Journal of Statistical Physics, Vol. 1, No. 1, 1969

Note on the Quantum Displacement of the Critical Point

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Received March 12, 1969

The quantum corrections to the law of corresponding states are studied by calculating the critical pressure, temperature, and density to first order in Planck's constant h on an exactly soluble model. The ratio of the critical parameters to the corresponding classical values are found to be $(p_c/p_c^0)^{1/2} = \rho_c/\rho_c^0 = T_c/T_c^0 = 1 - 0.67\Lambda$, with $\Lambda = h\rho_c^{1/3}(mkT_c)^{-1/2}$. The critical ratio is independent of h to first order. The results are compared with critical data for noble gases and hydrogen isotopes.

KEY WORDS: Critical point; Equation of state; Quantum effects; Corresponding states; Fluids.

1. INTRODUCTION

Assume that the intermolecular potential between each pair of particles in a fluid is of the form

$$\varphi(r) = \epsilon\psi(r/\sigma) \tag{1}$$

where ψ is a universal function, and σ (of dimension length) and ϵ are parameters varying from one substance to another. It is well-known prediction of *classical* statistical mechanics that all substances for which (1) holds have the same equation of state

$$p^* = p^*(\rho^*, T^*) \tag{2}$$

in terms of the reduced number density $\rho^* = \rho\sigma^3$, temperature $T^* = kT/\epsilon$, and pressure $p^* = p\sigma^3/\epsilon$. In particular the critical values ρ_c^*, p_c^* are universal.

Byk[(1)] suggested that quantum deviations from this principle of corresponding states occur, and proposed to use the dimensionless combination $h\rho_c^{1/3}(mkT_c)^{-1/2}$ as a measure of the quantum nature of a fluid. Experimental data[(2)] on light fluids

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(inert gases and hydrogen isotopes) support Byk's suggestion; $\rho_c{}^*$, $T_c{}^*$, and p_c^{*-1} become *systematically* smaller with increasing values of the Byk combination. As emphasized by de Boer,$^{(3)}$ the Byk parameter is not ideally suited for the study of quantum effects because the critical parameters ρ_c and T_c are themselves influenced by quantum phenomena.[2] A better choice for the quantum parameter is

$$\Lambda = h\rho_c^{0\frac{1}{3}}(mkT_c^0)^{-1/2} \tag{3}$$

where the superscript ^{0} always denotes the corresponding *classical* value. Then Λ is exactly proportional to $m^{-1/2}$.

The purpose of this note is to present a model calculation of the functions $\rho_c{}^*(\Lambda)$, $T_c{}^*(\Lambda)$, and $p_c{}^*(\Lambda)$ to first order in Λ. We were inspired by a recent study$^{(4)}$ of the critical properties of a one-dimensional model, *viz.*, hard rods with weak, long-range attraction. The one-dimensional model yielded results in qualitative agreement with experiments, but of course the three-dimensional version studied below is more relevant.

2. MODEL CALCULATION

The model is a quantum gas with an intermolecular potential consisting of a hard core of diameter d, plus a very weak long-range attraction $\varphi_a = \gamma^3 F(\gamma r)$. Lieb$^{(5)}$ has proved that in the so-called van der Waals limit $\gamma \to 0$ the equation of state is given by

$$p = p_h - a\rho^2 \tag{4}$$

Here p_h is the pressure of quantum hard-sphere gas, and $a = -\frac{1}{2}\int \varphi_a(r)\,dr$ is the "integrated strength" of the attraction, a finite quantity in the van der Waals limit.

The equation of state of the quantum hard-core gas is known exactly in one dimension, but the first quantum correction to the classical equations of state of hard spheres was determined only very recently.$^{(6)}$ The result is

$$p_h(\rho, T) = p_h{}^0(\rho, T) + \frac{3\lambda}{2\sqrt{2}d}\left(1 - \rho\frac{\partial}{\partial\rho}\right)p_h{}^0(\rho, T) + O\left(\frac{\lambda}{d}\right)^2 \tag{5}$$

to first order in the ratio of the thermal de Broglie wavelength $\lambda = h(2\pi mkT)^{-1/2}$ to the diameter d of the hard core.

We now determine the influence of the quantum correction of Eq. (5) by considering it a perturbation upon the classical limit of Eq. (4), *viz.*,

$$p^0 = p_h{}^0 - a\rho^2 \tag{6}$$

Using the fact that $p_h{}^0/kT$ is a function $\chi(\rho)$ of the density only, we have in the immediate neighborhood of the critical point[3]

$$\Delta p = k\chi_c\,\Delta T + k\chi_c{}'\,\Delta T\,\Delta\rho + \tfrac{1}{2}k\chi_c''\,\Delta T\,\Delta\rho^2 + \tfrac{1}{6}kT_c\chi_c'''\,\Delta\rho^3 \tag{7}$$

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[2] We are grateful to Professor J. de Boer for a helpful comment on this point.

[3] This expansion is possible since Eq. (6) is analytic at the critical point, a property almost certainly not shared by the equation of state of real fluids.

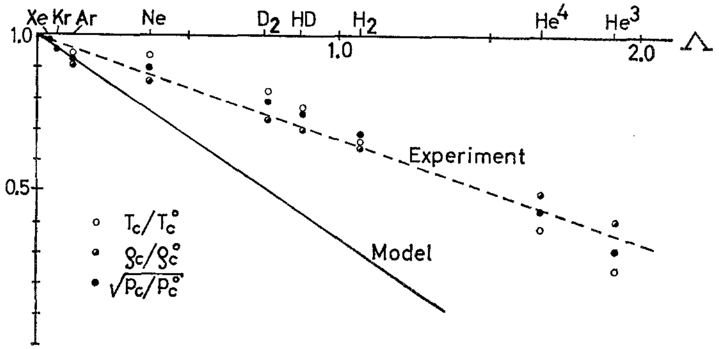

Fig. 1. The reduced critical temperature, density, and pressure for light fluids.[2] The classical values have been determined by requiring the experimental curve (dashed line) to fit the data for xenon.

Here $\Delta p = p - p_c^0$, $\Delta T = T - T_c^0$, and $\Delta\rho = \rho - \rho_c^0$ measure the deviations from the *classical* critical point. Perturbation of this equation with the quantum correction of Eq. (5) yields the following critical displacements:

$$\begin{aligned} \Delta p_c &= -p_c^0 \frac{3\lambda}{\sqrt{2}d} \\ \Delta T_c &= -T_c^0 \frac{3\lambda}{2\sqrt{2}d} \\ \Delta\rho_c &= -\rho_c^0 \frac{3\lambda}{2\sqrt{2}d} \end{aligned} \tag{8}$$

In terms of the parameter Λ this means that

$$\sqrt{p_c/p_c^0} = \rho_c/\rho_c^0 = T_c/T_c^0 = 1 - \frac{3}{4\sqrt{\pi}\,\rho_c^{0\frac{1}{3}}\,d}\Lambda \tag{9}$$

to first order in Λ. Numerically the classical critical density is[4] $\rho_c^0 \simeq 0.25d^{-3}$, so that the right-hand side of Eq. (9) equals $1 - 0{,}67\Lambda$.

3. DISCUSSION

Equation (9) predicts that $\sqrt{p_c/p_c^0}$, ρ_c/ρ_c^0, and T_c/T_c^0 *decrease* with Λ, to first order *linearly* and *in the same way.* Figure 1 shows that the experimental data are in qualitative agreement with this theoretical prediction. However, the slope of the theoretical curve is too steep, and the data favor a coefficient of Λ closer to -0.35.

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[4] To obtain this value we need the classical equation of state for hard spheres. Up to the critical density both the seventh-term virial expansion and the Percus–Yevick equation are excellent representations of the hard-sphere pressure, and both yield the quoted result. The exact Percus–Yevick value is $\rho_c = (\sqrt{73} - 7)/2\pi d^3$.

The one-dimensional version of the model yeilds $1 - 0.42\Lambda + O(\Lambda^2)$ for the ratios (9). We must conclude, therefore, that the very good agreement obtained by Burke *et al.*(4) with the one-dimensional model is accidental.

Furthermore, from the basic result given in Eq. (9) follows that the critical ratio $\kappa_c = p_c/\rho_c kT_c$ has no first-order dependence upon Λ,

$$\kappa_c = \kappa_c{}^0 + O(\Lambda^2) \tag{10}$$

This may be taken as an encouraging result since the experimental values of κ are almost constant (κ increases only 5 % from Xe to He^3).

As a final point, note that the quantum displacements discussed above imply *isotopic* shifts, each isotope having its own distinct critical point. (In addition, of course, the interactions between the various isotope species will differ slightly from one another.) For Xe, which displays a range of isotopes from Xe^{124} at 0.1 % abundance to Xe^{136} at 9 % abundance, Eq. (9) predicts a shift of the critical temperature equal to 0.03° per atomic weight unit, a large effect compared with present-day measuring accuracy.

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