Absence of criticality in the hypernetted chain equation for a truncated potential

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The three-dimensional HNC equation for a truncated Lennard–Jones potential is numerically solved. We have found that the direct correlation function asymptotically behaves as $r^{-2} \exp(-2r/\xi)$, ξ being the correlation length. The contribution coming from this behaviour has been incorporated into the computation of the isothermal compressibility κ_T. The results seem to indicate that the HNC equation does not have real solutions inside a certain region in the temperature-density plane, whose boundary line has been fitted to power laws. When approaching this boundary, κ_T and ξ tend to finite values. So, a true critical point, where κ_T and ξ would diverge, is not present.

1. INTRODUCTION

The question about the predictions of the classical integral equations in the liquid–vapour critical region has stimulated a great deal of studies in the last few years. For three-dimensional systems, both the mean spherical approximation and the Percus–Yevick equation predict the existence of a critical point, i.e. a state where the isothermal compressibility κ_T and the correlation length ξ diverge. In the mean spherical approximation, the critical exponents take the so-called spherical model values, at least for a potential with an attractive Yukawa tail [1]. In the case of the Percus–Yevick equation, the critical exponents take the classical values [2–4], but analytical [2] as well as numerical [3] studies show that the scaling function for the equation of state is not classical when the interaction potential is short-ranged. Some consequences of this are an asymmetry of the critical isotherm around the critical point, and the absence of the vapour-phase branch of the spinodal line. These anomalous features may disappear in the long-ranged interaction limit [4].

The critical behaviour of the Yvon–Born–Green (YBG) equation is, up to now, the best known one. Both analytical [5] and very careful numerical [6] studies indicate that this approximation does not predict a true critical point for spatial dimensionalities $d \leqslant 4$, although there does exist a 'quasicritical' region where the isothermal compressibility and the correlation length are large but finite. For $d > 4$ there exists a critical point and the behaviour around it is fully classical.

Concerning the remaining important integral equation, the hypernetted chain (HNC) equation, much less is known. The HNC approximation is given by the following relation between the net correlation function $h(r)$ and the direct correlation function $c(r)$

$$c(r) = h(r) - \ln\,[1 + h(r)] - u(r)/k_B\,T, \tag{1}$$

where $u(r)$ is the interaction potential, k_B is the Boltzmann constant, and T is the temperature. The equation (1) implies the asymptotic behaviour

$$c(r) \simeq \tfrac{1}{2}[h(r)]^2 - u(r)/k_B\,T. \tag{2}$$

Thus, just at the critical point, the HNC direct correlation function behaves as

$$c_c(r) \sim [h_c(r)]^2 \sim r^{-2(d-2+\eta)}, \tag{3}$$

where we have written $h_c(r) \sim r^{-(d-2+\eta)}$, which defines the critical exponent η. A generalization of an analysis due to Green [7] shows that, if

$$c_c(r) \sim [h_c(r)]^\varepsilon, \tag{4}$$

then

$$\eta = 2 - d\,\frac{\varepsilon - 1}{\varepsilon + 1} \tag{5}$$

for $d \leqslant d_> \equiv 2(\varepsilon + 1)/(\varepsilon - 1)$, whilst η takes the classical value zero if $d > d_>$. The HNC equation leads to $\varepsilon = 2$ and, then, for a three-dimensional fluid [7] $\eta = 1$, so that, at criticality, the net correlation function $h(r)$ decays as r^{-2}, and the direct correlation function $c(r)$ as r^{-4}.

Let us notice that in Green's analysis the existence of a critical point, where the correlation length ξ becomes infinite and $h(r)$ decays following a power law, is implicitly assumed. But, as far as we know, there is no general proof of the existence of such a criticality. In addition, the available numerical results for the three-dimensional case are rather inconclusive. According to Watts [8], the isothermal compressibility remains finite, so that there is not a true critical point. On the other hand, Guerrero et al. [9] have suggested that κ_T does diverge, but with a value of the corresponding critical exponent γ much less than unity. More recently, Foiles and Ashcroft [10] were not able to fit their κ_T data to any power or logarithmic divergence law. In the above numerical calculations, the analysis of the spatial correlations in the critical region is, in our opinion, quite poor. Moreover, they take $c(r) = 0$ from a given distance. Equation (2) suggests that this may be a too drastic approximation, even for truncated potentials, especially at the critical point. The isothermal compressibility in the critical region is expected to be sensitive to the details of the spatial correlations.

Here we present the results of a numerical solution of the HNC equation for a truncated Lennard–Jones (LJ) potential. We have found that the net correlation function decays following the Ornstein–Zernike (OZ) form, and this has been used for the computation of κ_T.

There is a region in the temperature-density plane inside which our iterative method fails to converge. We have analysed whether the boundary of this region could be understood as a spinodal line. According to our results, the answer is

negative. When one approaches any branch of the line, the values of κ_T and ξ do not seem to tend to infinity, but they remain finite.

So, the OZ decay for the net correlation function and the boundness of both κ_T and ξ suggest that, analogously to the YBG equation, the HNC equation does not predict a true critical point for a three-dimensional fluid, at least for truncated potentials.

The plan of this paper is the following. In §2 we describe the numerical algorithm and study the asymptotic behaviour of $h(r)$ and $c(r)$. In §3 the locus of points where convergence fails is analysed and the behaviour of κ_T and ξ in the outside region close to the locus is studied. Emphasis is put on the relation with previous works. We must point out that our calculations can be improved in several ways, as discussed along the text. In this sense, they can only be considered as a preliminary study.

2. Numerical algorithm

The compressibility equation of state for three dimensions reads

$$\chi \equiv \rho k_B T \kappa_T = 1 + 4\pi\rho \int_0^\infty dr\, r^2 h(r) \tag{6a}$$

$$= \left[1 - 4\pi\rho \int_0^\infty dr\, r^2 c(r) \right]^{-1}, \tag{6b}$$

where ρ is the number density. In the last step of (6) we have taken into account the definition of the direct correlation function $c(r)$ given by the (OZ) relation:

$$\tilde{h}(k) = \tilde{c}(k) + \rho\tilde{c}(k)\tilde{h}(k), \tag{7}$$

with the tilde denoting a Fourier transform. This relation has to be closed with an approximate equation relating $h(r)$ and $c(r)$. In the HNC approximation the closure is given by (1). We have considered a truncated LJ potential defined by

$$u(r) = 4(r^{-12} - r^{-6}), \quad r \leqslant 5,$$
$$= 0, \qquad\qquad\qquad r > 5, \tag{8}$$

where usual units of energy and length have been chosen.

As it is well known, it is convenient to introduce the auxiliary function $H(r) = h(r) - c(r)$. In terms of $H(r)$ and $c(r)$, the HNC equation and the OZ relation become

$$c(r) = \exp\left[-u(r)/k_B T + H(r)\right] - H(r) - 1 \tag{9}$$

and

$$\tilde{H}(k) = \frac{\rho[\tilde{c}(k)]^2}{1 - \rho\tilde{c}(k)}, \tag{10}$$

respectively. The Fourier transform $\tilde{c}(k)$ is numerically evaluated as

$$\tilde{c}(k) = \frac{4\pi}{k} \sum_{i=1}^N \Delta r\, r_i \sin(kr_i)c(r_i). \tag{11}$$

Here $\Delta r = R/N$, R being a sufficiently large cut-off distance, and $r_i = i \Delta r$, $i = 1$, ..., N. Analogously,

$$H(r) = \frac{1}{4\pi^2 r} \sum_{j=1}^{N} \Delta k k_j \sin (k_j r) \tilde{H}(k_j), \qquad (12)$$

where $\Delta k = \pi/R$ and $k_j = j \Delta k$. Now, let us suppose that certain asymptotic forms $c(r) = c_a(r)$ and $h(r) = h_a(r)$ are reached for r greater than a certain $R_0 \equiv N_0 \Delta r < R$. Then, the susceptibility χ is computed as

$$\chi = 1 + 4\pi\rho \left[\sum_{i=1}^{N_0} \Delta r r_i^2 h(r_i) + \int_{R_0}^{\infty} dr r^2 h_a(r) \right] \qquad (13\,a)$$

$$= \left\{ 1 - 4\pi\rho \left[\sum_{i=1}^{N_0} \Delta r r_i^2 c(r_i) + \int_{R_0}^{\infty} dr r^2 c_a(r) \right] \right\}^{-1}. \qquad (13\,b)$$

The numerical method employed to solve the HNC equation is iterative. We start from a guess function $H^{\text{in}}(r)$ and (9) gives the corresponding function $c(r)$. Once $\tilde{c}(k)$ has been obtained via (11), one gets $\tilde{H}(k)$ from (10). Finally, the inversion formula (12) allows to obtain the output function $H^{\text{out}}(r)$. The process is continued until the following convergence conditions are simultaneously satisfied:

$$\left\{ N^{-1} \sum_{i=1}^{N} r_i^2 [H^{\text{out}}(r_i) - H^{\text{in}}(r_i)]^2 \right\}^{1/2} < 10^{-3}, \qquad (14)$$

$$\max_i \left\{ r_i | H^{\text{out}}(r_i) - H^{\text{in}}(r_i) | \right\} < 10^{-3}, \qquad (15)$$

$$\left\{ N^{-1} \sum_{i=1}^{N} \left[\ln \frac{H^{\text{in}}(r_i)}{H^{\text{out}}(r_i)} \right]^2 \right\}^{1/2} < 10^{-3}, \qquad (16)$$

$$\max_i \left| \ln \frac{H^{\text{in}}(r_i)}{H^{\text{out}}(r_i)} \right| < 10^{-3}, \qquad (17)$$

$$|1 - \chi^{\text{out}}/\chi^{\text{in}}| < 10^{-3}. \qquad (18)$$

The last three conditions arise from the fact that we are interested in the behaviour of the correlation length and the isothermal compressibility. They have shown up to be much more stringent than the first two ones. As input function at the first iteration for a given state we have used the solution found for a thermodynamic state close to it.

Notice that we do not introduce the asymptotic forms $c_a(r)$ and $h_a(r)$ into the fourier transforms (11) and (12). In this sense, our method is not fully self-consistent. The numerical algorithm described here is similar to the ones previously considered by other authors [8–10]. The main difference is that the asymptotic spatial correlations are taken into account when numerically computing the susceptibility χ. This might be especially relevant in the possible critical region, where χ is expected to be very sensitive to the spatial correlations. The problem now is that we do not know $h_a(r)$ nor $c_a(r)$. On the basis of Green's analysis [7], one could expect that $h_a(r) \sim r^{-2} \exp (-r/\xi)$, where the correlation
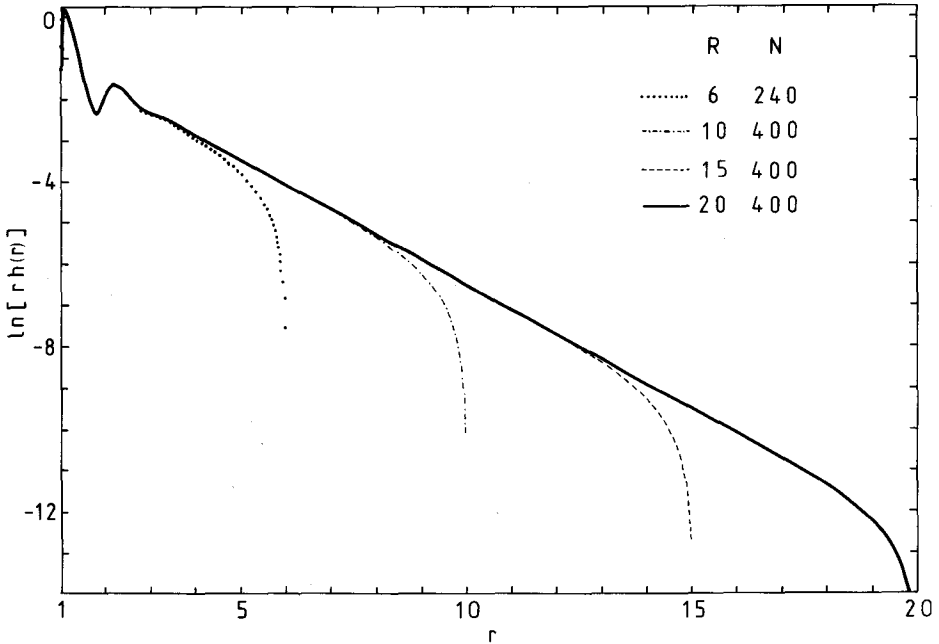
Figure 1. Plot of ln $[rh(r)]$ from the numerical method described in the text, for several values of the cut-off distance R and the number of points N considered in the interval $(0, R)$. The thermodynamical conditions are $T = 1.358$ and $\rho = 0.152$.

length ξ becomes infinite at the critical point. Nevertheless, our results do not fit to this law, but to the OZ form

$$h_a(r) = A\,\frac{\exp\,(-r/\xi)}{r}. \qquad (19\,a)$$

This can be seen from figure 1, where ln $[rh(r)]$ is plotted at $T = 1.358$ and $\rho = 0.152$ for several values of R and N. First, we comment on the unphysical abrupt decay of $h(r)$ when r approaches R. This decay is similar to the one observed in numerical solutions of the Percus–Yevick equation [11] and is a consequence of the method. The inversion formula (12) makes $H(r)$ to vanish at $r = R$, as $k_j R = j\pi$. So, $H(r)$ artificially tends to zero when r tends to R and so does $h(r)$. The truncation of the potential at $r = 5$ provokes a slight discontinuity $h(5^-) - h(5^+) \simeq -u(5)/k_B T$, which is not distinguishable on figure 1. The most important feature in this figure is the linear region observed for $r \gtrsim 5$. Since there is no reason to expect this linear behaviour to disappear if $R \to \infty$, $R/N \to 0$, we can conclude that the asymptotic form of $h(r)$ in the HNC approximation is given by $(19\,a)$.

In order to make $(19\,a)$ compatible with Green analysis [7], we see two possibilities: either the relation $(19\,a)$ is only valid for $r \gg \xi$ [12], in such a way that, just at the critical point (where $\xi \to \infty$), it is replaced by $h_a(r) \sim r^{-2}$, or ξ remains finite and there does not exist a true critical point. As we will see, we understand our results as supporting the latter possibility. The situation is similar to the one found in the YBG equation for three-dimensional fluids [5, 6]. Nevertheless, a
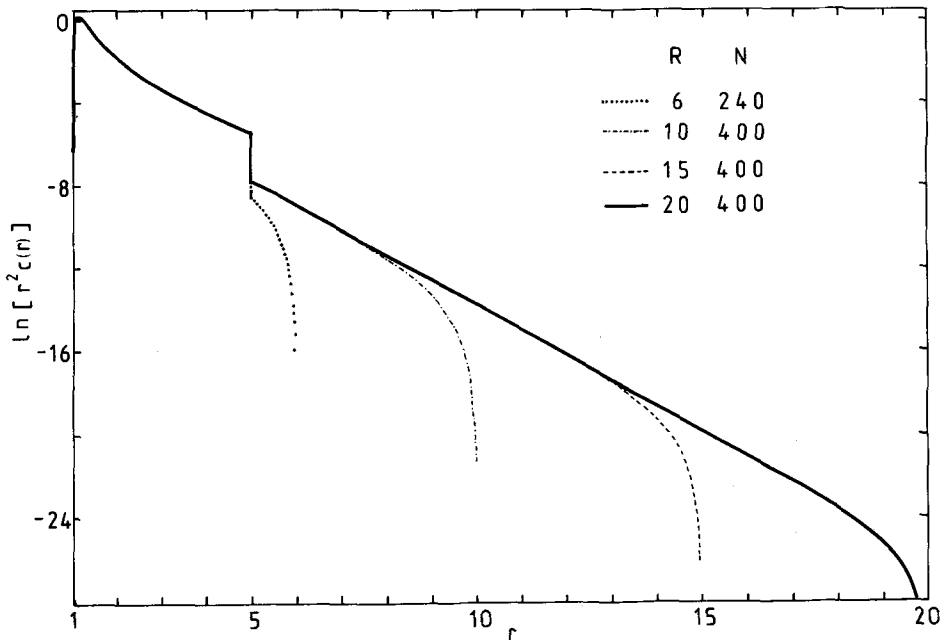
Figure 2.   Plot of ln $[r^2 c(r)]$ for the same cases as in figure 1.

more accurate approach should require to introduce the asymptotic forms (19 a) and (19 b) analytically into the fourier transforms performed along the numerical solution, and not only in the compressibility integral.

Let us now consider the asymptotic behaviour of the direct correlation function. Figure 2 shows ln $[r^2 c(r)]$ for the same cases as in figure 1. The artificial decay in the region $r \lesssim R$ is observed again, and the discontinuity $c(5^-)$ $- c(5^+) \simeq -u(5)/k_B T$ is here much more apparent than in figure 1. The linear region extending from $r \simeq 5$ confirms the law

$$c_a(r) = \tfrac{1}{2}[h_a(r)]^2 = \frac{A^2}{2} \frac{\exp{(-2r/\xi)}}{r^2}. \tag{19b}$$

So, the integrals appearing in (13 a, b) are, respectively,

$$\int_{R_0}^{\infty} dr r^2 h_a(r) = A\xi \exp{(-R_0/\xi)}(R_0 + \xi), \tag{20a}$$

$$\int_{R_0}^{\infty} dr r^2 c_a(r) = \frac{A^2}{4} \xi \exp{(-2R_0/\xi)}. \tag{20b}$$

Notice that the use of the asymptotic forms (19) eliminates the influence of the unphysical decay near R on the calculation of χ. All we need to know is the (discretized) values of the correlation function for $r < R_0$ and the fitting parameters A and ξ obtained from the linear regions.

In the numerical calculations presented in this paper we have taken $R = 20$, $N = 500$, and $R_0 = 5$. The linear fits have been carried out using the 125 points between $r = R_0$ and $r = 2R_0$. The statistical correlation coefficient has always

been greater than 0·99997, the fitting for the function $c(r)$ being slightly better than the one for the function $h(r)$. The relative differences between the fitting parameters obtained from $H(r)$ and those from $c(r)$ have been less than 0·9 per cent for A and less than 0·4 per cent for ξ. The relative difference between the susceptibility as obtained from (13 *a*) and (20 *a*) and the one from (13 *b*) and (20 *b*) has been no greater than 6 per cent. For the sake of consistency, as $h(r)$ does not enter into the numerical method, all the values of χ and ξ shown in the next section have been obtained from the function $c(r)$.

According to the results presented in the next section, ξ remains finite, which makes the value of χ computed from (13 *b*) not to differ appreciably from the one obtained by numerical integration over the full range of R. For instance, at $T = 1·3952$ and $\rho = 0·2873$, the relative difference between both values is about 2 per cent. However, it must be noticed that the smallness of this difference is a consequence of the absence of a true critical point. Otherwise, the correction (20 *b*) would play a quite important role.

3. RESULTS

When applying the numerical method described in the previous section, we observed that, as one approaches some points in the T-ρ plane, the rate of convergence of the iterative process becomes very slow. As a matter of fact, the numerical method fails to converge when approaching a dome shaped region in the T-ρ plane.

In figure 3 we have plotted the points defining the boundary of the region of convergence. The arrows indicate the path followed when approaching the points
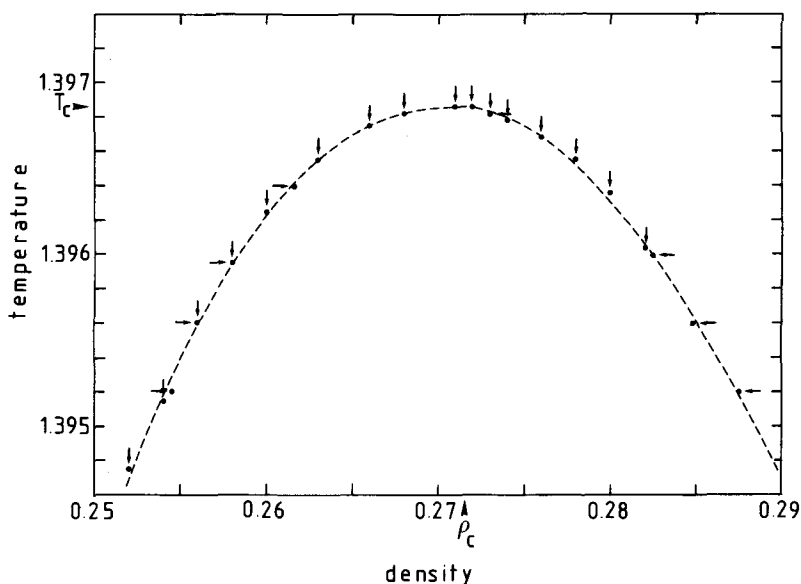

Figure 3. Temperature-density graph showing the points in which the iterative method seems to diverge, when approaching along the paths indicated by arrows. The apex defines a 'critical' point (ρ_c, T_c).
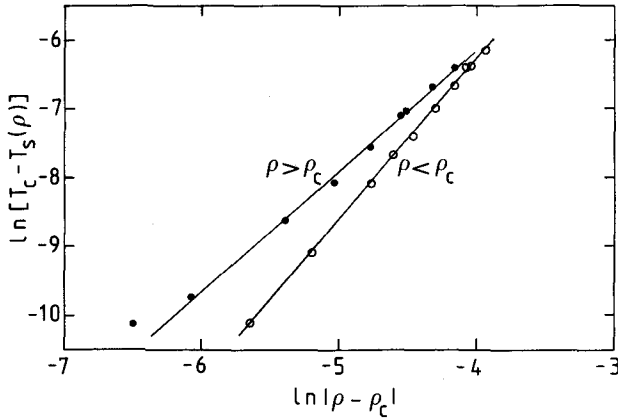
Figure 4.   Plot of $\ln [T_c - T_s(\rho)]$ vs $\ln |\rho - \rho_c|$ for the same points as in figure 3. $T_s(\rho)$ stands for the temperature at which the isochore ρ crosses the limiting line of the nonconvergence region. Dots refer to isochores $\rho > \rho_c$ and circles to $\rho < \rho_c$. The straight lines are linear fits.

in our calculations. The line drawn is a fit to be discussed below. The apex of the nonconvergence region determines a 'critical' point (ρ_c, T_c). For $T > T_c$, the HNC equation has a solution for any density, while for $T < T_c$, there is a density interval $\rho_s^{(-)}(T) < \rho < \rho_s^{(+)}(T)$ in which we have not been able to find a solution. When T tends to T_c from below, $\rho_s^{(-)}(T)$ and $\rho_s^{(+)}(T)$ tend to ρ_c. From figure 3 it follows that the 'critical' point is given by

$$\rho_c = 0 \cdot 2715 \pm 0 \cdot 0005, \tag{21}$$

$$T_c = 1 \cdot 39686 \pm 0 \cdot 00002. \tag{22}$$

To analyse the shape of the limiting line, let us assume a power law of the form

$$|\rho_s^{(\pm)}(T) - \rho_c| \approx B_\pm (T_c - T)^{\beta \pm}, \tag{23 a}$$

or, equivalently,

$$T_c - T_s(\rho) \approx \left\{ \frac{1}{B_\pm} |\rho - \rho_c| \right\}^{1/\beta_\pm}, \tag{23 b}$$

where the exponents $\beta_\pm$ play a role similar to the critical exponent β governing the shape of the coexistence curve. In figure 4, $\ln [T_c - T_s(\rho)]$ is plotted vs $\ln |\rho - \rho_c|$. The points fit very well to two straight lines, one for $\rho < \rho_c$ and another one for $\rho > \rho_c$, leading to values of the coefficients

$$\beta_+ \simeq 0 \cdot 5721, \tag{24}$$

$$B_+ \simeq 0 \cdot 6209, \tag{25}$$

$$\beta_- \simeq 0 \cdot 4285, \tag{26}$$

$$B_- \simeq 0 \cdot 2703. \tag{27}$$

When fitting the case $\rho > \rho_c$ we have omitted the lowest point, which corre-
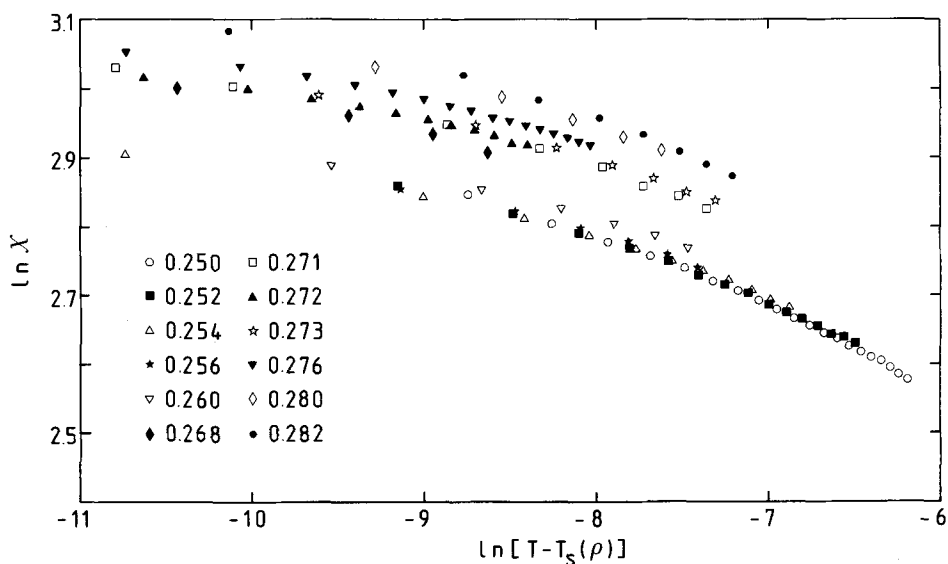
Figure 5. Behaviour of the susceptibility χ when approaching the limiting line along several isochores. The log-log plot has been taken in order to look for a possible power-law divergence.

sponds to $\rho = 0.273$, because in this case the value of $|\rho - \rho_c|$ is too close to the own uncertainty of ρ_c. The line in figure 3 corresponds to the laws (23) with the values (24)–(27).

So, we see that the limiting line is strongly asymmetrical with respect to the isochore $\rho = \rho_c$. Notice that $\beta_+ + \beta_- \simeq 1.0006$. As a matter of fact, $\beta_+ \simeq 4/7 \simeq 0.5714$ and $\beta_- \simeq 3/7 \simeq 0.4286$. In the classical theories one has $\beta_+ = \beta_- = \beta = 1/2$. It would be very interesting to check the above results by means of analytical studies.

In previous numerical solutions [8–10] the shape of the locus of singularities has not been studied. Foiles and Ashcroft [10] only give two points of the spinodal line, their values showing a certain asymmetry. Guerrero *et al.* [9] estimate $\beta = 0.53 \pm 0.05$ by extrapolating their results for $\rho > \rho_c$. However, their figure 1 can be used to define a limiting line of convergence, given by the points where the solid curves break. In this way, we have obtained a graph similar to our figure 4, allowing us to estimate $\beta_+ \simeq 0.60$, $B_+ \simeq 0.54$, $\beta_- \simeq 0.38$ and $B_- \simeq 0.28$. These values are quite close to ours in (24)–(27).

The relevant physical question now is whether the limiting line is a spinodal line, i.e. a line on which the susceptibility χ and the correlation length ξ become infinite. In that case, the apex of the line would be a true critical point. However, we will see that our results do not support this possibility.

In figure 5, we show $\ln \chi$ vs $\ln [T - T_s(\rho)]$ for several isochores close to the 'critical' one. The values of $T_s(\rho)$ were obtained from (23 *b*). If χ diverged following a power law, the graph should show straight lines. But no linear region is observed. The same was already noticed by Foiles and Ashcroft [10]. Our points seem to show that, when approaching the limiting line, $\chi(\rho, T)$ tends to a finite value $\chi_s(\rho)$. We have observed the same kind of behaviour for the correlation
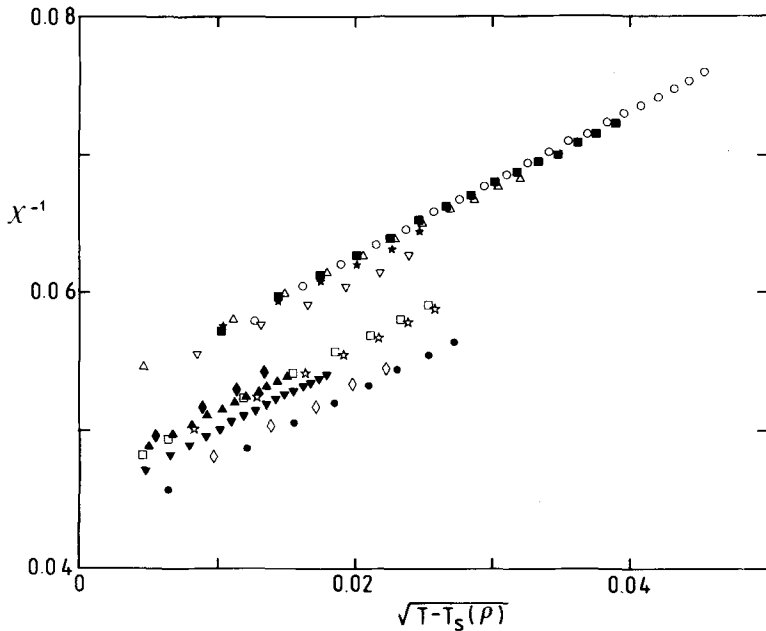
Figure 6.   Reciprocal susceptibility χ^{-1} vs $[T - T_s(\rho)]^{1/2}$ along the same isochores as in figure 5.

length ξ. The situation is similar to the one found in the Percus–Yevick equation for some short-ranged potentials [2] when $\rho < \rho_c$. In this case one gets

$$\chi^{-1}(\rho, \ T) \approx \chi_s^{-1}(\rho) + C(\rho)[T - T_s(\rho)]^{1/2}. \tag{28}$$

Although there is no reason to expect this law to hold for the HNC equation, we have plotted χ^{-1} vs $[T - T_s(\rho)]^{1/2}$ in figure 6 for the same isochores as in figure 5. The points fit quite well to straight lines with a typical value for C of the order of 0·5. But, rather than checking (28), we are interested in showing the absence of a true critical point. If one extrapolates to $T = T_s(\rho)$, one clearly observes that χ goes to a finite value χ_s, which seems to monotonically increase with the density. In figure 7 we present the results for the correlation length.

   Our conclusions are in agreement with the numerical results of other authors. From the points shown in figure 3 of [10] we have checked that the law (28) is satisfactorily verified for $\rho = 0\cdot274$ with $T_s(\rho) = 1\cdot4045$, leading to the values $\chi_s^{-1} \simeq 0\cdot057$ and $C \simeq 0\cdot21$. Also, the fact that $\chi_s(\rho)$ is an increasing function of ρ can be observed from figure 1 of [9]. Nevertheless, we must emphasize that our point of view is not the same as in those works. We claim that the numerical values cannot be extrapolated to get a divergent susceptibility, as a limiting line of convergence is reached in which χ is bounded.

   So, the approximate numerical solution of the HNC equation for a truncated Lennard–Jones potential presented in this paper does not seem to present a true critical point for three-dimensional systems. It is our conjecture that the same holds for any short-ranged potential, as it seems to be the case for the YBG
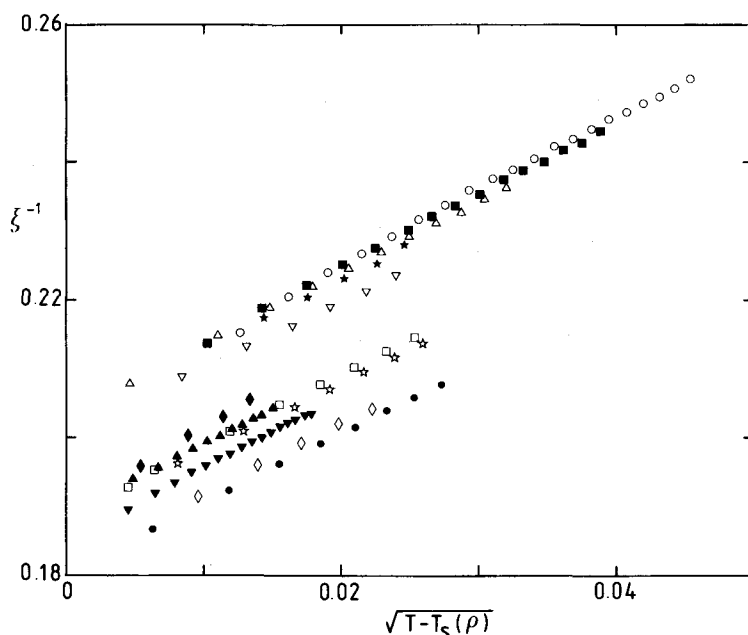
Figure 7. Reciprocal correlation length ξ^{-1} vs $[T - T_s(\rho)]^{1/2}$ along the same isochores as in figure 5.

equation. In this context, it would be interesting to see whether the analysis developed by Fisher and Fishman [5] could be extended to include the HNC equation. If that were the case, there would be a borderline dimensionally $d_>$, such that for $d > d_>$ the critical behaviour would be classical. For $d \leqslant d_>$, it is our guess that there is no true criticality. The result (5) leads us to expect that $d_> = 6$. Of course, more accurate numerical studies are also needed. On one hand, it is necessary to carry out the calculations by introducing the asymptotic behaviour of $h(r)$ and $c(r)$ in a self-consistent way. Also, it is necessary to explore whether the results are a consequence of the Picard method by trying more elaborate numerical techniques. In particular, it would be interesting to know whether or not solutions exist inside the region bounded by the limiting line.

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