Location of melting point at 300 K of nitrogen by Monte Carlo simulation

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We present an accurate new method to compute absolute free energies of molecular solids by computer simulations. As a first application, we computed the thermodynamic phase transition between the fluid phase and the orientational disordered solid β phase of nitrogen at 300 K, using a well tested pair potential. The computed coexistence pressure and the volume change coincides within the error margins with the experimental values. The coexistence volume differed by 2% from the experimental value. To our knowledge these results constitutes the first numerical calculation of the thermodynamic stability for a model of a realistic molecular solid.

INTRODUCTION

Computer simulation studies of the mechanical or thermodynamic stability of model systems provide a good test for theories of phase transitions. A second important application is the study of models of realistic systems under conditions that can not be probed experimentally. However, in computer simulations it is usually not possible to observe coexistence between two solid phases in thermodynamic equilibrium. As small periodic systems are used in most simulations, first-order transitions have pronounced hysteresis effects; there is a pressure range in which both phases are mechanically stable. To locate the thermodynamic phase transition, the free energies of both phases in the region of the phase transition must be known.

Several techniques have been developed to calculate free energies of solids by computer simulation. They all rely on a reversible transformation of the solid to a reference solid of known free energy. The earliest method, called the single-occupancy cell (SOC) method, was developed by Hoover and Ree.[1] In this method, the original solid is changed to a lattice gas with the same crystal structure, with the particles confined to their Wigner–Seitz cells by artificial walls. In practice this method has certain drawbacks. At the density where the solid in absence of the artificial walls would become unstable a weak first-order phase transition is found to occur. Furthermore, the calculation of the free energy of the low-density reference state is not straightforward for particles with complex interactions. A second method, is to transform the solid into a harmonic solid by decreasing the temperature to zero.[2] However, this method cannot been used when a first-order phase transition occurs somewhere along the thermodynamic integration path. This happens, for instance, in the case of molecular solids in the rotator phase. In a third method, developed by Frenkel and Ladd,[3,4] the solid under consideration is changed reversibly into an Einstein crystal by gradually switching off the interparticle interaction and switching on an attractive coupling between each

particle and its equilibrium lattice site. In principle, this method can be applied to any solid, but it also has a drawback in that the derivative of the free energy with respect to the coupling parameter has, for a large class of potentials, a weak but integrable divergence in the Einstein-crystal limit. For atomic systems, integration of the divergent function does not usually lead to significant numerical inaccuracy, but in the case of molecular solids with orientational disorder it may result in large numerical errors.

In the present paper we present a new method to calculate free energies of molecular solids by computer simulations. This method can be applied into situations where other methods, just described, cannot been used, for instance, molecular solids in the rotator phase. As an application, we have studied the melting of a realistic model of nitrogen. We calculated the absolute free energy of the orientationally disordered solid β phase at 300 K and determined the nitrogen solid–fluid melting transition at that temperature.

METHOD

In the present section, we describe a new method to calculate absolute free energies of arbitrary solids. We will refer to this method as the lattice-coupling expansion method. The basic idea is to change the solid reversibly, in two stages, to a reference crystal with known free energy. First each particle is coupled to its corresponding equilibrium lattice site, as in the Frenkel–Ladd method.[3] In the second stage the system is expanded to zero density so that it becomes equivalent to a lattice site-coupled solid without interparticle interactions.

Consider a system of N particles (atoms or molecules) arranged in a particular crystal structure. In the first stage the crystal is changed by introducing an artificial attractive interaction between the particles and their equilibrium lattice sites. If there is, in case of molecular solids, orientational order, a force constraining the orientation must also be imposed. The artificial coupling of the particles to their lattice

sites and the orientational constraint must be such that when the interparticle potential is switched off, the crystal will keep the same structure. In general, the lattice site or orientational coupling can have an independent coupling parameter for each degree of freedom in the unit cell. In the following we assume, for clarity, a crystal with only translational order and use one coupling parameter. In that case the lattice site coupling is imposed by adding a term αV to the original Hamiltonian H_0:

$$H_1(\mathbf{r}_i,\alpha) = H_0(\mathbf{r}_i) + \alpha V(\mathbf{r}_i - \mathbf{r}_i^0), \qquad (1)$$

where $\mathbf{r}_i$ and $\mathbf{r}_i^0$ denote the coordinate of the center-of-mass position of atom (or molecule) i, respectively, its lattice site and α is the coupling strength parameter. The coordinates $\mathbf{r}_i^0$ of the lattice sites are defined with respect to the center-of-mass of the N-particle crystal. We refer to the solid described by H_1 as the lattice-coupled solid. A convenient choice for V is a harmonic coupling: $V(\mathbf{r}_i - \mathbf{r}_i^0) = \Sigma_{i=1}^N (\mathbf{r}_i - \mathbf{r}_i^0)^2$. The initial solid is gradually changed by increasing α from zero to a finite value. The derivative of the free energy with respect to α is given by

$$\frac{\partial F_1}{\partial \alpha} = \langle V \rangle_\alpha, \qquad (2)$$

from which it follows that the free energy of initial solid F_0 is related to the free energy of the lattice-coupled solid F_1 by

$$F_0(\alpha = 0) = F_1(\alpha) + \int_\alpha^0 \langle V \rangle_{\alpha'} d\alpha'. \qquad (3)$$

The integrand can be evaluated by determining $\langle V \rangle_\alpha$ for several values of α by Monte Carlo or molecular dynamics simulations.

In the second stage the lattice-coupled solid is expanded. We introduce a linear expansion parameter γ which is related to the density ρ by $\rho = \rho_0/\gamma^3$, where ρ_0 is the initial density. The Hamiltionian H_1 for the expanded crystal is then given by

$$H_1(\mathbf{r}_i,\alpha,\gamma) = H_0(\mathbf{r}_i) + \alpha V(\mathbf{r}_i - \gamma \mathbf{r}_i^0). \qquad (4)$$

During expansion, the influence of interparticle potential will smoothly decrease. However, the lattice-coupled solid will not melt but instead it keeps its original ordering as the coupling αV forces the particles to stay around the sites $\gamma \mathbf{r}_i^0$ of the expanded lattice. Hence there will be no (first-order) phase transition. For infinite expansion the interparticle interaction has vanished and the potential energy of the system is given by the function αV. In the case of harmonic coupling this (reference) system is an Einstein crystal. The derivative of the free energy with respect to the linear expansion is given by

$$\frac{\partial F_1}{\partial \gamma} = -\left\langle \sum_{i<j} \mathbf{f}_{ij} \cdot \mathbf{r}_{ij}^0 \right\rangle_{\alpha,\gamma} = -\langle W_1 \rangle_{\alpha,\gamma}, \qquad (5)$$

where $\mathbf{f}_{ij}$ denotes the force of particle j on particle i and $\mathbf{r}_{ij}^0 = \mathbf{r}_i^0 - \mathbf{r}_j^0$ is the lattice-site separation at the initial density ρ_0. Note that the expression for the modified viral W_1 of the lattice-coupled solid contains $\mathbf{r}_{ij}^0$ instead of the usual $\mathbf{r}_{ij}$. From Eq. (5) it follows that the free energy of the nonexpanded lattice-coupled solid is related to the infinitely expanded solid by

$$F_1(\alpha,\gamma = 1) = F_1(\alpha,\gamma = \infty) - \int_\infty^1 \langle W \rangle_{\alpha,\gamma'} d\gamma'. \qquad (6)$$

The integrand in Eq. (6) can be evaluated by determining $\langle W_1 \rangle_{\alpha,\gamma}$ for several values of γ by Monte Carlo or molecular dynamics simulations.

We have now completed the construction of a reversible path between a solid described by Hamiltonian H_0 and a reference crystal described by Hamiltonian αV_1: first a lattice-site coupling is imposed and subsequently the lattice-coupled solid is expanded until the intermolecular forces vanish. Combining the Eqs. (3) and (6) gives an expression for the free energy F_0 of the initial solid in terms of the free energy of the reference crystal and an integral over a reversible path.

The lattice-coupling expansion method presented here combines elements of the single-occupancy method with the Frenkel–Ladd method. It can be applied to any solid phase, with the important advantage that the integrands in the thermodynamic integrations [Eqs. (3) and (6)] are expected to be well behaved. Another practical advantage is that the properties of the reference crystal depend only on a one-particle Hamiltonian.

NITROGEN FLUID TO β-SOLID PHASE TRANSITION AT 300 K

As an application of the lattice-coupling expansion method, we determined the thermodynamic fluid–solid phase transition of nitrogen along the 300 K isotherm by computer simulations. The solid phase at the transition is orientational disordered, but at lower temperatures it transforms into a orientationally ordered solid phase. Consequently, the free energy of the solid near the melting line cannot be obtained by reversibly cooling the system to a state where it becomes harmonic. Hence we decided to calculate the melting point at 300 K using the lattice-coupling method. To our knowledge this constitutes the first numerical simulation of the thermodynamic solid–fluid phase transition for a realistic model of any molecular system.

Nitrogen freezes at 300 K into a rotator phase, called the β phase, with an experimentally determined coexistence pressure of 2.44 GPa.[6] In this phase the centers of mass of the molecules are arranged in a hexagonal closed packed structure, but there is still controversy about the orientational order in this phase. Recent experiments[7,8] can be interpreted with a model where all particles are precessing around the *c* axis at an angle of 54°, but can equally well be explained by a model with complete orientational disorder. Both theory[9,10] and computer simulation results[11,12] indicate a nearly spherical distribution for the orientational order.

In recent years several computer simulation studies of nitrogen have been reported. They yield the fluid equation of state over a wide range of pressures and temperatures,[13–15] a study of the structure in a low temperature β-solid state[11] and a study of the mechanism for the transitions in the solid phase at high pressure.[16,17] There has also been a study of the microscopic configurational properties of the fluid phase and the solid β and δ phases along the 300 K isotherm,[12] but

a thermodynamic melting point could not be located in that study.

The nitrogen pair potential used in this work was derived by Etters *et al.*[5] by a fit to both theoretical and experimental data. The intermoleculer potential is represented by site–site interactions. There are two sites per molecule interacting with an exponential short range repulsion and an r^{-6} longe range attraction, while the region around the minimum is described by a cubic spline fit connecting the two other regions; four point charges along the molecular axis represent the quadrupole interaction. Computer simulation results[14,15] for the density in the fluid region obtained with this potential, agree to within 0.3% with experimental data[18] over a wide range of pressure and temperature. Moreover zero-temperature properties predicted with this potential agree well with experimental observations of the crystalline solid.[5] The effect of the high frequency intramolecular vibrations can be ignored, thus the bond length of the nitrogen molecules, i.e., the distance between the two sites, is fixed at the gas-phase equilibrium value.

Equation-of-state data were obtained by Monte Carlo (MC) simulations of a 180 particle system with periodic boundary conditions. The solid phase MC simulations were performed with the particles arranged in ABAB··· stacked triangular layers, in a rectangular box; the fluid phase simulations were performed in a box of the same shape. In the solid phase simulations, all interactions up to a separation midway between the fifth and sixth neighboring shells were taken into account. For the fluid phase simulations the cutoff radius was 9 Å in the low-density region and slightly less than 9 Å in the high-density region. Interactions between particles outside the cutoff radius were taken into account by assuming a uniform distribution of the center of mass and the orientation. The initial configuration was, for most of the simulations, the final configuration of a previous run. Before data were collected, the system was equilibrated by 1000 MC cycles, with each cycle corresponding to one trial move per particle.

To determine the thermodynamic phase transition for the nitrogen model at 300 K, the fluid and solid states with equal pressure and Gibbs free energy must be located. The free energy of the fluid phase is determined by thermodynamic integration along the 300 K isotherm using

$$\frac{F(\rho)}{NkT} = \frac{F^{id}(\rho)}{NkT} + \int_0^\rho \left[\frac{P(\rho') - \rho'T}{\rho'^2 T} \right] d\rho', \qquad (7)$$

where F^{id} denotes the free energy of an ideal gas. We determined the equation of state at 300 K by performing constant-volume MC simulations for 11 densities consisting of 10 000 MC moves per molecule. The estimated errors in the pressure varied from 0.004 GPa in the low-density region to 0.015 GPa in the high-density region. The simulation results as well as experimental data are shown in Fig. 1 (low-density region) and Fig. 2 (high-density region) in density vs pressure plots. The solid line is a sixth order polynomial fit ($\chi^2 = 0.1$) to the simulation data. The dashed line represents the experimental results of Mills *et al.*[18] in the pressure range from 0.3 up to 2.5 GPa. The triangles represent the experimental data of Kortbeek *et al.*,[19] which cover a range
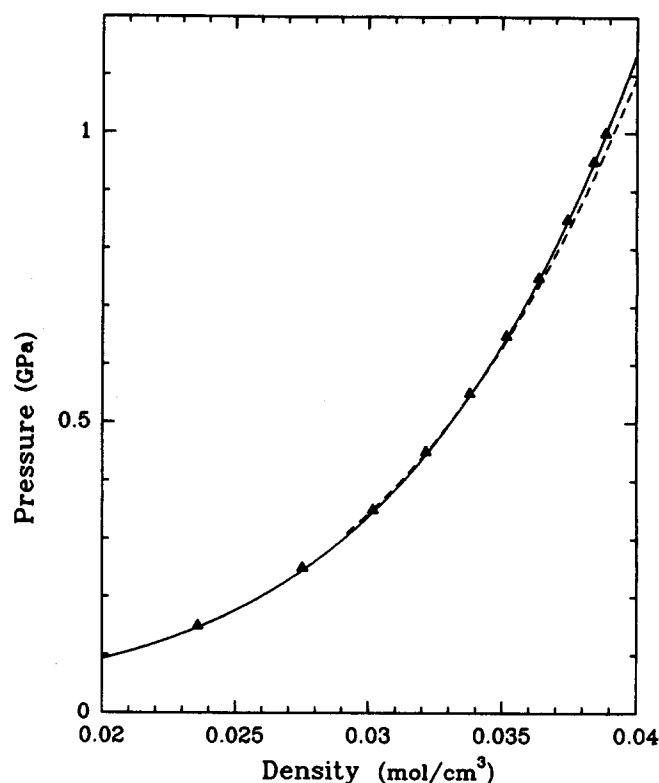

FIG. 1. Equation of state for fluid nitrogen in the low-density region. The solid line is a polynomial least-square fit to the simulation data. The dashed line (Ref. 18) and the triangles (Ref. 19) represent experimental results.

from 0.08 to 1 GPa. Above 0.75 GPa the simulation data differ significantly from the results of Mills *et al.* Therefore we extrapolated the results of Kortbeek *et al.* to 2.5 GPa in the following way. We assumed that the increase in relative density difference between both experimental data was linear with respect to the pressure. The slope of the increase was fixed as the slope at 1 GPa. The extrapolated data are indicated by squares in Fig. 2.

Up to 0.75 GPa the simulation results fit within the error margins with both sets of experimental data. Above 0.75 GPa the results of Mills *et al.* (dashed line) show an increasingly lower pressure (up to 0.2 GPa) compared with our simulations, whereas the data of Kortbeek *et al.* (triangles in Fig. 1) coincide with the simulation results. Furthermore, we see that in the region from 1.0 up to 2.5 GPa (Fig. 2) the simulation data agree quite well with the extrapolated experimental data (squares), with an increasingly small difference (max. 0.05 GPa) in the high-pressure region.

The free energy along the solid branch of the 300 K isotherm is determined in two steps. The absolute free energy of the 3.5 GPa solid β-phase state is determined with the lattice-coupling expansion method. Then thermodynamic integration (7) is used to obtain the free energy along the isotherm. The equation of state of the solid branch was determined by performing constant-stress MC simulations for seven pressures between 2.0 and 4.0 GPa. In these simulations the volume was varied by independent changes in the ABAB··· stacking plane direction and in the direction per-
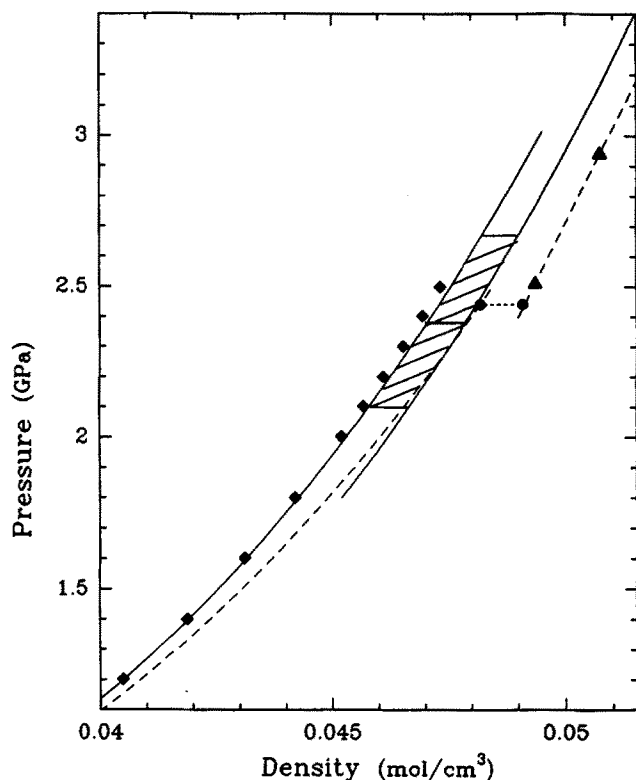
FIG. 2. Equation of state for fluid and β-nitrogen in the high-density region. The solid lines are polynomial least-square fits to the simulation data for the fluid branch (left line) and the solid branch (right line). The dashed line and the squares represents, respectively, experimental results (Ref. 18) and extrapolated experimental data (Ref. 19) (see the text) for the fluid phase. The triangles are experimental results for the solid phase (Refs. 7 and 8), which are for clarity connected by a dashed line. The coexistence density and pressure with estimated error, obtained with the simulation data, are indicated by the horizontal solid line and the dashed area. The experimental coexistence values (Ref. 6) for the fluid and the solid are indicated by two circles and the connecting horizontal dashed line.

where θ_i denotes the orientation of molecule i. Here, we have also fixed the center of mass of the nitrogen crystal with respect to the lattice. This accounts for the following change in free energy with respect to the 3.5 GPa state with freely moving center of mass: $\Delta F^I/NkT = -(\ln V_{box})/N = -0.0481$. The maximum value of the coupling parameter α_{max} was chosen to be such that the mean square displacement $\langle \Sigma_{i=1}^N (\mathbf{r}_i - \mathbf{r}_i^0)^2 \rangle/N$ of an Einstein crystal with α_{max} equals the mean square displacement of the nitrogen crystal at 3.5 GPa. With this choice the reference state (i.e., the infinitely expanded lattice-coupled nitrogen crystal) will most closely approximate the initial 3.5 GPa nitrogen state, which leads to a minimal change in free energy and a maximal numerical accuracy. The difference in free energy between the noncoupled crystal ($\alpha = 0$) and the maximal coupled crystal (α_{max}) is evaluated by determining $\partial F_1/\partial \alpha = \langle \Sigma_{i=1}^N (\mathbf{r}_i - \mathbf{r}_i^0)^2 \rangle_\alpha$ for five values of α between 0 and α_{max} and integrating numerically with a Gauss–Legendre quadrature. The five MC runs consisted of 10 000 moves for each particle. The calculated change in free energy is: $\Delta F^{II}/NkT = -0.812 \pm 0.008$.

Subsequently, the lattice-coupled nitrogen crystal is expanded to zero density. The equation of state is determined by calculating the modified virial $\langle W_1 \rangle_{\alpha_{max},\gamma}$ [see Eq. (6)] for nine values of the density. These values were obtained with constant-volume MC runs consisting of 5000 moves for each particle. Figure 3 shows the simulation results (open circles) in a plot of linear expansion $\gamma [= (\rho_0/\rho)^{1/3}]$ vs the modified virial. The solid line is a cubic spline fit. The curve is quite smooth and reflects the form of the intermolecular force. This smoothness suggests that there is no first-order phase transition associated with a change in orientational order of the molecules upon expansion.

The change in free energy ΔF^{III} during expansion is given by the integral, up to infinite expansion, of the curve shown in Fig. 3. In order to improve the numerical accuracy

pendicular to it. Each run consisted of at least 10 000 MC cycles. We observed a stable hcp structure for all pressures. We did not systematically study the orientational order but relied on results of Belak *et al.*[12] who observed in simulations of the same nitrogen model nearly complete orientational disorder. The estimated errors in the pressure were about 0.015 GPa. The simulation data are shown in Fig. 2. The right-hand solid line is a third order polynomial fit ($\chi^2 = 0.02$) to the simulation data. The solid triangles are experimental results[7,8] which show significantly lower pressures (0.25 GPa) then the simulation results. Note that the estimate of Schiferl *et al.*[7] for the pressure of the lower density solid-state point relies on an extrapolation of the earlier measurements of the melting behavior by Mills *et al.*[6]

The absolute free energy at 3.5 GPa is calculated with the lattice-coupling expansion method. The 3.5 GPa state is gradually changed by adding to the nitrogen Hamiltonian H_0 a harmonic coupling between the center of masses of the molecules $\mathbf{r}_{i,c.m.}$ and their corresponding lattice sites $\mathbf{r}_i^0$:

$$H_1 (\mathbf{r}_{i,c.m.},\theta_i,\alpha) = H_0 (\mathbf{r}_{i,c.m.},\theta_i) + \alpha \sum_{i=1}^N (\mathbf{r}_{i,c.m.} - \mathbf{r}_i^0)^2,$$
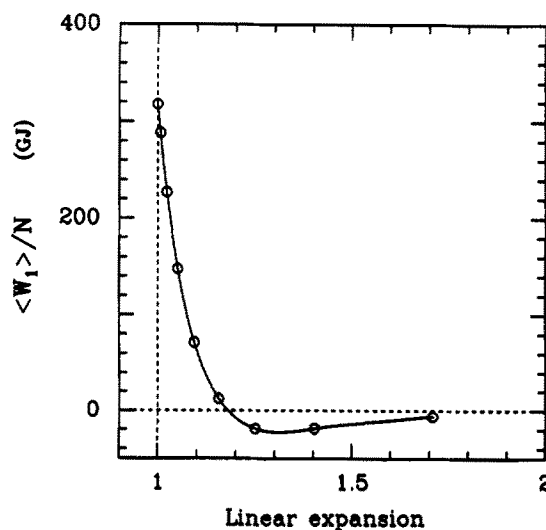
(8)

FIG. 3. Linear expansion vs modified virial.

of the quadrature we converted the infinite integral to a finite one with a smoother integrand. We write the integrand $\langle W_1 \rangle_{\alpha_{max}, \gamma}$ as

$$\frac{\langle W_1 \rangle_{\alpha_{max}, \gamma}}{\langle W_1 \rangle_{\gamma}^0} \langle W_1 \rangle_{\gamma}^0,$$

where $\langle W_1 \rangle_{\gamma}^0$ is the modified virial for r^{-6}-interacting particles on the lattice sites:

$$\langle W_1 \rangle_{\gamma}^0 = C_6 \sum_{i<j} \frac{24}{(r_{ij}^0)^6} \frac{1}{\gamma^7}. \tag{9}$$

Here C_6 is the coefficient of the long range r^{-6} interaction.[5] With λ, defined by $d\lambda(\gamma) = \langle W_1 \rangle_{\gamma}^0 d\gamma$, as new integration variable, we obtain the finite interval integration

$$\Delta F^{III} = F_1(\alpha_{max}, \rho_0) - F_1(\alpha_{max}, \rho = 0)$$

$$= -\int_0^{\lambda_1} \frac{\langle W_1 \rangle_{\lambda}}{\langle W_1 \rangle_{\lambda}^0} d\lambda. \tag{10}$$

When approaching infinite volume the integrand has the limit 1. Figure 4 shows a plot of λ vs $-\langle W_1 \rangle_{\lambda} / \langle W_1 \rangle_{\lambda}^0$, where the solid line is a cubic spline fit. The left border corresponds with infinite expansion and the right border with the nonexpanded system: $\lambda_1 = \lambda(\gamma = 1)$. In the region near $\lambda = 0$ (low density) the long range r^{-6} interaction dominates. As the particles are there confined to a small but finite region around their lattice site, $\langle W_1 \rangle_{\lambda}$ is, in absolute value, somewhat larger than $\langle W_1 \rangle_{\lambda}^0$, which accounts for the bump near $\lambda = 0$. Overall the curve is quite smooth. The integration is numerically evaluated with a 10-point Gauss–Lobatto quadrature giving $\Delta F^{III}/NkT = 2.331 \pm 0.010$.

The infinitely expanded system is an Einstein crystal with fixed center of mass. The expression for its excess free energy is given in Ref. 3 and gives $F_1(\alpha_{max}, \rho = 0)/NkT = F^{Ein}/NkT = -0.518\,80$. Combining the values ΔF^I, ΔF^{II}, and ΔF^{III} and F^{Ein} gives as
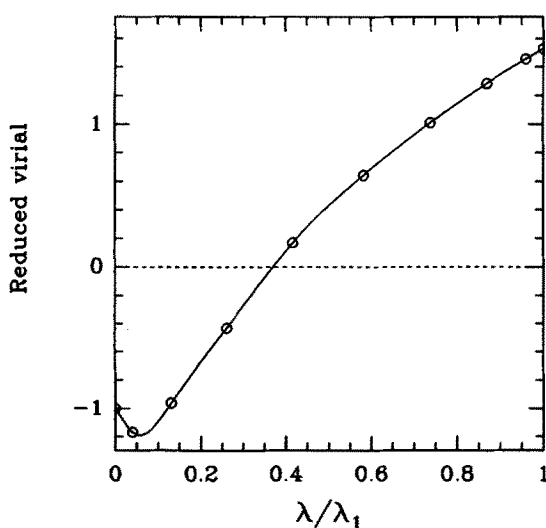
FIG. 4. Reduced λ vs reduced virial, where λ is related to the linear expansion. For the definition of λ and λ_1 see the text. The reduced virial is defined as $-\langle W_1 \rangle_{\lambda} / \langle W_1 \rangle_{\lambda}^0$.

excess free energy for the 3.5 GPa nitrogen state: $F^{ex}/NkT = 0.953 \pm 0.013$.

With the free energy results for the fluid and the solid branch of the nitrogen model, we are now able to locate the phase transition at 300 K. In Table I, the calculated and experimental coexistence quantities are listed. They are indicated in Fig. 2 by the horizontal solid line (simulation) and the horizontal dashed line (experiment[6]). Recently Vos and Schouten[20] measured the coexistence pressure at 2.42(3) GPa. Note that their error is much larger than the error (0.001 GPa) reported in Ref. 6. P, $\Delta\rho_{coex}$, and ΔS denote, respectively, the pressure, the density difference between the fluid and the solid β phase, and the entropy of fusion. The experimental value for the entropy of fusion is calculated with the Clausius–Claperon relation. The coexistence densities are obtained from the equation of state. The calculated fluid coexistence density is 0.0471(12) mol/cm³, with the error mainly due to the error in the calculated coexistence pressure and only slightly to the uncertainty in the density-pressure relation. The experimental fluid coexistence density is 0.0482(2) mol/cm³. Recall that at a fixed pressure in the region near melting the calculated and the experimental densities differ considerably (see Fig. 2). Consequently, the density at the experimental coexistence pressure calculated with the density-pressure relation obtained with the simulations [0.0474(1) mol/cm³], is considerably lower then the experimental density.

DISCUSSION

We have presented a new method to calculate absolute free energies of molecular solids by computer simulation, and we have used this technique to determine the 300 K fluid-solid phase transitions for a realistic model of nitrogen.

In the high pressure region (0.75–3.0 GPa) the densities, for both solid and fluid phases obtained by the simulations are significantly lower than the experimental values reported by Mills *et al.*[18] and Schiferl *et al.*[7,8] Hence, in this region the model potential does not describe those experimental results as well as in the fluid regions studied in Ref. 15 where the densities agreed within 0.3%. However, our simulation results for the fluid region do agree very well with experimental isothermal density-pressure data (0.08–1.0 GPa) obtained by Kortbeek *et al.*[19] Furthermore, the simulation data fit quite well to the extrapolated density-pressure data of Kortbeek *et al.* in the region up to 2.5 GPa. The computer simulation results are thus consistent with the suggestion of Kortbeek *et al.* that the room temperature fluid densities above 0.75 GPa reported by Mills *et al.* are too

TABLE I. Calculated and experimental (Ref. 6) coexistence values for nitrogen at 300 K.

	Simulation	Experimental
P_{coex} (GPa)	2.4(3)	2.441(1)
$\Delta\rho_{coex}$ (mol/cm³)	0.000 82(14)	0.000 84(4)
$\Delta S/NkT$	0.67(8)	0.664

high. On the other hand, in the region near melting the extrapolated data are not very reliable. So it cannot been excluded that the discrepancy between the simulation data and the experimental data in the melting region are partly due to inaccuracy of the model potential. This should then imply that the site–site potential is too repulsive at nearest neighbor distances for densities in the region near melting. More accurate experimental density–pressure data in the melting region are required in order to make a more detailed comparison with our simulation results in that region.

The error in the calculated absolute free energy of the nitrogen model at 3.5 GPa β-phase solid is roughly 10 times larger then errors in free energy calculations of atomic systems obtained with the same number of MC cycles per run (see, e.g., Refs. 3 and 4). This is partly due to the longer thermodynamic integration path. Another factor is that the nitrogen model has a nonspherical pair potential so that longer simulation runs are required to obtain the same accuracy as for atomic systems which have spherical pair potentials. However, the error margins in the calculated coexistence values are mainly due (90%) to statistical errors in the free energy change along the isotherm. The remaining 10% is due to the error in the absolute free energy calculation of the 3.5 GPa β-phase solid. The calculated coexistence pressure agrees within the error margins with the experimental value. The coexistence densities differ considerably as a consequence of the difference in the calculated and experimental[18] equation of state. Furthermore, we see that the calculated and experimental values for the volume change and the entropy of fusion agree within two standard deviations.

Finally, we conclude that the calculated coexistence quantities for the nitrogen model indicates that the lattice-coupling expansion method presented here is a powerful tool to study free-energy related properties of molecular solids. Furthermore, our results may be an indication that the experimental equation of state near the room-temperature freezing point[18] is not quite accurate.

ACKNOWLEDGMENTS

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