

## Equation of state for "classical" helium

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(Received 28 September 1992)

A classical base-line equation of state for fluid helium is calculated from a recent accurate pair potential and a classical statistical-mechanical theory. The range covered is 2.5–1400 K and densities up to 90 mol/dm<sup>3</sup>. Comparison with experimental data shows how quantum effects in <sup>4</sup>He behave in the dense-fluid region. A pseudoclassical calculation based on experimental second virial coefficients fails to account for the high-density quantum effects. The volume expansion caused by zero-point motion can be directly seen in the curvature of the Zeno line.

PACS number(s): 05.70.-a, 67.20.+k, 64.30.+t

In discussing quantum effects in fluids, it is useful to have an accurate classical result as a base line. Such a result has usually been calculated with a pairwise additive Lennard-Jones (12,6) potential [1–3]. For example, Barocchi, Neumann, and Zoppi [4] calculated the thermodynamic properties of quantum fluids by the Wigner-Kirkwood expansion up to order  $h^6$ , using as a base line the classical equation of state (EOS) for a Lennard-Jones fluid [3]. Unfortunately, the Lennard-Jones potential give only a rather crude representation of the pair potentials of real substances.

Two recent results make possible an easy improvement of this situation for helium. One is the development of an accurate pair potential for helium [5,6] and the other is the derivation of a statistical-mechanical classical EOS for simple fluids at all densities [7].

We have used these results to calculate the base-line classical EOS for fluid helium, which is the same for both <sup>4</sup>He and <sup>3</sup>He, from 2.5 to 1400 K and densities up to 90 mol/dm<sup>3</sup> (1 dm<sup>3</sup> ≡ 1 liter). Comparison with experimental  $p$ - $v$ - $T$  data then gives information on the quantum effects.

Another way to estimate quantum effects is to simulate a real quantum fluid as a fictitious classical one by means of an effective potential [2,8]. The present EOS furnishes a convenient procedure for such a pseudoclassical calculation, since it allows the entire fluid  $p$ - $v$ - $T$  surface to be calculated from just the experimental second virial coefficient as a function of temperature [7]. We find that this procedure produces an improvement over the completely classical result calculated directly from the pair potential, but that it still fails to fit the experimental data.

In all studies involving base-line classical results, it has not been possible to separate the effects of many-body forces from the quantum effects, because too little is known about such forces. However, some indication of their relative importance can be obtained from a new strong principle of corresponding states obtained from the statistical-mechanical EOS [9]. Application to the heavy noble-gas fluids indicates that many-body forces can have significant effects on the EOS (e.g., up to a maximum of about 10% at densities of the order of the critical density, and less at both lower and higher densities

[9]), but their magnitude is much less than the quantum effects in helium at temperatures below about 50 K.

The EOS has the form [7]

$$\frac{p}{\rho kT} = 1 + B_2 \rho + \alpha \rho [g(\sigma^+) - 1], \quad (1)$$

where  $p$  is the pressure,  $\rho$  is the number density,  $kT$  has its usual meaning,  $B_2$  is the second virial coefficient,  $\alpha$  is a temperature-dependent scaling factor for the softness of the interatomic repulsive forces, and  $g(\sigma^+)$  is the pair distribution at contact for equivalent hard spheres of diameter  $\sigma$ , a diameter which is temperature dependent. The quantities  $B_2$ ,  $\alpha$ , and  $\sigma$  are related to the interatomic potential  $u(r)$  by integration,

$$B_2(T) = 2\pi \int_0^\infty [1 - e^{-u(r)/kT}] r^2 dr, \quad (2)$$

$$\alpha(T) = 2\pi \int_0^{r_m} [1 - e^{u_0(r)/kT}] r^2 dr, \quad (3)$$

$$\frac{2}{3}\pi\sigma^3 \equiv b(T) = \alpha + T \frac{d\alpha}{dT}. \quad (4)$$

Here  $u_0(r)$  is the repulsive part of  $u(r)$ ,

$$u_0(r) = \begin{cases} u(r) + \varepsilon, & r < r_m \\ 0, & r > r_m \end{cases}, \quad (5)$$

where  $\varepsilon$  is the depth of the potential well and  $r_m$  is the position of its minimum. This is the Weeks-Chandler-Andersen [10] decomposition of  $u(r)$ . Notice that  $\alpha$  is just the contribution of the repulsive forces to  $B_2$  and that  $b$  is an equivalent van der Waals covolume. For  $g(\sigma^+)$  we have used the Carnahan-Starling expression [11],

$$g(\sigma^+) = \frac{1 - \eta/2}{(1 - \eta)^3}, \quad (6)$$

where  $\eta = b\rho/4$  is the packing fraction.

For the completely classical calculation we have used the LM2M2 helium potential recommended by Aziz and Slaman [6], with  $\varepsilon/k = 10.97$  K and  $r_m = 2.9695$  Å. For the pseudoclassical calculation we have taken the experimental values of  $B_2(T)$  for <sup>4</sup>He from the International Union of Pure and Applied Chemistry compilation [12].

In particular, we used  $B_2(T)$  to determine the Boyle temperature  $T_B=22.48$  K and the Boyle volume  $v_B=18.16$  cm<sup>3</sup>/mol, and used these values to find  $\alpha(T)$  and  $b(T)$  from tables based on a (12,6) potential [7]. The parameters  $\alpha$  and  $b$  are insensitive to details of the shape of  $u(r)$ . For comparison, the classical values of the Boyle parameters calculated from the LM2M2 potential are  $T_B=33.75$  K and  $v_B=18.84$  cm<sup>3</sup>/mol.

Calculated and experimental  $p$  vs  $\rho$  plots are shown in Figs. 1–4 for fluid <sup>4</sup>He. The experimental uncertainty is less than the size of the symbols. For the high-temperature result shown in Fig. 1 the classical and pseudoclassical calculations are essentially indistinguishable, and both are in good agreement with the IUPAC compilations [12]. Quantum deviations become quite noticeable at high densities at 50 K (Fig. 2), and are relatively enormous at 10 K and below (Figs. 2–4). The effect of many-body forces on the classical calculations is to lower the calculated pressure, at least up to densities about three times the critical density [9], which would increase the discrepancy between the calculated and experimental results. That is, the many-body effects tend to conceal the quantum effects at high densities. For reference the critical constants of <sup>4</sup>He are  $T_c=5.2014$  K,  $p_c=2.2746$  bar, and  $\rho_c=17.399$  mol/dm<sup>3</sup> [12]. The pseudoclassical calculations move the isotherms in the right direction, but are still far from the experimental points, except at low densities where  $B_2$  dominates.

In Fig. 5 we show the Zeno contours, the locus of  $T$  vs  $\rho$  points at which the compression factor,  $Z \equiv p/\rho kT$ , is unity. (The intercept on the  $T$  axis is the Boyle temperature  $T_B$ ). The Zeno contour has been found to be nearly linear for a wide variety of normal fluids [13,14], and also for the strong principle of corresponding states [15]. The

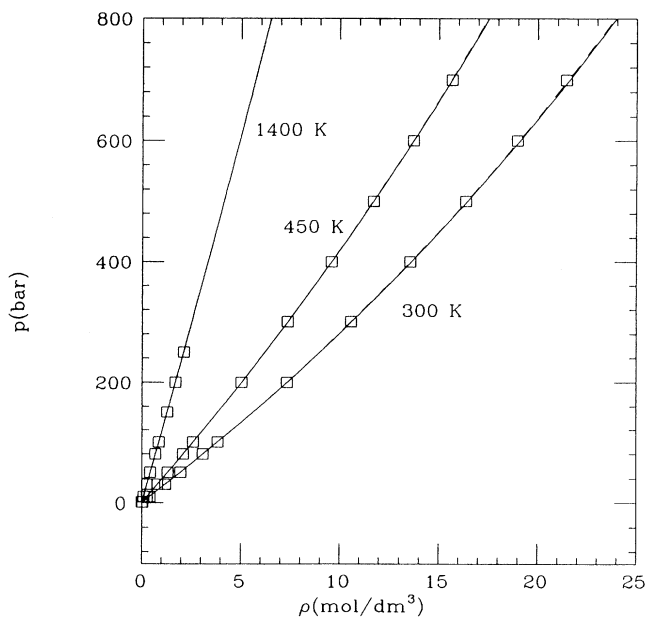


FIG. 1. High-temperature  $p$ - $\rho$  isotherms for <sup>4</sup>He. The curves are the classical calculation and the points are from the IUPAC compilation [12]. 1 dm<sup>3</sup>  $\equiv$  1 liter.

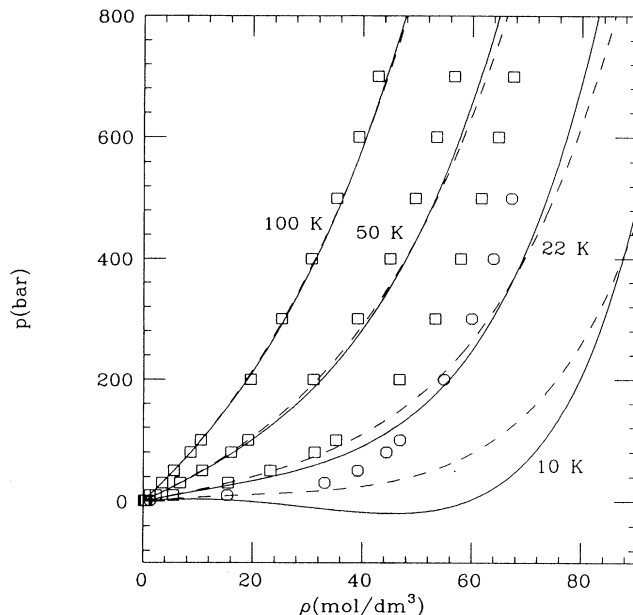


FIG. 2. Intermediate-temperature  $p$ - $\rho$  isotherms for <sup>4</sup>He. The solid curves are classical and the dashed curves are pseudoclassical. The points are from Ref. [12], with those for 10 K shown as circles.

calculated classical and pseudoclassical contours are concave upward, whereas the experimental contour curves strongly downward. This seems to be clearly a quantum effect, in which the volume at a given temperature is expanded by the zero-point motion, reducing the density. Also shown in Fig. 5 is the empirical Zeno contour for

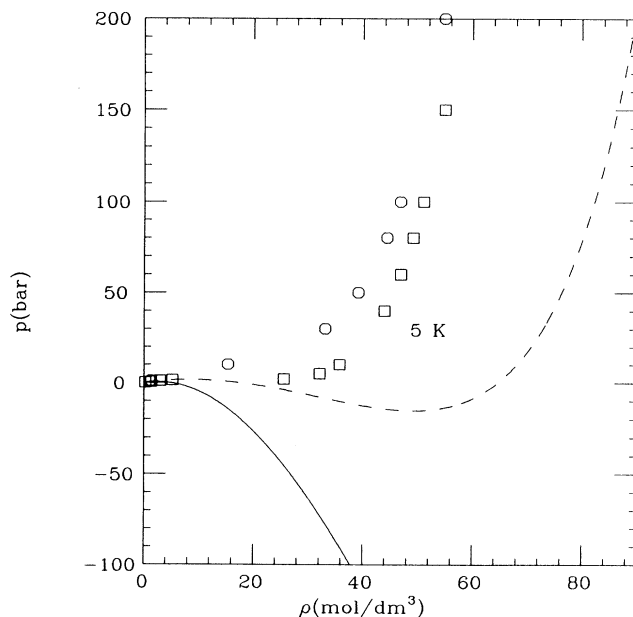


FIG. 3. Same as Fig. 2, for 5 K. The 10-K points (circles) are repeated to facilitate comparison with Fig. 2.

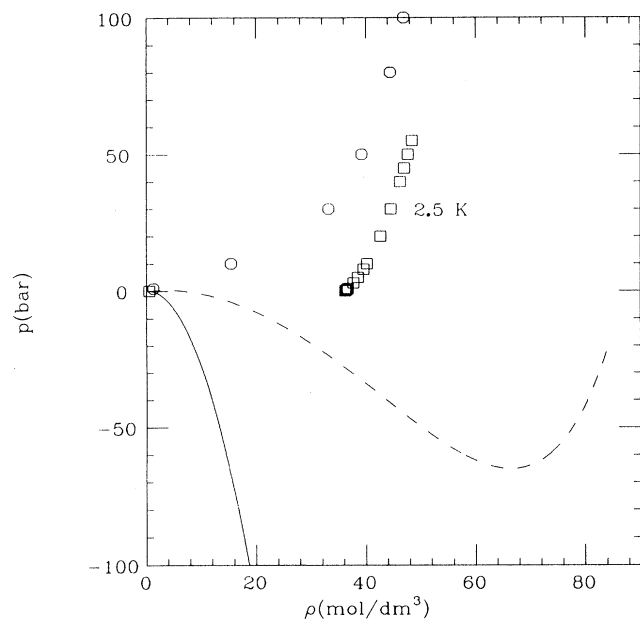


FIG. 4. Same as Fig. 3, for 2.5 K.

the heavy noble-gas fluids, scaled to the classical  $T_B$  and  $v_B$  of He, which is indeed nearly straight [15].

Another route to a classical base-line EOS would be to scale the empirical data for the classical noble-gas fluids (Ar, Kr, Xe). For example, reduced plots of  $pr_m^3/\epsilon$  vs  $\rho r_m^3$  for reduced isotherms  $kT/\epsilon$  of the classical fluids would serve as the base line for similar plots for He. Although this would no doubt be an improvement over use of the Lennard-Jones potential, we prefer the present procedure for two reasons. First, it is still necessary to know accurate scaling factors  $\epsilon$  and  $r_m$  from a potential for He; if one has an accurate potential, it is just as easy to do the numerical integrations to find  $B_2$ ,  $\alpha$ , and  $b$ , as we have done. Second, the procedure requires that the noble-gas potentials all have the same shape—that is, the potentials would coincide when plotted as  $u/\epsilon$  vs  $r/r_m$ . While this is almost the case [16], there are quite noticeable devia-

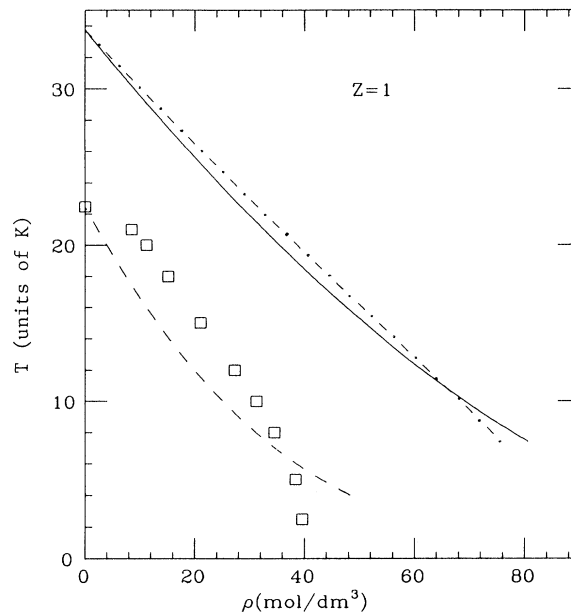


FIG. 5. Zeno contours ( $T$  vs  $\rho$  for  $Z \equiv p/\rho kT = 1$ ) for  $^4\text{He}$ . Solid curve is classical, dashed curve is pseudoclassical, points are experimental [12], and dashed-dotted curve corresponds to Ar, Kr, Xe.

tions from such a universal shape [17–19].

To summarize, a classical base-line EOS for fluid helium has been calculated from an accurate pair potential and statistical-mechanical theory. As expected, quantum effects are large at low temperatures, and especially at high densities. The results can serve as a base line for the calculation of quantum effects, for example, by a Wigner-Kirkwood expansion. A pseudoclassical calculation using experimental second virial coefficients fails to account for the quantum effects at high densities. The unusual deviation from linearity of the Zeno contours can be explained as the result of volume expansion caused by zero-point motion.

We thank Dr. Steven Rick for his help.

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