

Correlated-cell-model calculation of the high-pressure phase diagram of helium

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A correlated cell model which takes into account the low-frequency collective sliding mode along the [110] direction in the bcc crystal is shown to reproduce semiquantitatively the high-pressure fcc-bcc transition recently discovered in solid helium at room temperature.

Recent diamond-anvil measurements of the equation of state of ⁴He at high pressures point to the existence of a fcc-bcc solid-phase transition prior to melting, with a triple point near $T = 300$ K.¹ This transition has been confirmed by an isobaric-isoenthalpic molecular dynamics simulation² which revealed the sequence fcc-bcc-fluid as the temperature is increased at a pressure of 16 GPa. Such a sequence of stable phases has also been observed in other compounds characterized by "soft" interatomic repulsions;³ the transition is due to a larger bcc entropy which, at sufficiently high temperature, compensates the higher internal energy of that phase. For metals, Friedel⁴ showed, on the basis of a central-force nearest-neighbor model, that the excess bcc vibrational entropy is simply related to a lower Einstein frequency. In helium this interpretation does not hold, since the Einstein frequency, calculated from a lattice sum of the Laplacian of the interatomic pair potential $v(r)$, turns out to be higher for the bcc than for the fcc lattice, indicating that anisotropy and correlations cannot be neglected. Hone, Alexander, Chaikin, and Pincus⁵ predicted the existence of a fcc-bcc-liquid sequence in colloidal suspensions, on the basis of a mean-field anisotropic cell model. The anisotropic cell model will be the starting point of our own calculation on solid helium, but to obtain a quantitatively reliable description of the fcc-bcc transition, the inclusion of microscopic correlations will prove to be essential. The importance of correlations in determining the close packed to bcc transition has been clearly revealed by earlier work on the hcp-bcc transition observed at low pressures and temperatures in solid ³He.^{6,7}

In the cell model,^{5,8} each atom is constrained to a volume V/N and moves in the mean-field potential due to the $N - 1$ other atoms. The He atoms are assumed to interact through the modified Aziz pair potential^{1,9} and we use classical statistical mechanics, since quantum corrections have been shown to be small in the temperature range of interest.¹⁰ The configuration integral reads in the cell-model approximation

$$z_{\text{cell}} = \left(\int \exp[-\beta\Phi(\vec{r})] d^3\vec{r} \right)^N, \tag{1}$$

where $\beta = 1/k_B T$, and the mean-field potential inside a cell centered at the origin is given by

$$\Phi(\vec{r}) = \int \rho(\vec{r}') \sum_i v(|\vec{r} - \vec{r}' - \vec{R}_i|) d^3\vec{r}'. \tag{2}$$

In Eq. (2), \vec{R}_i and \vec{r} are, respectively, the equilibrium lattice positions and the displacements of the interacting atoms. Although it turns out to be essential to include terms of higher order than the harmonic one in the mean-field potential $\Phi(\vec{r})$ experienced by any one atom, the anharmonicity of the average motion of the surrounding atoms is a higher-order effect so that it is sufficient to assume, for the evaluation of $\Phi(\vec{r})$ from Eq. (2), a self-consistent Gaussian form for the one-particle density

$$\rho(\vec{r}) = \left(\frac{2\pi}{3\sigma^2} \right)^{3/2} \exp\left[-\frac{3r^2}{2\sigma^2} \right], \tag{3}$$

where $\sigma^2 = \langle r^2 \rangle$ is the mean-square displacement. We expand the pair potentials in Eq. (2) to fourth order in the displacements, then perform the lattice sums taking into account the cubic symmetry of the crystal and finally perform the Gaussian average, with the result⁵

$$\Phi(\vec{r}) = v_0 + v_2 r^2 + v_{40} r^4 + v_{41} (r_x^4 + r_y^4 + r_z^4). \tag{4}$$

Indicating partial derivatives by subscripts x or y , the coefficients are explicitly given by

$$v_0 = \sum_i v(R_i) + \frac{\sigma^2}{6} \sum_i \nabla^2 v(R_i) + \frac{\sigma^4}{24} \sum_i [v_{xxxx}(R_i) + 2v_{xyxy}(R_i)], \tag{5a}$$

$$v_2 = \frac{1}{6} \sum_i \nabla^2 v(R_i) + \frac{\sigma^2}{12} \sum_i [v_{xxxx}(R_i) + 2v_{xyxy}(R_i)], \tag{5b}$$

$$v_{40} = \frac{1}{8} \sum_i v_{xyxy}(R_i), \tag{5c}$$

$$v_{41} = \frac{1}{24} \sum_i [v_{xxxx}(R_i) - 3v_{xyxy}(R_i)]. \tag{5d}$$

The excess Helmholtz free energy can be calculated from the resulting one-particle density $X(\vec{r}) \sim \exp[-\beta\Phi(\vec{r})]$ via^{5,8}

$$\frac{\beta F^{\text{ex}}}{N} = \int_{\text{cell}} X(\vec{r}) \ln[X(\vec{r})] d^3\vec{r} + \frac{\beta}{2} \int_{\text{cell}} d^3\vec{r} \int_{\text{cell}} d^3\vec{r}' X(\vec{r}) X(\vec{r}') \times \sum_i v(|\vec{R}_i + \vec{r}' - \vec{r}|). \tag{6}$$

Approximating the exponential of the anharmonic terms by its first-order expansion, we obtain after rearrangement

$$\frac{\beta F^{ex}}{N} = \frac{v_0}{2} - \frac{3}{2} k_B T + \frac{3}{8\beta^2 v_2^2} [5v_{40} + 3v_{41}] \quad (7)$$

The mean-square displacement σ^2 is determined by the self-consistency condition

$$\langle r^2 \rangle = \frac{3k_B T}{2v_2} \quad (8)$$

To illustrate the validity of the various approximations made in deriving Eq. (7), we quote typical results obtained in the fcc phase at $T=400$ K and a molar volume $V=4.515$ cm³/mole (the bcc phase leads to similar conclusions) $\sigma^2=4.68 \times 10^{-2}$ Å²; $\beta v_0=9.28$; $\beta v_2=32$; $\beta v_{40}=42$; $\beta v_{41}=-27$. From these results it can be verified that the anharmonic part of the free energy is only 5% of the harmonic contribution, indicating a good convergence of the potential expansion; moreover the exponential of the anharmonic term (≈ 0.09) is well approximated by its linear expansion.

In Table I we report the total free energies of both phases for various volumes at $T=400$ K. At that temperature the experimental melting pressure is $P=183$ kbar, while the volume of the coexisting solid is 4.32 cm³/mole. Hence, we conclude that the anharmonic cell model does not predict a stable bcc phase before melting. This failure of the cell model must be traced back to the neglect of correlated motions between neighboring atoms.

In order to include correlations, we write the exact configuration integral of the crystal in the form

$$z = z_{cell} \langle \exp(-\beta \Delta H) \rangle \quad (9)$$

where ΔH is the difference between the exact Hamiltonian for N interacting He atoms and the cell model Hamiltonian; the statistical average is over a cell-model ensemble. Taking ΔH to second order in the Taylor expansion of the potential, we obtain

$$\exp(-\beta \Delta F_{corr}) = \left\langle \prod_{i < j} (1 + f_{ij}) \right\rangle \quad (10)$$

where ΔF_{corr} denotes the correlation part of the free energy and the f_{ij} are the Mayer functions

$$f_{ij} = \exp[-\beta v_{\alpha\beta}(R_{ij}) r_{i\alpha} r_{j\beta}] - 1 \quad (11)$$

In Eq. (11) summation over repeated indices ($\alpha, \beta = x, y, z$) is implied. Restricting ourselves to the contribution of pair correlations, we decouple the statistical average of the prod-

uct in Eq. (10) into the product of pair averages, with the result

$$\frac{\beta \Delta F_{corr}}{N} = \frac{1}{4} \sum_l \left[\ln \left(1 - \frac{v''(R_l)^2}{4v_2^2} \right) + 2 \ln \left(1 - \frac{v'(R_l)^2}{4R_l^2 v_2^2} \right) \right] \quad (12)$$

where v' and v'' denote the first and second derivatives of the pair potential. It can be seen from the results given in Table I that pair correlations lower the free energies of both phases by roughly equal amounts so that there is still no stable bcc phase before melting. The pair-correlation approximation can be expected to be adequate for the fcc phase, since the predicted free energies lie very close to those obtained from the Domb-Salter approximation of lattice dynamics, an approximation which is known to be very good for close-packed rare-gas crystals.¹¹ The predicted fcc free energies lie also very close to the results of a variational calculation based on "exact" Monte Carlo data for the close-packed phase.¹ On the other hand, the pair-correlated cell model may not be sufficiently accurate for the bcc phase in which anharmonic collective modes are known to yield significant contributions to the entropy.⁷ In particular, for hard spheres the bcc is known to be unstable with respect to a sliding motion of the 110 planes in the direction of the face diagonal. The 110 plane is almost close packed and if alternate such close-packed layers are shifted parallel to each other in the direction of the face diagonal, holding the remaining layers fixed, it is possible to convert a bcc crystal into a fcc structure. For continuous interatomic potentials this sliding motion is expected to give rise to a low-frequency mode and could hence stabilize the bcc phase by increasing the entropy.⁷ We have incorporated this mode into our correlated bcc cell model by adding strong correlations in the 110 plane. To achieve this we let an atom and its four nearest neighbors in the 110 plane move as a rigid unit. We neglect the resulting correlation effects on the anharmonic terms, whereas the harmonic part $v_2 r^2$ of the mean-field potential is changed into an anisotropic contribution $v_{2x} r_x^2 + v_{2y} r_y^2 + v_{2z} r_z^2$, where the x and y directions are now in the 110 plane; the previously considered pair correlations are unchanged in the orthogonal (z) direction. Because of the Gaussian average, the difference in free energy comes from the entropic term

$$\frac{\beta \Delta F_{corr}^{110}}{N} = \frac{1}{2} \ln \left(\frac{v_{2x} v_{2y}}{v_2^2} \right) \quad (13)$$

The 110 correlations are limited to groups of five atoms; each atom has probability $\frac{1}{5}$ to be at the center and probability $\frac{4}{5}$ to be at the edge of a rectangle in the 110 plane. With lattice sums weighted accordingly, v_{2x} and v_{2y} are given by

$$v_{2\alpha} = v_2 - \frac{2}{5} v_{\alpha\alpha}(R_{24}) - \frac{4}{5} v_{\alpha\alpha}(R_{01}) - \frac{2}{5} v_{\alpha\alpha}(R_{12}) \quad (14)$$

where 0 and 1,2,3,4 label the center and edge atoms, respectively.

As can be seen from Table I, the resulting bcc free energy falls now below the corresponding fcc free energy for volumes greater than 3.90 cm³/mole at $T=400$ K; this volume being less than the melting volume, a stable bcc phase is found between the fcc and fluid phases. Our calcu-

TABLE I. Total free energies of the fcc and bcc phases of solid ⁴He at $T=400$ K within various approximations; the free energies are given in their reduced form $f = \beta F/N$.

v (cm ³ /mole)	Cell model		Pair-correlated cell model		Correlated cell model
	f_{fcc}	f_{bcc}	f_{fcc}	f_{bcc}	f_{bcc}
3.31	14.35	14.56	13.98	14.19	14.02
3.91	8.39	8.56	8.07	8.23	8.06
4.51	4.94	5.08	4.66	4.78	4.62
5.11	2.79	2.91	2.55	2.65	2.49
5.71	1.35	1.45	1.15	1.23	1.07

TABLE II. Pressure and molar volumes (in cm³/mole) at the fcc-bcc transition as functions of temperature.

T (K)	P (kbar)	⁴ He		³ He		
		v_{fcc}	v_{bcc}	P (kbar)	v_{fcc}	v_{bcc}
200	61.47	5.608	5.632	60.39	5.668	5.692
250	95.82	5.022	5.040	94.49	5.066	5.085
300	137.85	4.577	4.592	136.20	4.611	4.627
350	188.75	4.217	4.229	186.70	4.245	4.258
400	249.3	3.916	3.927			

lation confirms the essential role played by the low frequency 110 modes in stabilizing the bcc phase.⁷

Since quantum corrections are not entirely negligible,¹⁰ we have added the leading \hbar^2 term of the Wigner-Kirkwood expansion to the free energy of both solid phases. Retaining only the dominant harmonic part of the mean-field potential, the correction reads

$$\frac{\beta F_p}{N} = \frac{\lambda^2}{8\pi} \beta v_2, \quad (15)$$

where λ is the thermal de Broglie wavelength.

Summing the cell model, correlation, and quantum contributions, we have plotted the total free energy versus volume curves for both phases at several temperatures and determined the fcc-bcc transition line by the Maxwell double-tangent construction. Results are summarized in Table II and in Fig. 1. The melting curve is determined in a similar way, using the theoretical fluid free energies calculated in Ref. 1 with the same interatomic potential. The calculated $\frac{3}{1000}$ volume discontinuity at the fcc-bcc transition is in good agreement with the results of molecular dynamics simulations.² The predicted triple point of ⁴He at 216 K can be regarded as being in good agreement with experiment¹ in view of the sensitivity of the results to alterations of the model. The isotopic shift of the triple point in going from ⁴He to ³He (215 K) is negligible and this finding is expected to remain valid for more accurate calculations.

A final important point relates to the interatomic potential. All the results quoted in this Rapid Communication were obtained with the modified Aziz potential⁹ which is

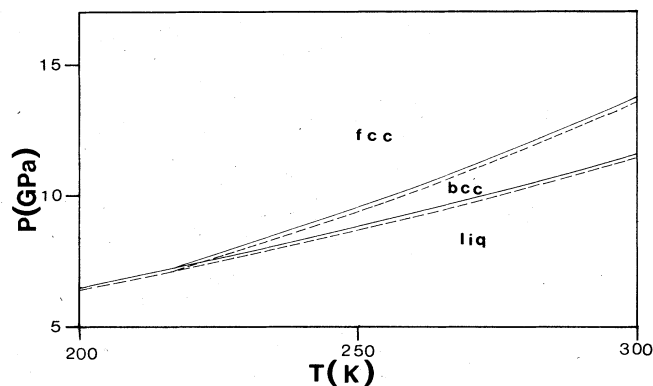


FIG. 1. The high-pressure phase diagram of ⁴He (full lines) and of ³He (dashed lines).

known to yield a reasonable description of the high-pressure thermodynamics of helium.¹ The standard Lennard-Jones potential yields melting pressures which are systematically too low. If the Lennard-Jones potential is used in our calculations, the bcc free energy is always found to lie above its fcc value. This illustrated the sensitivity of the phase diagram to the pair potential and represents a good test of the validity of the correlated cell model, since it is generally accepted that a "hard" interatomic repulsion (like in the Lennard-Jones potential) favors the close-packed solid phase, while a "softer" repulsion favors the bcc phase.³ The exponential repulsion in the Aziz potential becomes effectively softer with increasing pressure and temperature, so that the appearance of a bcc phase above a triple point may not have been totally unexpected.

In summary, by improving the crude cell model, we have been able to pin down the essential physical ingredients of the fcc-bcc phase transition and understand semiquantitatively the high-pressure phase diagram of helium. Our calculation has shown that a description of the solid phases with an accuracy of better than $\frac{2}{1000}$ is needed to obtain the proper transition line.

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