clear [17, 18]. For integral equations that can be derived from the minimization of a certain functional, the no-solution line simply represents a loss of convexity of the functional with respect to variations in $g(r)$. It is fair to say that it is now known why

the HNC or RHNC do not present a critical character. However, for other closures of the OZ equation, as for instance, the mean spherical approximation (MSA), the no-solution line is also a critical line [11, 20–22]. An interesting question is, which is the key feature of an approximate closure of the OZ equation that provokes the presence of true criticality along the no-solution line?

4. Conclusions

The RHNC equation has been solved for a finite ranged potential. It was found that the RHNC equation has no-solution in a certain region of the phase diagram, where the decay of the function $rh(r)$ is exponential. Hence the correlation length close to the no-solution line can be obtained by analyzing the behaviour of the purely imaginary pole of the structure factor. It is shown that neither the correlation length nor the isothermal compressibility diverge when the no-solution line is approached. Therefore the RHNC equation does not exhibit criticality. Although the RHNC equation is found to be more efficient that the HNC equation when considering structural predictions, both equations are equivalent in their failure to exhibit criticality.

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