Isotopic Shift of Helium Melting Pressure: Path Integral Monte Carlo Study

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We compute by a path integral Monte Carlo calculation the isotopic shift of helium melting pressure in the temperature range ($T > 100$ K) where a discrepancy between theory and experiment has been recently reported. We use a realistic Aziz pair potential together with Bruch-McGee three-body forces for the interaction. The isotopic shift predicted in this work is in agreement with experiment; its measurement provides a good test of the interatomic potential of helium, as the isotopic shift is sensitive to the kinetic energy, which is determined by the short-range pair interaction.

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Quantum effects [1] cause the two helium isotopes (^{4}He and ^{3}He) in the solid phase to melt at two slightly different pressures, π_4 and π_3. A path integral Monte Carlo (PIMC) calculation [2] yielded an isotopic shift $\Delta\pi = \pi_3 - \pi_4$ monotonically decreasing in the 0–250 K temperature range, becoming negative at $T \approx 100$ K; in this study an effective pair potential was used for the atomic interaction [3] reproducing a number of experimental high-pressure data. However, recent diamond-anvil-cell measurements of the melting curves of ^{4}He and ^{3}He show a behavior of $\Delta\pi$ in marked qualitative disagreement with the above predictions. The experiment finds that $\Delta\pi$ attains a minimum (close to zero) at $T \approx 180$ K and increases at higher temperatures [4]. Thus there is a puzzle in understanding the simplest quantum solid.

There is an exact relationship between $\Delta\pi$ and the difference between the kinetic energy of the solid and liquid phases at melting, if one neglects the effect of the nuclear statistics, which is small at these densities. For a given temperature T, let $f_\alpha(x)$ and $v_\alpha(x)$ be the free energy and volume per particle at melting of the isotope of mass $m = 1/x$ in the phase α, with $\alpha = S$ (solid) or L (liquid). Then, the equation of phase equilibrium is

$$f_S(x) + \pi(x)v_S(x) = f_L(x) + \pi(x)v_L(x),\qquad(1)$$

$\pi(x)$ being the melting pressure. But the derivative of the free energy with respect to x is proportional to the kinetic energy of the nuclei, since the inverse mass is the coupling constant in the (nonrelativistic) Hamiltonian: $(\partial f_\alpha/\partial x)_V = k_\alpha(x)/x$. Taking the derivative with respect to x of each side of (1) at constant volume and integrating from $x_4 = 1/m_4$ to $x_3 = 1/m_3$, one obtains

$$\Delta\pi = \int_{x_4}^{x_3} \frac{dx}{x} \frac{k_S(x,v_S(x)) - k_L(x,v_L(x))}{v_L(x) - v_S(x)}.\qquad(2)$$

The denominator of the integrand is positive, slowly varying with mass, and can be determined independently from experiment. Hence, the measurement of the isotopic shift is essentially a measurement of the kinetic energy difference between the coexisting liquid and solid phases.

Figure 1 shows calculated kinetic energies per atom for the two isotopes of helium in the liquid and solid phases, at 250 K. We first note that the kinetic energy is higher than its classical value, 375 K, by 40% in ^{3}He and 30% in
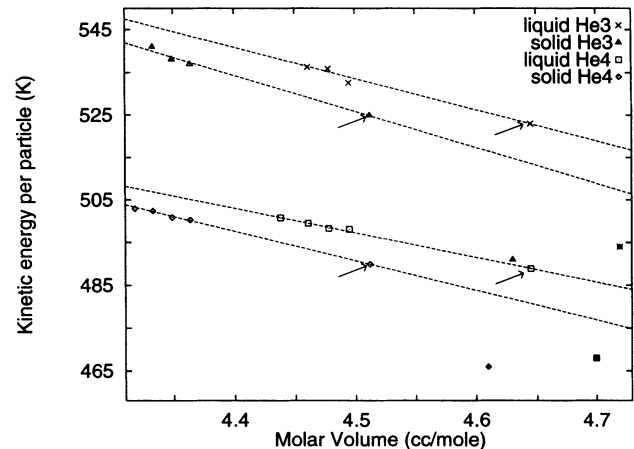

FIG. 1. Kinetic energies per particles (K) vs molar volume (cm^3/mole) computed by PIMC, at $T = 250$ K, for solid (diamonds) and liquid (squares) ^{4}He and for solid (triangles) and liquid (crosses) ^{3}He. Dashed lines are linear fits to the data. Arrows point to the values obtained in the solid (liquid) phase of both isotopes at the experimental melting density of solid (liquid) ^{4}He. Also shown for comparison are the kinetic energy values from Ref. [2] for solid (filled triangle) and liquid (star) ^{3}He and for solid (filled diamond) and liquid (filled square) ^{4}He.

⁴He. Thus, quantum effects are important even at this high temperature. We also see that there is a strong dependence on density, mass, and phase. Remarkably, the kinetic energy in the liquid is higher than in the solid, at the same density. In the solid the particles keep away from their neighbors more effectively (as revealed by the pair correlation function) and this causes a slight lowering of the kinetic energy. For coexisting liquid and solid phases, the solid has a slightly greater kinetic energy due to its higher density; however, there is clearly a delicate cancellation which may account for the negative value of $\Delta\pi$ found in Ref. [2]. In Fig. 1 we also report for comparison the kinetic energies calculated in Ref. [2] at the estimated melting densities; they are lower than ours by as much as ∼25 K (for liquid ³He). The isotopic shift is rather small (∼0.2% of the melting pressure) and can only be resolved by determining the kinetic energy to better than 0.1%. The shift is also very sensitive to the volume change at melting.

We have carried out PIMC calculations to obtain these kinetic energies assuming a semiempirical pair and three-body potential. Using (1) we have obtained estimates for $\Delta\pi$ in excellent agreement with experiment: at $T=250$ K we find $\Delta\pi=21\pm5$ MPa, to be compared with the experimental value 25 ± 15 MPa [4]. At $T=300$ K, for which no experimental data are available yet, we find $\Delta\pi=41\pm7$ MPa. In the remainder of this Letter we first motivate our choice of the interatomic potential; we then describe the main elements of the PIMC method and details of the calculation of the isotopic shift and finally discuss our results.

We begin by making the Born-Oppenheimer approximation. Our elementary particles are distinguishable helium atoms interacting via a semiempirical potential. Thus the kinetic energy that we compute is of an atom, not strictly of the nucleus. The determination of a potential to describe the interactions among atoms in helium has been the goal of a long-lasting research effort. Aziz and collaborators [5] have carefully combined all theoretical and experimental gas phase data on the interaction of two atoms to obtain a highly reliable pair potential, which has proven itself adequate to describe the energetic and structural properties of liquid ⁴He in the superfluid regime. At higher density, calculations based upon it predict equilibrium pressures significantly higher than the ones experimentally measured. This fact signals the existence of attractive many-body forces [6]. The effective potential approach [3] attempts to incorporate many-body effects into a pair potential whose parameters are determined by fitting high-pressure experimental data.

Another way of treating interactions of many atoms is to include them explicitly as three-body terms in the interatomic potential; extensively studied ab initio three-body contributions are the triple-dipole Axilrod-Teller [7] and the effects related to the changes in the electronic clouds of two interacting atoms due to the presence of a third one. The Bruch-McGee potential [8] combines

these two contributions in the following expression:

$$\hat{V}_3 = [-Ae^{-a(r+s+t)} + C(rst)^{-3}]f(t_1,t_2,t_3), \qquad (3)$$

where r,s,t are the sides and t_1,t_2,t_3 the angles of the triangle formed by three atoms and $f(t_1,t_2,t_3) = 1 + 3\cos(t_1)\cos(t_2)\cos(t_3)$. The interaction $\hat{V}_3$, together with the Aziz two-body potential [5], was shown by Loubeyre [9] to yield a reasonable quantitative description of ⁴He, in the 1-10 GPa pressure range. In Fig. 2 we show the good agreement with available experimental data on liquid and solid ⁴He up to pressures of 17 GPa. We obtained such an agreement by adjusting the constant A to a value equal to $\frac{2}{3}$ of the value given in Ref. [9]; for the other constants we use the values suggested in the same reference. It is worth mentioning that no agreement exists as to the exact values of the constants, and even the analytical form of the potential (3) may be questionable [10].

Next we give an outline of the PIMC method (for a thorough description, see, for instance, [11]), a well-established computational tool which can calculate exact properties of quantum many-particle systems at finite temperature. Given a system of N particles, characterized by a Hamiltonian $\hat{H}$, the average of a physical observable $\hat{O}$ is

$$\langle O \rangle = \frac{1}{Z} \int d\mathbf{R}\, O(\mathbf{R}) \rho(\mathbf{R},\mathbf{R};\beta), \qquad (4)$$

where $\mathbf{R} \equiv \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ are the coordinates of the N particles, $\rho(\mathbf{R},\mathbf{R};\beta) = \langle \mathbf{R} | e^{-\beta\hat{H}} | \mathbf{R} \rangle$ (with $\beta = 1/kT$) is the many-body density matrix, and $Z = \int d\mathbf{R}\, \rho(\mathbf{R},\mathbf{R};\beta)$ is the
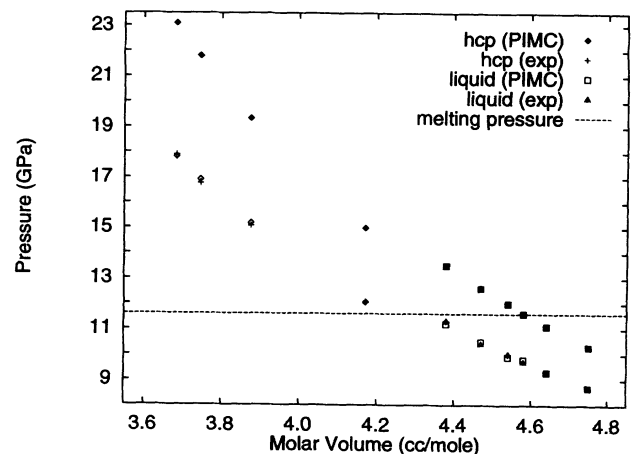

FIG. 2. Comparison between experimental (crosses) and PIMC (open diamonds) data for hcp solid ⁴He, and between experimental (triangles) and PIMC (open squares) data for liquid ⁴He, at $T=300$ K. The dashed line indicates the melting pressure. For comparison, we also show pressure estimates for the liquid (filled squares) and the solid (filled diamonds) obtained without the inclusion of the three-body term, i.e., with the Aziz two-body potential only.

partition function. A PIMC calculation consists of generating stochastically a set of configurations $\{R_i\}$ statistically sampled from a probability density proportional to $\rho(R,R;\beta)$; the quantity $\langle O \rangle$ can thus be evaluated as a statistical average over the set of values $\{O(R_i)\}$. Now, since the explicit form of $\rho(R,R;\beta)$ is not known, one uses the identity $e^{-\beta H} = (e^{-\tau H})^M$, with $\tau = \beta/M$. As M increases, explicit approximations for $\rho(R,R';\tau)$ can be obtained. Thus, it is possible to generate the configuration sample $\{R_i\}$ by sampling "paths" through the configuration space from a probability density proportional to $\rho(R_0,R_1;\tau)\rho(R_1,R_2;\tau)\cdots\rho(R_{M-1},R_0;\tau)$.

The number M of intermediate points ("slices") in which the interval β must be partitioned crucially depends on how accurate an approximation one can obtain for $\rho(R,R';\tau)$; it is highly desirable [11] to keep the number M down to a minimum, in order for the calculation to be efficient. To this aim, a remarkably effective form for $\rho(R,R';\tau)$ is given by

$$\rho(R,R';\tau) = \rho^{(0)}(R,R';\tau)\exp\left[-\sum_{i<j} u(r_{ij},r'_{ij};\tau)\right], \quad (5)$$

where $\rho^{(0)}(R,R';\tau)$ is the density matrix for a system of N free particles and u is defined to be exact for two interacting atoms; r_{ij},r'_{ij} are the vectors between two He atoms at two successive slices, separated by τ. This density matrix is considerably more accurate than the commonly used "primitive" approximation, which consists of setting $u(r_{ij},r'_{ij};\tau) = (\tau/2)[V(r_{ij})+V(r'_{ij})]$, $V(r)$ being the two-body potential. Using the pair density matrix (5) we observe convergence in the kinetic energy with $M = 4$, whereas with the primitive approximation one needs at least $M = 20$. This results in much larger statistical errors, making the evaluation of the isotopic shift extremely difficult.

For computational convenience, only the Aziz two-body part of the potential is included in the action of our PIMC simulation. The contributions of the three-body term to the thermodynamic averages of the observables are evaluated "perturbatively," i.e., as averages over a set (typically 100) of PIMC-generated N-particle configurations, following a procedure analogous to the one outlined in Ref. [12]. Because the three-body potential does not appear in the action, the kinetic energy [11] depends only on the pair potential. To lowest order in V_3, the change in the kinetic energy due to V_3 is given by the correlation between the kinetic energy and the three-body potential:

$$\Delta k \approx -\beta\langle \hat{k}\hat{V}_3 \rangle + \beta\langle \hat{k}\rangle\langle \hat{V}_3\rangle, \quad (6)$$

where $\langle \cdots \rangle$ is an average over the configurations generated with the two-body potential only. Although the estimates are noisy, we find that the change in the kinetic energy is smaller than 0.1 K in both the solid and liquid phases. This establishes that it is the two-body potential which determines the kinetic energy.

We have performed a path integral Monte Carlo simu-

lation of 108 He atoms either in the liquid or in the solid (fcc or hcp) phase. In Fig. 2 we compare our PIMC estimates of the equilibrium pressure at different molar volumes in liquid and solid (hcp) ^{4}He at $T = 300$ K with experimental diamond-anvil-cell data from Refs. [13] and [14]. We show PIMC results obtained with (open symbols) and without (filled symbols) the inclusion of the three-body potential (3); it is evident from the figure that the three-body term is essential to reproduce the experimental data in this pressure range. It is worth mentioning that the contribution to the pressure from the Axilrod-Teller part of (3) is positive and its absolute value is an order of magnitude smaller than the absolute value of the contribution from the exchange part, which is negative.

Calculating the isotopic shift directly from the interatomic potential is notoriously difficult computationally, because small systems do not spontaneously melt or freeze; it is necessary to evaluate the free energy of each phase by integrating the energy from high or low temperature. Instead we follow a procedure similar to the one in Ref. [2]. Our calculation accurately reproduces the experimental pressure in the density range of interest; therefore, we perform isochoric simulations of the two phases at the experimental melting and freezing densities. This is an important point, as the kinetic energy is strongly dependent on the density and it is therefore crucial to perform the simulations at the correct values of v_a. We then use Eq. (2) to estimate the isotopic pressure shift. Let us use a three-point trapezoidal approximation to the integral in (2) and neglect the dependence of $v_S(x)$ and $v_L(x)$ on x [15]:

$$\Delta\pi \approx \tfrac{1}{4} \ln(m_4/m_3) \left[\frac{\Lambda(x_4)+2\Lambda(x')+\Lambda(x_3)}{v_L(x_4)-v_S(x_4)}\right], \quad (7)$$

where $\Lambda(x) = k_S(x,v_S(x_4)) - k_L(x,v_L(x_4))$; x' refers to an isotope of intermediate mass $1/x' = \sqrt{m_3 m_4}$. We evaluate (7) by performing isochoric simulations of the three isotopes in the liquid and solid fcc phases at $v_S(x_4)$ and $v_L(x_4)$, which are known from experiment [14,16].

In Table I we report our PIMC results for the kinetic

TABLE I. Kinetic energy per particle (in K) in the solid and liquid phases of ^{4}He, ^{3}He, and of an isotope of intermediate mass $m_7 = \sqrt{m_4 m_3}$, at $T = 250$ K and $T = 300$ K. The volumes per particle (in cm^3/mole) are those of ^{4}He at melting. Statistical errors (in parentheses) are on the last digit.

T	v	^{3}He	^{7}He	^{4}He
		fcc solid		
250	4.51	524.9(3)	505.7(3)	489.9(4)
300	4.18	607.7(3)	588.9(4)	571.5(3)
		Liquid		
250	4.64	523.0(3)	504.7(3)	488.9(3)
300	4.30	605.0(4)	586.5(4)	570.7(3)

energy per particle in the three isotopes at $T=250$ and 300 K. The predicted value of $\Delta\pi$ from (7) at $T=250$ K is 21 ± 5 MPa, in excellent agreement with the experimental value of 25 ± 15 MPa [4] and in contrast with the value of $\Delta\pi \approx -120$ MPa predicted in Ref. [2]. At $T=300$ K we find $\Delta\pi=41 \pm 7$ MPa.

Summarizing, the isotopic shift is determined mostly by differences of kinetic energy which are in turn influenced by the pair potential. Thus the measurement of the isotopic shift of the melting pressure provides a test for the interatomic potential in solid helium at high pressures. Use of the low-pressure pair potential gives agreement with experiment. A three-body potential is necessary to reproduce the experimental equation of state but has little effect on the kinetic energy. The effective pair potential utilized in Ref. [2] may be the cause of the disagreement with experiment. By softening the pair potential to mimic the effect of higher-order many-body potentials, there is good agreement with the high-pressure experimental equation of state but significantly smaller kinetic energies. The measurement of the influence of mass on pressure is not confined to the melting line. One can use the Maxwell relation

$$\frac{d\pi}{d\ln(x)}\bigg|_T = -\frac{dk}{dv}\bigg|_T \tag{8}$$

to estimate the kinetic energy of solid helium. These measurements in combination with PIMC calculations would provide a significant test of interatomic potentials.

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