NUMERICAL CALCULATION OF CRITICAL EXPONENTS FROM THE PERCUS–YEVICK EQUATION

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We have solved numerically the Percus–Yevick equation with a Lennard–Jones (12, 6) potential, using an iterative procedure. The behaviour of the system near the critical point has been studied and the critical exponents γ, γ' and δ have been obtained.

A few years ago, Baxter [1] proposed a modified Percus–Yevick equation valid for cases in which the interaction potential vanishes for distances bigger than a certain R. Since the Baxter equation is self-contained in the interval $(0,R)$, it is not necessary to assume any asymptotic form either for the radial distribution function $g(r)$ or for the direct correlation function $c(r)$, in order to calculate the thermodynamical properties of the system.

Henderson and Murphy [2] have used Baxter's equation to determine the critical exponents. Using a truncated Lennard–Jones potential,

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad r < 6\sigma,$$

$$u(r) = 0, \quad r > 6\sigma,$$

and the method of solution suggested by Watts [3], they were able to find the values $\gamma = \gamma' = 1$, $\delta = 3$, in the equation of state for the compressibility.

We have obtained the same values considering a Lennard–Jones potential without truncation and assuming that $c(r)$ behaves asymptotically like $-\beta u(r)$ for $r > 5\sigma$. We solve the Percus–Yevick equation using an iterative procedure analogous to the one used by other authors [4,5], but modifying the convergency conditions.

Lado [5] proposes the following convergence criteria:

$$D_{\mathrm{rms}} = \left\{ N^{-1} \sum_{j=1}^{N} r_j^2 [H^{\mathrm{out}}(r_j) - H^{\mathrm{in}}(r_j)]^2 \right\}^{1/2} < 10^{-3},$$

$$D_{\max} = \max_j \{ r_j | H^{\mathrm{out}}(r_j) - H^{\mathrm{in}}(r_j)| \} < 10^{-3},$$

where $H(r) \equiv g(r) - 1 - c(r)$. Nevertheless, these requirements are not sufficient in the vicinity of the critical point. We introduce the additional requirements

$$\frac{Z^{i+1} - Z^i}{Z^i} < 10^{-3}, \quad \frac{B^{i+1} - B^i}{B^i} < 10^{-3},$$

where Z^i is the compressibility factor $\beta p/\rho$, and B^i is the isothermal bulk modulus $(\rho K_T/\beta)^{-1} = \beta \times (\partial p/\partial \rho)_T$, both obtained after the ith order iteration. The values for the critical constants obtained with the compressibility equation of state are

$$T_c = 1.3197\epsilon/k_B, \quad \rho_c = 0.2880\sigma^{-3}.$$

These values are slightly higher than those obtained in ref. [2]. The dependence of the critical constants on the range of the potential has been studied by Watts [3].

From the slope of the graph $\ln K_T$ versus $\ln(T-T_c)$ along the critical isochorous line for $T > T_c$ in the linear region we find $\gamma = 1$. There is a non-linear region of the curve which corresponds to values of $T-T_c$ of the same order of magnitude as the uncertainty in the value of the critical temperature. In a similar way the value $\gamma' = 1$ is obtained.

Fig. 1 represents $\ln|p-p_c|$ versus $\ln|\rho-\rho_c|$ along the critical isothermal line. From it the value $\delta = 3$ is obtained. But in this case, the values of $|\rho-\rho_c|$ in

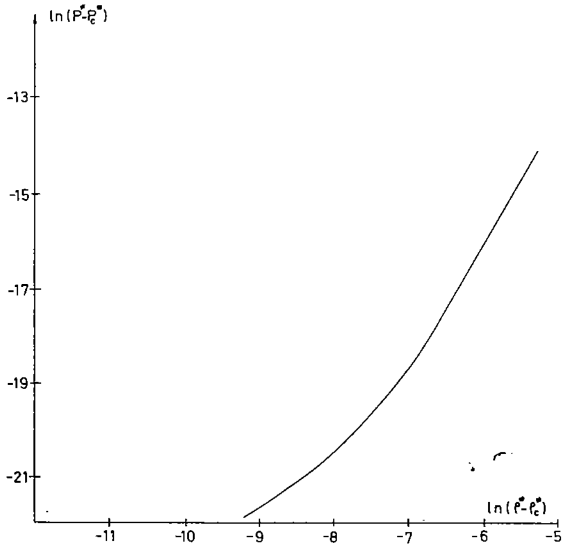

Fig. 1. Ln $|p^* - p_c^*|$ versus ln $|\rho^* - \rho_c^*|$ along the critical isothermal line. $p^* = p\sigma^3\epsilon^{-1}$ and $\rho^* = \rho\sigma^3$.

the non-linear region are higher than the uncertainty in the critical density. We are now studying this point.

We conclude that we do not have to assume a truncated potential in order to solve the Percus–Yevick equation in the vicinity of the critical point, because the critical point and the critical exponents have been obtained from the compressibility equation of state, where only the function $c(r)$ is needed, and this function has a finite range even near the critical point.

We think, with Henderson and Murphy [2], that the same values for the critical exponents would be obtained using any other realistic potential. Furthermore we think the above conclusion is also valid in the HNC approximation.

References

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