Quantum corrections for the liquid-gas transition of Lennard-Jones particles in two dimensions

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The quantum corrections in first-order perturbation theory are semiquantitatively reproduced in the low temperature behavior of the liquid-gas coexistence curve of the simulations—at least for reduced masses down to $m^*=50$.

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I. INTRODUCTION

The mass effect on the phase diagram of a fluid at temperatures below the critical temperature is of great interest. The phase diagram of two-dimensional Lennard-Jones fluids in mass regions where exchange effects are negligible has only been obtained recently [1] by path integral Monte Carlo (PIMC) simulations [2]. By simulation methods the coexistence region can be computed quantitatively correctly. In order to see how well such quantum effects on the phase diagram can be estimated approximately we have used in addition a perturbative approach.

II. THE MODEL AND THE SIMULATION

We study the behavior of a Lennard-Jones system in two dimensions at different reduced masses $m^*=m/(\hbar^2/\varepsilon\sigma^2)$. For comparison, for three dimensions a reduced mass of 1148 corresponds to argon and 112 to neon [2].

In order to compute the phase diagram we use the path integral Monte Carlo method [2] for particles with mass m interacting with Lennard-Jones potentials. In Ref. [2] Ceperley derived, by comparing the quantum delocalization length scale at a given temperature T with the average distance between particles at a given density ρ, an expression for the degeneracy temperature $T_D=\rho\hbar^2/mk_B$, below which effects due to quantum statistics can be expected. Our fluid density is always below the value $\rho^*=\rho\sigma^2=1$, and with this density we obtain an upper bound for the degeneracy temperature $T_D^*=k_BT_D/\varepsilon=1/m^*$. For reduced masses 100 and 50 we investigated the gas-liquid coexistence region for temperatures above $T^*=0.3$, which is well above T_D^*, for $m^*=10$ we show the resulting phase diagram as well for comparison, neglecting quantum statistics. The Trotter index in the PIMC simulations has been chosen to be 5, 20, and 75 for the reduced masses 100, 50, and 10, respectively, approximating sufficiently well the quantum limit. The number of quantum particles was 576, by which a direct comparison with earlier simulations of the phase diagram [3] became possible for the classical case, and good agreement was found. The liquid-gas coexistence curve was computed by subdividing the simulation box of size $S\times S$ in subsystems of size $L\times L$, taking histograms $P_L(\rho)$ of the density ρ in subsystems, and mapping the histogram maxima in the density-temperature plane. The results for the phase diagram presented here are obtained with $S/L=8$, a typical run for a data point of the phase diagram took about 10^6 Monte Carlo steps.

The phase diagram is shown in Fig. 1. In Fig. 1 the coexistence region is shown for masses $m^*=10$, 50, 100, and in the classical limit. Due to the quantum delocalization the phase transition temperature decreases with smaller particle masses and the resulting coexistence region is reduced. The ordering phenomena can be studied by the order parameter $\phi=\rho_l^*-\rho_g^*$, the difference in densities of the liquid and gas, as a function of the temperature, see Fig. 2.

III. FREE ENERGY AND PERTURBATION THEORY

In order to compute the phase diagram we approximated the free energy for hard disks in the Percus-Yevick (PY) or hypernetted chain (HNC) closure [4–7] and treated quantum effects in first-order perturbation theory [8]

$$f=f_{cl}+\frac{\hbar^2}{24(k_BT)^2}2\rho\frac{1}{m}\frac{\rho}{4}\int u'(r)g_{HS}(r)2\pi r dr \qquad (1)$$

with

$$f_{cl}=\rho^2\int u(r)g_{HS}(r)2\pi r dr. \qquad (2)$$

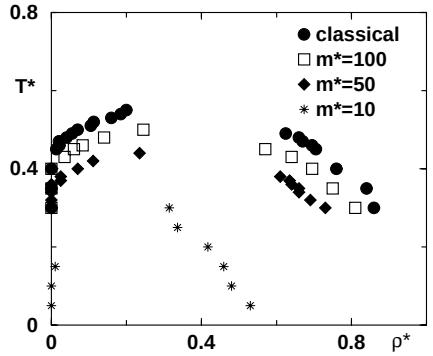

FIG. 1. Phase diagram for Lennard-Jones particles with reduced masses $m^*=10,50,100$, and in the classical limit (path integral Monte Carlo simulations).

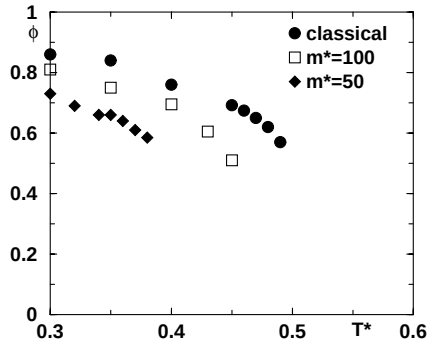

FIG. 2. Order parameter vs temperature, PIMC simulations.

The hard disk correlation function $g_{HS}(r)$ has been computed iteratively in the PY or HNC closure with a reference system with an effective hard disk diameter [9,10] of $d(T) = \int_0^\sigma dr(1-\exp[-\beta u(r)])$.

The liquid-gas coexistence region has been computed by the double-tangent method to the free energy. The resulting phase diagram is shown in Fig. 3. In the low temperature region we get semiquantitative agreement between the results in the PY approximation [Fig. 3(a)]; the results in the HNC approximation are slightly worse due to the fact that the PY can approximate the hard disk system better. In the region of the critical temperature however (Fig. 3) both closures cannot obtain the proper shape of the coexistence curve and the correct critical exponents due to the diverging correlation length.

The order parameter is presented in Figs. 2 and 3. At low temperatures we obtain semiquantitative agreement with the simulation data, at higher temperatures, however, the perturbation theory overestimates the coexistence region due to the molecular field character of the perturbation approach.

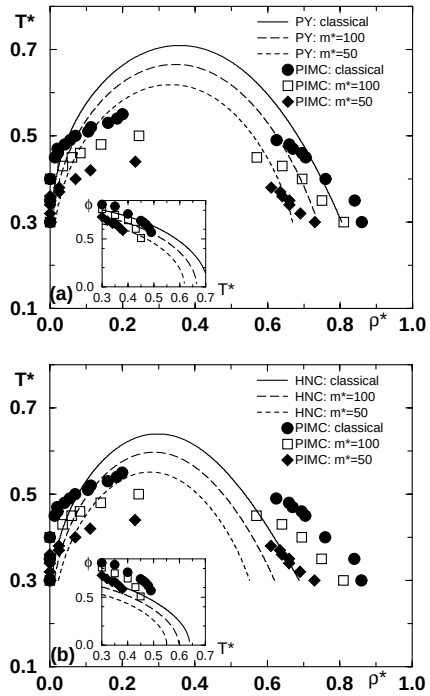

FIG. 3. Phase diagram for Lennard-Jones particles with reduced masses $m^*=50$, 100, and in the classical limit, obtained by PIMC (symbols) and in the PY approximation (a) and the HNC approximation (b). Insets show the order parameters vs temperature.

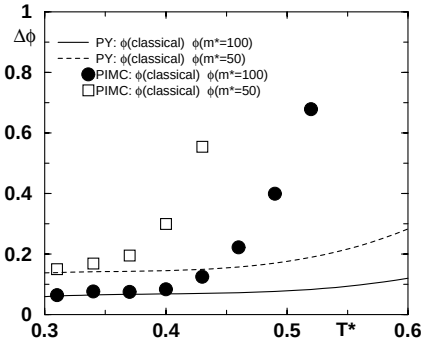

FIG. 4. Order parameter differences $\Delta\phi$ of systems with different reduced masses vs temperature. The upper curves at $T^*=0.3$ correspond to the difference in the order parameters for the classical limit and $m^*=50$, the lower curve between the classical limit and $m^*=100$. The results are obtained by fits through the order parameter data.

IV. DISCUSSION

The phase diagram shows interesting mass-dependent phenomena. In particular the coexistence region is shifted to smaller temperatures with decreasing masses. In order to analyze to what extent the perturbation theory can estimate the quantum effects we have computed the phase diagram and the order parameter in perturbation theory, taking the hard disk system with an effective diameter as reference system. In first-order perturbation theory we obtain surprisingly semiquantitative agreement with simulation data for the coexistence region and the order parameter. Of course this crude approximation has its limitations. In particular the critical exponents are the mean-field exponents in contrast to the exact exponents. Thus close to the critical temperature the approximate treatment is not reliable and the critical parameters are not correct. We do however get semiquantitative agreement for the liquid and gas densities with simulation results at low temperatures. In particular the differences between the order parameter values for systems with different particle masses are in semiquantitative agreement with the simulation results, as shown in Fig. 4. This shows that the main problem is the computation of the proper free energy of the reference system, the quantum corrections are treated well within first-order perturbation theory, at least for particle masses down to $m^*=50$. If the particle masses are much smaller, first-order perturbation theory cannot treat the quantum effects correctly, for example, see the phase coexistence curve for $m^*=10$ in Fig. 1.

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