Molecular Physics, 1989, Vol. 66, No. 3, 695–700

RESEARCH NOTE

Nonclassical critical exponents in the mean spherical approximation

by F. CASTAÑO
Departamento de Fisica, Universidad de Extremadura,
06071 Badajoz, Spain

J. J. BREY and A. SANTOS
Departamento de Fisica Teórica, Universidad de Sevilla,
Apdo. Correos 1065, Sector Sur, 41080 Sevilla, Spain

(*Received 29 July 1988; accepted 26 September 1988*)

Using a numerical solution of the MSA for a hard core Yukawa potential, the critical exponents are calculated. Although the results differ from the exact ones, they are much closer to them than to the classical values. The tendency of the numerical solution towards the analytical one is shown.

In the last decade a great deal of work has been devoted to the study of the critical region as predicted by the integral equations for fluids [1, 2]. In most of the cases one has to resort to approximate numerical methods to solve the equations. A general feature of these methods is that a cutoff is introduced for the correlation function $h(r)$. Since $h(r)$ presents a long tail in the neighbourhood of the critical point, one might expect that the above numerical methods are not accurate enough to study the critical region. This suggests the need of carrying out tests for the numerical techniques. Of course, the most direct way is to compare with analytical solutions. Two analytical solutions for the integral equations exhibiting critical behaviour are known. One corresponds to the Percus–Yevick equation with an adhesive-hard-sphere interaction [1], and the other one refers to the mean spherical approximation (MSA) for the hard core Yukawa fluid (HCYF) [3]. In this paper we will be concerned with the latter. In fact, this work has been prompted and motivated by previous results for the same model [2, 4].

The HCYF is defined by the interaction potential

$$\phi(r) = \begin{cases} \infty, & r < \sigma, \\ -\dfrac{J}{r/\sigma} \exp\left(-z\,\dfrac{r-\sigma}{\sigma}\right), & r > \sigma, \end{cases} \tag{1}$$

where σ is the diameter of the hard core, J is the depth of the attractive well, and z characterizes the range of the potential. The MSA is defined by the closure relations

$$\left.\begin{aligned} h(r) &= -1, && r < \sigma, \\ c(r) &= -\phi(r)/k_B T, && r > \sigma. \end{aligned}\right\} \tag{2}$$

Here, k_B is Boltzmann's constant, T is the temperature, and $c(r)$ is the direct correlation function, that is related to the correlation function $h(r)$ through the Ornstein–Zernike equation

$$h(r) = c(r) + \rho \int d\mathbf{s} h(|\mathbf{r} - \mathbf{s}|)c(s), \tag{3}$$

ρ being the density. This model has been solved analytically. By using the compressibility equation of state

$$\chi^{-1} \equiv \frac{1}{k_B T}\left(\frac{\partial p}{\partial \rho}\right)_T = 1 - \rho \int d\mathbf{r} c(r), \tag{4}$$

where p is the pressure, it has been shown [3] that there exists a critical region characterized by the so-called spherical model critical exponents, i.e. $\delta = 2$ and $\gamma = 5$. These exponents describe the behaviour near the critical point of the critical isochore and the critical isotherm, respectively.

Cummings and Monson [2] have solved the MSA numerically for an HCYF with $z = 2$, and compared their results with the analytical solution. They conclude that their method is unable to approach the critical point sufficiently closely to enable the critical exponents to be determined unequivocally. A similar study, but for $z = 7{\cdot}5$, has been carried out by Mier-y-Terán and Fernández-Fassnacht [4]. Again, the numerical results disagree with the analytical solution. In particular, the numerical critical exponents are very close to the classical values $\gamma = 1$ and $\delta = 3$. In both papers the discrepancy is attributed to the truncation of the correlation function at a finite distance used in the numerical method.

Here, the same problem is reconsidered. We will show that a careful use of the conventional Picard method leads to quite a good agreement with the analytical solution close to the critical point. Although we have not reached a region where the spherical model critical exponents are clearly identified, the tendency towards them is seen fairly well.

The details of the numerical method have been described elsewhere [5]. It must be noticed that the simplicity of the MSA allows the analytical calculation of the contribution to the Fourier transform of $c(r)$ coming from $r > \sigma$. On the other hand, the method implies the truncation of $h(r)$ at a certain distance $r = R$. In the calculations we have used a grid size $\Delta r = 0{\cdot}0125\sigma$ and cutoff distances $R/\sigma = 6{\cdot}4$, $12{\cdot}8$, $25{\cdot}6$, $51{\cdot}2$, and $102{\cdot}4$.

In order to compare the analytical and the numerical solutions, we have chosen the value $z = 2$, for which the analytical solution gives a critical point defined by [2] $K_c \equiv J/k_B T_c = 1{\cdot}114384$ and $\eta_c = \pi \rho_c \sigma^3/6 = 0{\cdot}165978$. Then, we have numerically solved the model along the isotherm $K = 1{\cdot}114$. The results for χ^{-1} are shown in figure 1 for the different values of R. Also, the analytical solution for the same value of K is plotted. It is seen that, for each value of R, there is a density interval for which the compressibility takes unphysical negative values. In fact, the numerical iterative method becomes unstable for those values of the density. More precisely, we have observed that the iterated values of $h(r)$ tend to oscillate between two functions $h_+(r)$ and $h_-(r)$. In order to stabilize the solution, a mixing parameter α is introduced. We have found that a value $\alpha = 0{\cdot}75$ leads to a quite fast convergence. The plotted negative value of χ^{-1} are the ones obtained in this way.

Figure 1 shows that the numerical solution approaches the analytical one as the cutoff distance R increases. The agreement is fairly good for $R = 102{\cdot}4\sigma$. It must be

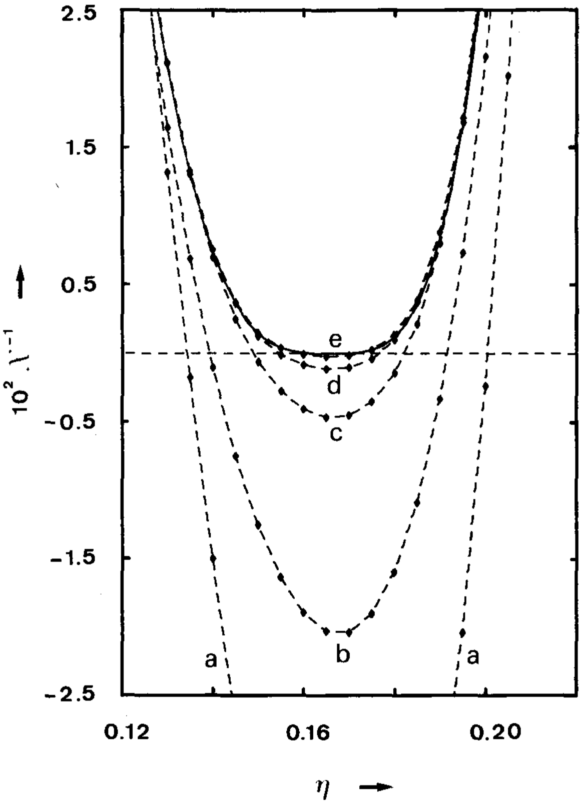

Figure 1. Inverse compressibility χ^{-1} versus reduced density along the isotherm $K = 1{\cdot}114$. The dots correspond to the numerical solution with a cutoff distance $R/\sigma = 6{\cdot}4$ (*a*), $12{\cdot}8$ (*b*), $25{\cdot}6$ (*c*), $51{\cdot}2$ (*d*), and $102{\cdot}4$ (*e*). The solid line is the analytical solution.

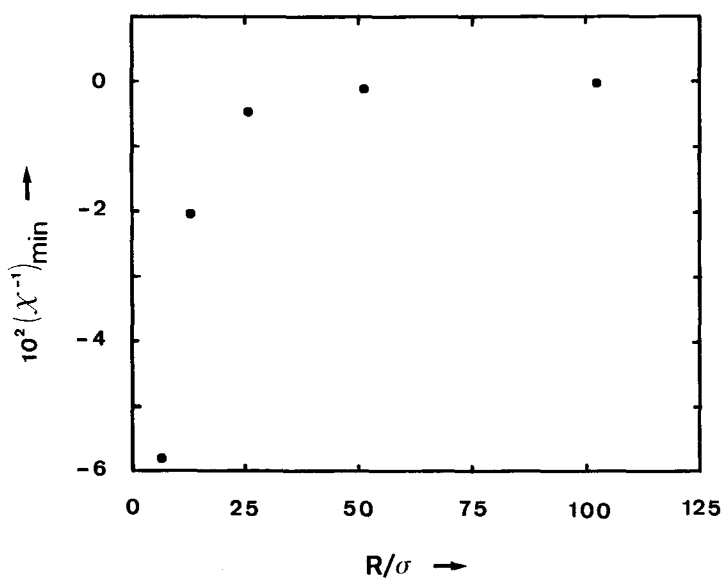

Figure 2. Minimum value of the numerical χ^{-1} along the isotherm $K = 1{\cdot}114$ versus the cutoff distance R.

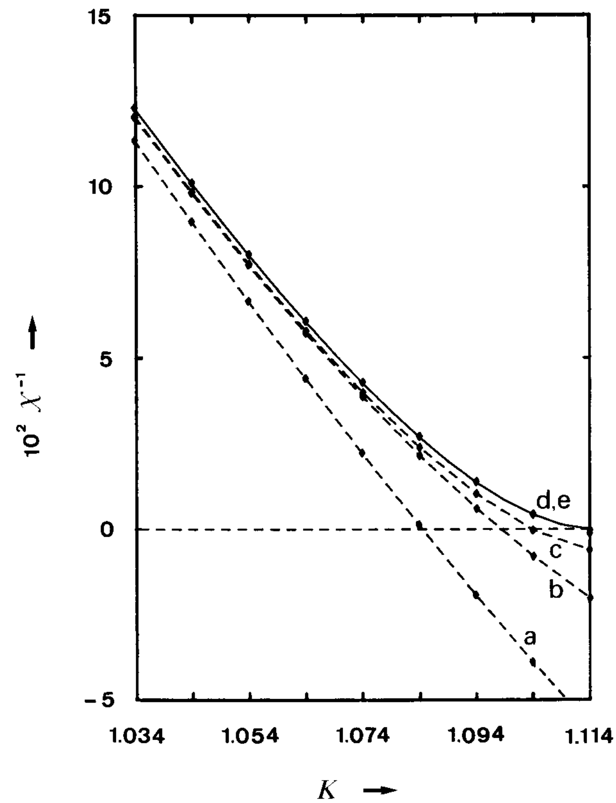

Figure 3. Inverse compressibility versus inverse reduced temperature K along the isochore $\eta = 0{\cdot}165$. The dots and the solid line have the same meaning as in figure 1. Notice that the data in the cases (*d*) and (*e*) are undistinguishable except at $K = 1{\cdot}114$.

noticed that not very close to the critical density, smaller values of R seem to be accurate enough. As a measure of the influence of the cutoff, we have plotted in figure 2 the value of the minimum inverse compressibility $(\chi^{-1})_{min}$ versus R. It is seen that $(\chi^{-1})_{min}$ rapidly approaches the analytical value. For $R = 102{\cdot}4\sigma$, it is $(\chi^{-1})_{min} \approx -0{\cdot}24 \times 10^{-3}$, while the analytical value is of the order of 10^{-5}.

A similar analysis has been carried out along the isochore $\eta = 0{\cdot}165$, and the results are shown in figure 3. Again, the agreement between the numerical and the analytical solutions improves as R increases, and it is quite good for $R = 102{\cdot}4\sigma$.

The values of K and η considered are close to the analytical critical ones, and in this sense the above graphs indicate that the numerical method is able to reproduce the analytical results even in the critical region. Of course, the accuracy will depend on the value of the cutoff distance. The natural question now is whether the method allows to determine the spherical model critical exponents. For the analysis of this point, we will restrict ourselves to the data with $R = 102{\cdot}4\sigma$. In figure 4 we plot $-\ln \chi^{-1}$ vs. $-\ln|\eta/\eta_c - 1|$ along the isotherm $K = 1{\cdot}114$ for $\eta > \eta_c$. Also, the analytical solution is shown. From figure 1 we have estimated $\eta_c = 0{\cdot}1675 \pm 0{\cdot}0025$. For consistency, this is the value we have used rather than the exact theoretical one. A least-square fit of the points yields $\delta(\eta > \eta_c) \approx 4{\cdot}30$. A similar analysis for $\eta < \eta_c$ leads to $\delta(\eta < \eta_c) \approx 4{\cdot}51$. These values show in a definite way that the behaviour is

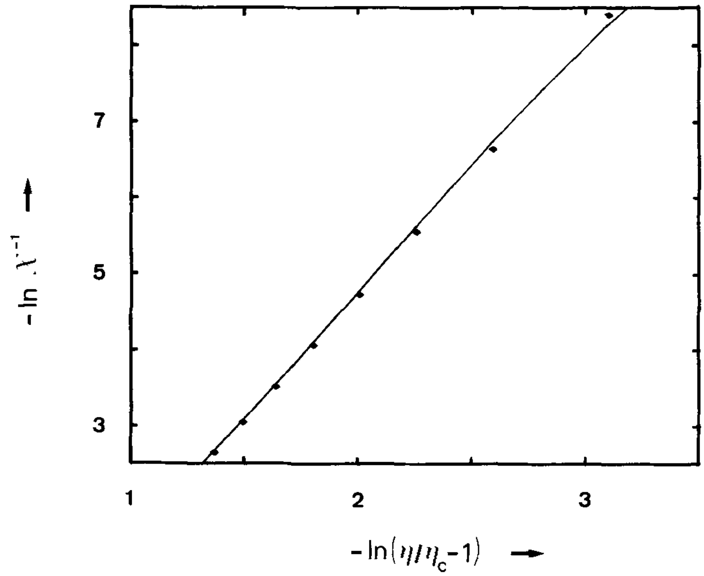

Figure 4. Log–log plot of χ^{-1} versus $|1 - \eta/\eta_c|$ along the isotherm $K = 1{\cdot}114$ for $\eta > \eta_c$, where $\eta_c = 0{\cdot}1675$. The dots represent the numerical data, while the solid line corresponds to the analytical solution.

nonclassical, although they are smaller than the exact result $\delta = 5$. This discrepancy is mainly due to the fact that the critical point used is not accurate enough. In fact, the analytical solution along $K = 1{\cdot}114$ gives apparent critical exponents $\delta(\eta > \eta_c) \approx 4{\cdot}28$ and $\delta(\eta < \eta_c) \approx 4{\cdot}51$.

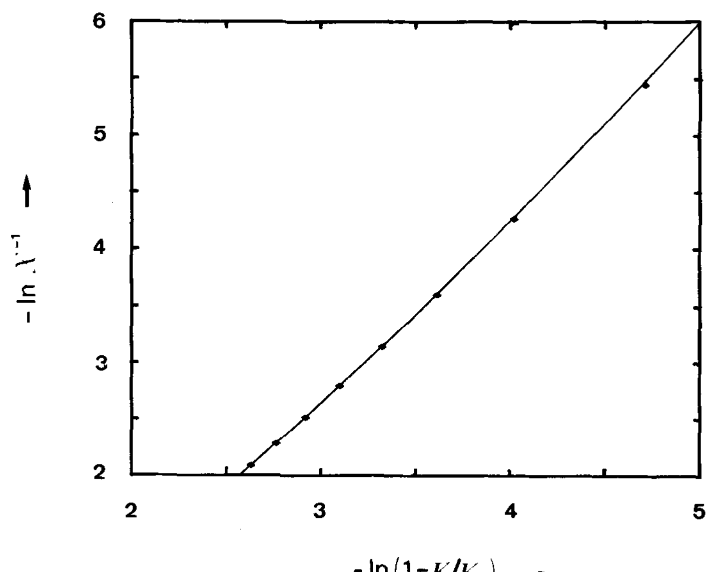

Figure 5. Log–log plot of χ^{-1} versus $(1 - K/K_c)$ along the isochore $\eta = 0{\cdot}165$, with $K_c = 1{\cdot}114$.

Finally, in order to estimate the critical exponent γ, $-\ln \chi^{-1}$ vs. $-\ln(1 - K/K_c)$ for $\eta = 0{\cdot}165$ is plotted in figure 5, where we have taken $K_c = 1{\cdot}114$. Using again a least-square fit, one gets $\gamma = 1{\cdot}65$ from the numerical data and $\gamma = 1{\cdot}67$ from the analytical solution. As above, the main reason for the discrepancy with the exact value $\gamma = 2$ is associated with the uncertainty of the critical point.

In summary, the numerical method we have used (with a cutoff distance $R = 102{\cdot}4\sigma$) is able to reproduce the analytical solution fairly well in a region where χ^{-1} takes values of the order of 10^{-3}. This is not enough to identify unequivocally the critical exponents, although our results are clearly closer to the spherical model values than to the classical ones. In order to get more accurate values, there are two possibilities. The cutoff distance R must be increased or an asymptotic behaviour of $h(r)$ in the critical region must be introduced into the calculations. The latter seems to be much more efficient and work is now in progress to apply that technique to cases where an analytical solution is not available.

Two of is (J.J.B. and A.S.) acknowledge partial support from the Dirección General de Investigación Cientifica y Técnica (Spain) through PB86-0205.

References

[1] FISHMAN, S., and FISHER, M. E., 1981, *Physica* A, **108**, 1, and references therein.
[2] CUMMINGS, P. T., and MONSON, P. A., 1985, *J. chem. Phys.*, **82**, 4303.
[3] CUMMINGS, P. T., and STELL, G., 1983, *J. chem. Phys.*, **78**, 1917.
[4] MIER-Y-TERÁN, L., and FERNÁNDEZ-FASSNACHT, E., 1986, *Physics Lett.* A, **117**, 43.
[5] BREY, J. J., SANTOS, A., and ROMERO, F., 1982, *J. chem. Phys.*, **77**, 5058.