About the numerical solution of the Percus–Yevick equation in the critical region for nontruncated potentials

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In a recent paper[1] we presented the results of a numerical solution of the Percus–Yevick (PY) equation near the critical point for a Lennard-Jones (LJ) fluid. According to those results, the PY equation exhibited a purely classical critical behavior, i.e., we obtained classical values for the critical exponents and the symmetry relations for the critical amplitudes.

In Ref. 1, the Fourier transforms were carried out[2] by substituting the upper limit ∞ by a cutoff distance R and considering N points in the interval $(0, R)$. Furthermore, in order to take into account the infinite range of the LJ potential, we assumed the asymptotic behavior $-u(r)/k_BT$ for $c(r)$. Obviously, the greater R and N are, the more accurate the method is. In Ref. 1 we took $R = 5\sigma$ and $N = 200$. These values seemed to be good enough, but the results we present here leave some doubts about them.

We have solved the PY equation for several pairs of values (R, N) using the method described in Ref. 1. The results for some of these pairs are presented in Fig. 1, where $\ln[rh(r)]$ and $h(r)$ are plotted vs r for $T = 1.3195\ \epsilon/k_B$ and $\rho = 0.225\sigma^{-3}$. In the $h(r)$ plot one hardly may see a significative difference between the curves corresponding to $R = 5\sigma$ and $R = 30\sigma$. However, the influence of a finite cutoff distance R is dramatically clear in the representation of $\ln[rh(r)]$. Thus, we observe in Fig. 1, a nonphysical, abrupt decay of $h(r)$ near R, which is caused by the numerical method [see Eq. (2.10) and the relations following it in Ref. 1]. But the error introduced by the method seems to affect even the small distances, especially in the cases $R = 5\sigma$ and $R = 10\sigma$. On the other hand, we have checked that, for a given value of R, an increase of N does not ameliorate the results substantially.

Figure 1 also shows a linear behavior of $\ln[rh(r)]$ from $r \simeq 4\sigma$ to the neighborhood of R. By extrapolation to the exact solution $(R \to \infty, R/N \to 0)$, we can confirm the expected Ornstein–Zernike form for the asymptotic behavior of the net correlation function in the critical

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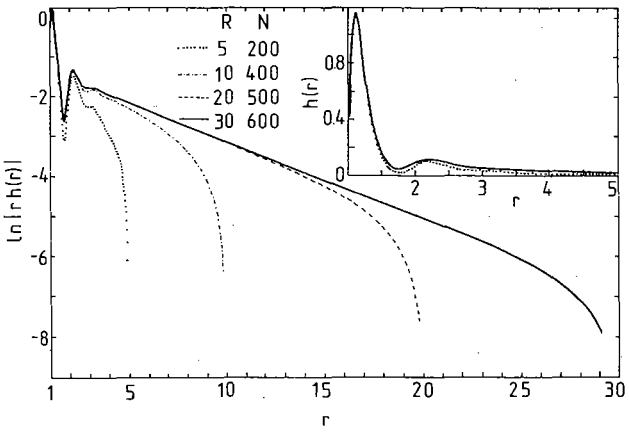

FIG. 1. Plot of $h(r)$ and $\ln[rh(r)]$ obtained using the numerical method described in Ref. 1, for several pairs of the cutoff distance (R) and the number of points (N) considered in the interval $(0, R)$. The thermodynamical conditions are $T = 1.3195\,\epsilon/k_B$ and $\rho = 0.225\,\sigma^{-3}$, where ϵ and σ are the parameters of the Lennard-Jones potential. The distances are measured in units of σ.

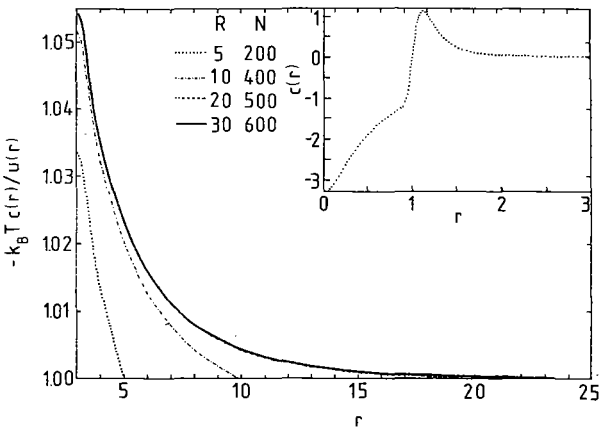

FIG. 2. Plot of $c(r)$ and $-k_B T\, c(r)/u(r)$ for the same conditions as in Fig. 1.

region, namely $h(r) \sim \exp(-r/\xi)/r$, where ξ is the correlation length.

In our previous work[1] the system was described by the compressibility equation of state written in terms of the direct correlation function $c(r)$. How is this function affected by the errors introduced by the numerical method? To answer this question we have plotted in Fig. 2, $-k_B T\, c(r)/u(r)$ and $c(r)$ for the same conditions as in Fig. 1. For $c(r)$, we have only considered the curve corresponding to $R = 5\sigma$ as the ones corresponding to greater values of R overlap it, over the scale employed in this graph. Thus, $R = 5\sigma$ is *apparently* a good cutoff distance. Nonetheless, the representation of $-k_B T\, c(r)/u(r)$ shows that this is not so. Since the algorithm employed in Ref. 1 makes $H(r) \equiv h(r) - c(r)$ to tend to zero when $r \to R$, the function $c(r)$ [obtained from $H(r)$ by means of Eq. (2.6) in Ref. 1] is compelled to tend to its asymptotic behavior $-u(r)/k_B T$ when r approaches to R. This fact is worthless if R is great enough because, then, it really is $c(r) \simeq -u(r)/k_B T$ for $r > R$.

This criticism about the numerical method shows that, near the critical point, $R = 5\sigma$ is not a very good cutoff distance. So, the numerical results presented in Ref. 1 should be revised. One of the main features of the PY approximation is that $c(r)$ has the asymptotic law $-u(r)/k_B T$ even at the critical point. By making $R = 5\sigma$ in our calculations we have anticipated this asymptotic behavior. However, we think that only the location of the critical point and, perhaps, the values of the critical amplitudes must have been affected by the use of $R = 5\sigma$ as a cutoff distance, in such a way that the conclusions[1] about the classicity of the PY approximation are still valid. Of course a more definitive answer to this problem should imply to solve the PY equation in the critical region by means of a numerical method more reliable than the one used in Ref. 1 (for instance, choosing $R \geq 20\sigma$). But this would require an enormous deal of computer time. In the case $R = 20\sigma$ we have observed that the convergence rate of iterations is so slow that the immediate vicinity of the critical point (where $\rho K_T / k_B T > 10^2$) becomes practically inaccessible. Furthermore, if, for a given value of R, one were able to reach a region very close to the critical point, that R would likely be inadequate in this region. A better value of R would modify the position of the critical point and so on. We are now studying these difficulties and we will report some results in a forthcoming paper.

These numerical problems do not appear in the case of the PY equation for a truncated potential,[3] but we are interested in infinite-range potentials. Not only are they more realistic, but the attractive tail seems to play an important role in the critical region.[4]

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