

Critical behavior in the Percus-Yevick equation for a Lennard-Jones potential

J. J. Brey, A. Santos, and L. F. Rull

Departamento de Física Teórica, Facultad de Física, Sevilla, Spain

(Received 23 March 1982)

The behavior of the critical isotherm near the critical point has been studied starting from a numerical solution of the Percus-Yevick equation for the Lennard-Jones potential. The results show the usual asymptotic gas-liquid symmetry, i.e., a purely classical behavior. This result solves a problem brought up recently by Fishman and Fisher.

Recently, the detailed study of the behavior of a fluid near its critical point by means of the several integral equations has received great attention. This behavior is described by the critical exponents and also by the critical amplitudes.¹⁻³ In particular, from the behavior of the critical isotherm T_c near the critical point (ρ_c, p_c) , the critical exponent δ and the critical amplitudes W_{\pm} are defined by

$$|p/p_c - 1| \approx W_{\pm} |\rho/\rho_c - 1|^{\delta}, \quad (1)$$

where W_+ and W_- refer to the limits $\rho > \rho_c$ and $\rho < \rho_c$, respectively.

Classical theories, such as the van der Waals equation and the Landau phenomenological theory, predict the value $\delta=3$ for a three-dimensional fluid. They also predict the symmetry of the critical isotherm about the critical point, which implies $W_- = W_+ = W$. Concretely, for a van der Waals fluid W takes the value $\frac{3}{2}$.

Baxter¹ has solved analytically the Percus-Yevick (PY) equation for "sticky hard spheres," showing the existence of a critical point and obtaining the classical values for the critical exponents. Nevertheless, the critical isotherm shows a strong asymmetry around the critical point ($W_-/W_+ \approx 34$) disagreeing with the classical theories. Fishman and Fisher² have shown that this asymmetry is related to the fact that the scaling functions for the equation of state are nonclassical.

The PY equation has been solved numerically near the critical point by Henderson and Murphy⁴ for a truncated Lennard-Jones (LJ) potential. The critical exponents obtained by these authors coincide with those predicted by the classical theories. Although they do not explicitly consider the behavior of the critical amplitudes, Fishman and Fisher² have estimated an amplitude ratio for the critical isotherm of $W_-/W_+ \approx 1.6$ using a graph reported in Ref. 4. Nonetheless, Fishman and Fisher remark that the data of Henderson and Murphy do not approach the critical point very closely and that the iterative method of solution used may not be adequate in the vicinity of the critical point. For these reasons, they

do not definitively conclude whether the PY equation predicts nonuniversal critical behavior for general potentials or that only special limit models lead to a nonclassical behavior in the PY equation. So they remark that it would be interesting to carry out more extensive and accurate numerical calculations.

We have solved the PY equation for a LJ potential without truncation,

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (2)$$

assuming that the direct correlation function $c(r)$ behaves like $-u(r)/k_B T$ for $r > 5\sigma$ and using an iterative method with convergence conditions especially useful in the vicinity of the critical point. Namely, we use the compressibility factor and the isothermal bulk modulus to define additional convergence criteria.⁵

From the compressibility equation of state we have obtained

$$\begin{aligned} k_B T_c / \epsilon &= 1.319678 \pm 0.000002, \\ \rho_c \sigma^3 &= 0.2880 \pm 0.0001, \\ p_c / \rho_c k_B T_c &= 0.3352 \pm 0.0004, \end{aligned} \quad (3)$$

and the classical values for the critical exponents. In particular, the value $\delta=3$ is confirmed by Fig. 1, where $\chi_c^{-1/2}$ vs $(\rho - \rho_c)$ is represented; χ_c is defined by

$$\chi_c = k_B T_c \left(\frac{\partial \rho}{\partial p} \right)_{T_c} \approx \frac{\rho_c k_B T_c}{p_c} (\delta W_{\pm})^{-1} \left| \frac{\rho}{\rho_c} - 1 \right|^{1-\delta}. \quad (4)$$

The nonlinear behavior near the origin is a consequence of the error in the determination of the critical temperature.

Figure 2 shows $(\rho/\rho_c - 1)^2 \chi_c$ vs $(\rho/\rho_c - 1)$. The lowering of the values on both sides of the critical density is due again to the indetermination of the critical point. Actually, χ_c^{-1} does not vanish at the calculated critical point but its value is $\sim 10^{-6}$. The extrapolation of the linear regions of the curve on both sides of ρ_c coincides within the error range,

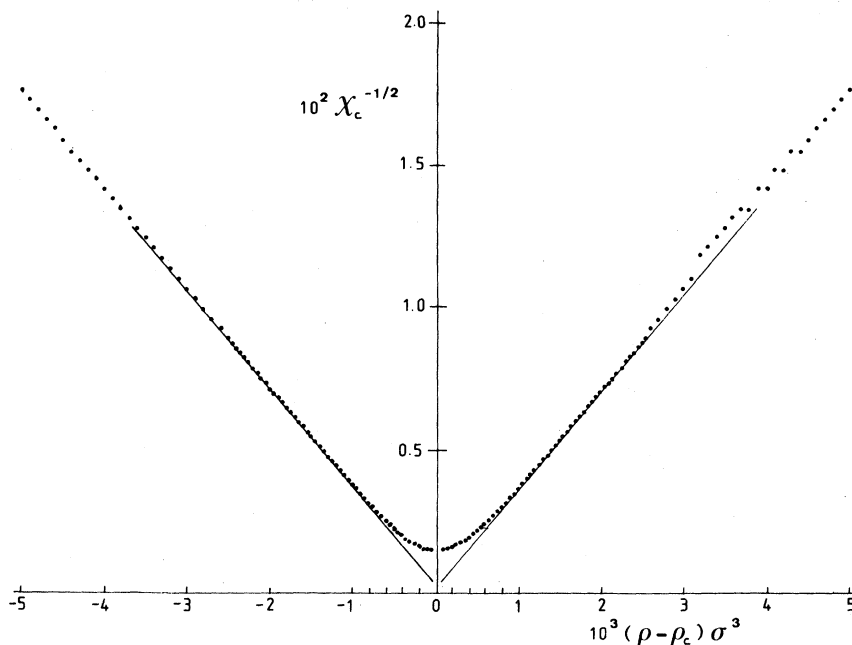


FIG. 1. Reciprocal square root of the critical susceptibility χ_c vs the density $(\rho - \rho_c)\sigma^3$ for a LJ interaction according to the PY equation. The points correspond to the obtained results and the straight line to a linear fit.

showing that $W_- = W_+ = W (\approx 1.02)$, in agreement with classical theories. Let us notice that the symmetry of the isotherm that we consider as critical is maintained even in the region affected by the uncertainty of the critical point. This shows that more precision would not change our above conclusion about

the symmetry of the critical isotherm.

We notice that from Fig. 1 one sees linear behavior for $|\rho/\rho_c - 1| \geq 0.0035$. Thus in Fig. 2 a constant behavior for $|\rho/\rho_c - 1|$ outside 0.0035 could be expected. However, there is a strong variation up to $|\rho/\rho_c - 1| \approx 0.02$, which differs by a factor of 10.

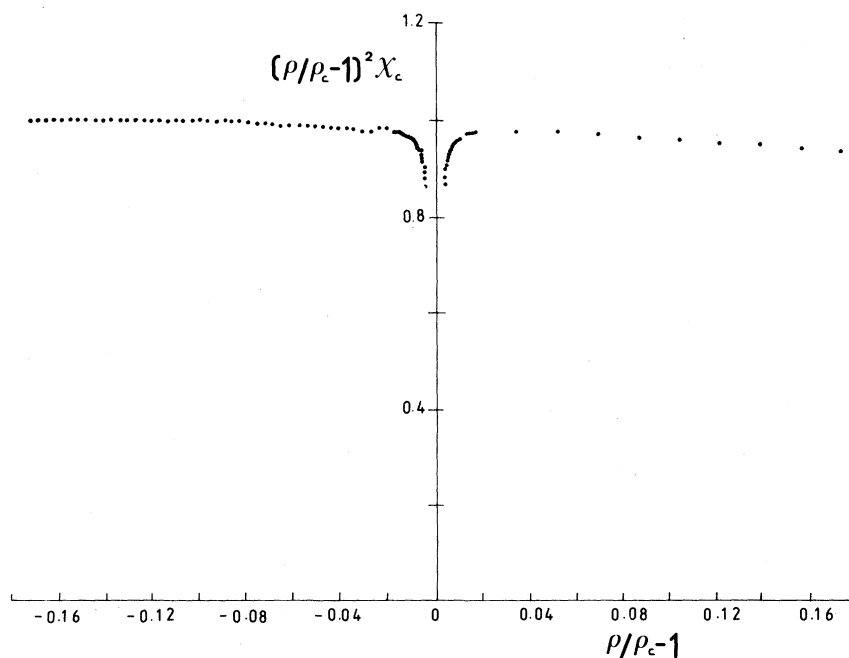


FIG. 2. $(\rho/\rho_c - 1)^2 \chi_c$ vs $(\rho/\rho_c - 1)$ for a LJ interaction according to the PY equation. The points correspond to the results obtained.

The reason for this apparent discrepancy is the following. As said above, the nonlinear behavior in Fig. 1 is associated with the error in the determination of the critical temperature, whereas in Fig. 2 the strong variation is due to the uncertainty of both the critical temperature and the critical density. In other words, even if we had two straight lines joining themselves for $\chi_c^{-1/2}=0$, but $\rho-\rho_c=0$, we would have almost the same variation in Fig. 2. To be more explicit, let us consider

$$A(\rho) = (\rho/\rho_c - 1)^2 \chi_c(\rho), \quad T = T_c, \quad (5)$$

and assume that if T_c and ρ_c are the exact critical temperature and density, $A(\rho)$ becomes ρ independent. We are going to study the quantity

$$A^*(\rho) = (\rho/\rho_c^* - 1)^2 \chi_c(\rho), \quad T = T_c, \quad (6)$$

where $\rho_c^* = \rho_c + \Delta\rho_c$ is the approximate value used for the critical density. From (3) we have that $\Delta\rho_c/\rho_c \approx 3.47 \times 10^{-4}$. A simple calculation shows

that

$$\Delta A(\rho)/A(\rho) = 2(1+1/x)\Delta\rho_c/\rho_c, \quad (7)$$

with $\Delta A(\rho) = A^*(\rho) - A(\rho)$ and $x = \rho/\rho_c - 1$. Considering Eq. (7) for small values of x it is seen that the behavior shown in Fig. 2 can be explained by the uncertainty in the value of the critical density.

We conclude that the deviation of the PY equation from the classical behavior is reduced to a class of special models of potentials (even though the classical values of the critical exponents can be obtained with these model potentials). Of course, it would be interesting to determine the interaction potentials belonging to this class.

ACKNOWLEDGMENT

It is a pleasure to thank Professor M. E. Fisher for a critical reading of the manuscript and for suggesting to us to relate the two nonlinear regions in Figs. 1 and 2.

¹R. J. Baxter, J. Chem. Phys. 49, 2770 (1968).

²S. Fishman and M. E. Fisher, Physica (Utrecht) 108A, 1 (1981).

³M. E. Fisher and S. Fishman, Phys. Rev. Lett. 47, 421 (1981).

⁴D. Henderson and R. D. Murphy, Phys. Rev. A 6, 1224 (1972).

⁵J. J. Brey, A. Santos, and L. F. Rull, Phys. Lett. 67A, 383 (1978).