Monte Carlo study of a simple model bulk-ice-Ih system: *P-T* melting behavior at constant volume

K. Han* and B. N. Hale
Department of Physics and Graduate Center for Cloud Physics Research, University of Missouri-Rolla, Rolla, Missouri 65401
(Received 15 July 1991)

An *NVT* Metropolis Monte Carlo computer simulation is used to examine the *P-T* behavior of a constant-density model periodic ice-Ih sample near melting. The ice unit cell with density 0.904 g/cm^3 consists of 192 rigid water molecules interacting via the revised central-force potentials (RSL2) of Stillinger and Rahman [J. Chem. Phys. **68**, 666 (1978)] with a cutoff. Intramolecular parameters are determined from a minimization of the total potential energy of the ice-Ih structure at 0 K. In the *P-T* plot, emergence of the liquid-solid coexistence region is signaled by a change in sign of dP/dT (when expansion occurs upon freezing) and gives an approximate value for the onset of constant-density "melting." In this simulation, the expected pressure slope reversal occurs near 280 K. Internal energy, specific heat, and two-dimensional structure factors for the constant-density H_2O system are also monitored at 14 temperatures from 100 to 370 K and support the *P-T* analysis.

I. INTRODUCTION

Ice formation on surfaces is a crucial process occurring in the atmosphere and several of our previous studies[1-3] have been directed toward understanding this phenomenon. In particular, we have carried out Monte Carlo studies of water adsorbed on model substrates of silver iodide—the most recent of which is a two monolayer water-ice system on the iodine exposed AgI basal face.[3] This latter simulation uses (for the water-water interactions) a rigid-body version of the Rahman and Stillinger[4] revised central-force (RSL2) potentials and employs a cutoff to reduce computer time. A constant area unit cell of H_2O with periodic boundary conditions parallel to the substrate is used. The short-range goal has been to evaluate the effect of the substrate in lowering ice nucleation threshold temperatures. There can be, however, no conclusive statement about the effect of the substrate without a reasonable estimate of the freezing (melting) temperature for the model ice-Ih system. The need for this relatively limited information about the model ice phase diagram is the fundamental motivation for the present (and previous) studies of ice models using the RSL2 potentials.[5,6] It has not been our intent to carry out a liquid-solid coexistence study for the general RSL2 potentials nor to address the merits of other frequently used model water-water potentials[7-10] for use in modeling ice Ih—though certainly all of the latter information is of great interest.

Clearly, phase diagrams for model water potentials are complex and simulations of coexistence phenomena are tedious. Weber and Stillinger[11] have used ST2 water-water potentials[10] in molecular dynamics studies of the melting of a 250-molecule ice crystallite. This work finds a 300-K melting temperature at low pressure and a 23 °C depression in the melting temperature with increased pressure (about 2 kbars). These microcrystalline ice systems are confined with a wall potential but appear to have been at neither constant density nor constant pressure. In some very interesting bulk system studies, Karim and Haymet[12-14] have used a rigid molecule transferable intermolecular potential–4 points (TIP4P) potential[7,8] and the simple point charge (SPC) potential[9] to study an ice-Ih–water interface. The initial ordered ice system unit cells are built from eight molecule, zero dipole moment periodic ice-Ih cells. From their molecular dynamics studies Karim and Haymet report stable interfaces at 240 and 200 K for the TIP4P[12,13] and SPC[14] models, respectively. The average pressures, *P*, are near zero; for the TIP4P model $P = -105 \pm 118$ atm. Assuming these ice-Ih–water interface systems are unequivocally equilibrated, Karim and Haymet's results suggest "melting temperatures" near 200 and 240 K for the SPC and TIP4P models, respectively. These low melting temperatures are surprising—particularly for the TIP4P potential which appears to do a good job of reproducing the properties of bulk water.[15,16] However, complicating factors could emerge in the water systems—including lower energy "ice" structures at these temperatures.[17]

In preliminary studies (from which the present work evolved) Deutsch *et al.*[5,6] carried out constant number, volume, and temperature (*NVT*) Metropolis Monte Carlo simulations on a model ice-Ih system which was subsequently used in the adsorbed water layer system described above. This density 0.904 g/cm^3 model ice-Ih system has a periodic 192-rigid-molecule unit cell with slightly disordered hydrogen configurations giving zero dipole moment and small quadrupole moments at 0 K.[5] The model also includes a cutoff on the potentials. Deutsch *et al.*[6] simulated the system at 20, 100, 200, and 300 K and reported that the basal face structure factors indicated a significant breakdown of ice-Ih structure between 200 and 300 K. These simulations were limited by available computer resources and system equilibration after only 3 to 4 million steps was suspect (particularly near liquid-solid coexistence). The same ice-Ih model was used in a flexible molecule *NVE* (constant *N*, *V*, and energy *E*) molecular dynamics simulation at approximate

temperatures 20, 100, 175, 260, 330, and 340 K by Kerr and Kiefer;[18] they report that the system "melts" between 260 and 330 K.

A direct Metropolis Monte Carlo approach for obtaining the model ice melting temperature would appear to be an *NPT* (constant number, pressure, and temperature) simulation at 1 atm pressure. Some preliminary *NPT* simulations have been made by Han.[20] However (in addition to generating a model ice-Ih cell with cross-sectional area different from that in the adsorbed water layer studies) at each *NPT* density change the total interaction energy must be recalculated. This energy calculation increases the computing time by a factor of $N/2$. In the present work an alternative approach is used. The pressure P is calculated in constant volume Monte Carlo simulations for temperatures ranging from 100 to 370 K. Emergence of the liquid-solid coexistence region is then looked for on the P-T plot—where (in a good ice model) dP/dT changes sign. The P-T path for an ideal infinite constant density ice system is indicated by the solid curve in Fig. 1. The point A where the system enters the solid-liquid coexistence region, and the point B, where the system leaves the liquid-vapor coexistence region can depend on the density. If finite size and nucleation hysteresis effects are minimal in the simulated system, onset of the P-T liquid-solid coexistence region should be detectable. Since for water the experimental value of dP/dT near the triple point is ≈ -133 atm/K one expects that in a reasonable model ice system the pressure slope reversal should be detectable even in the presence of nucleation hysteresis. Such a P-T analysis for systems which expand upon freezing allows one to predict a temperature corresponding to onset of "melting" (in this case onset of solid-liquid coexistence) without constructing an entire van der Waals (finite-size effect) loop. Our intent in adopting such an approach is to examine the usefulness, and/or shortcomings, of the *NVT* P-T curve approach, as well as to extract information on the model ice system.

In order to compare results of the generated P-T path data with standard phase transition probes, the internal energy, U, specific heat, C_v, and basal face structure factors, $S(\mathbf{k}_i)$ (as well as the pressure, P) are monitored for the constant density ice sample. In this study the monitored quantities support the predictions of the P-T plot and illustrate the sensitivity of the pressure data to the onset of liquid-solid coexistence. The computational details are given in Sec. II, the results in Sec. III, and comments and conclusions in Sec. IV.

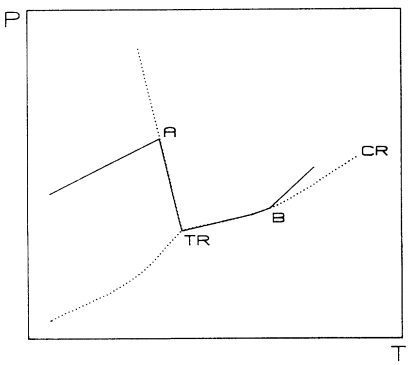

FIG. 1. Schematic of a P-T path of the water system in equilibrium at constant density. The dotted lines locate the P-T coexistence curves. The solid curve along increasing T represents the intersection of a plane of constant density with the *PVT* surface of water. *TR* and *CR* indicate the triple and critical points, respectively; *A* and *B* are described in the text.

II. COMPUTATIONAL DETAILS

The calculations use a periodic ice-Ih unit cell with 192 rigid H_2O molecules and density 0.904 g/cm^3. In order to generate a stable ice-Ih configuration at low temperatures an "initial" unit cell (at 0 K) was constructed by Deutsch *et al.*[5] with oxygens on a wurtzite lattice and H_2O dipole moments bisecting the O—O—O tetrahedral angles. A disordered hydrogen arrangement consistent with periodic boundary conditions was then determined (see Appendix of Ref. 5 and note in Ref. 19) so that the 192-molecule-unit cell has zero dipole moment and small quadrupole moments. (All subsequent Monte Carlo simulations impose no restrictions on molecular dipole orientations.) A potential cutoff (5 Å on O-O separation) was then assumed and the intramolecular O-H distance (0.972 Å), intramolecular H—O—H angle (101°), and density (0.904 g/cm^3) were determined by Deutsch *et al.*[5] from a static RSL2 potential energy minimization on the initial periodic 192-molecule-unit cell without image interactions.

In the present P-T plot approach it is important to begin with a stable low temperature ($\approx$0 K) model ice-Ih unit cell to avoid (to the extent this is possible) disordering (or reduced pressure) arising from transitions into lower energy "ice" structures. It would also be preferable to avoid a unit cell density which produces large pressures at higher temperatures. To examine the range of possibilities, Han[20] performed static potential energy minimizations on the same initial periodic cell with image interactions for different cutoffs and carried out a preliminary (6 million step) *NPT* simulations with a 6-Å cutoff (see Table I). Han[20] also examined anisotropic volume expansions of the initial unit cell and found results similar to those given in Table I. For a 6-Å cutoff a density of 0.917 g/cm^3 gives a stable ice-Ih model at 0 K; but at high temperatures (200 and 260 K) a density of the order of 0.89 g/cm^3 is required to maintain a pressure as low as 220 atm. We note that Stillinger and Rahman[4] report a pressure of 125 atm at 303 K using the same potentials (with nonrigid molecules and an Ewald summation) in a *NVT* molecular dynamics simulation of liquid water at density 1 g/cm^3. In view of these results—and the primary objective of studying the ice model used in the adsorbed water layer simulations—it was decided to continue the simulations begun with density 0.904 g/cm^3. This allows use of starting configurations for the unit cell at a few temperatures from the previous work.[6] To reduce the computational effort, a 5-Å cutoff is used.[21] Unfortunately, any selection of parameters (indeed any potential model with or without cutoff) can at best be termed a model ice-Ih. The present choice allows execution of the P-T constant density method on our model ice-Ih system

TABLE I. The cutoff (Å), optimal density (g/cm^3), intramolecular O-H distance (Å), and intramolecular H—O—H bond angle from the static minimization of the RSL2 total potential energy in the initial ice-Ih unit cell. The density is altered by varying the O-O distance in the wurtzite lattice. The last rows indicate results for *NPT* simulations. In the last column is the pressure in atm for the *NPT* simulations.

Cutoff (Å)	Density (g/cm^3)	$R_{O\text{-}H}$ (Å)	H—O—H angle (deg)	P (atm)
5.0	0.8800	0.9735	101.04	
5.5	0.9166	0.9742	100.89	
6.0	0.9166	0.9742	100.89	
6.5	0.9185	0.9743	100.86	
10.0	0.9193	0.9744	100.81	
12.0	0.9211	0.9746	100.75	
14.5	0.9262	0.9745	100.80	
6.0 (*NPT*, 200 K)	0.897	0.974	101	224
6.0 (*NPT*, 260 K)	0.886	0.974	101	228

with some degree of efficiency, and examines the short-range part of the RSL2 water-water potentials for crucial properties which support ice-Ih at low temperatures and produce expansion upon freezing.

In the Metropolis Monte Carlo simulations new configurations are generated by randomly translating a randomly selected molecule in all three Cartesian directions and randomly rotating the molecule about a randomly chosen (x, y, or z) axis.[22] Further details are given in Ref. 1. System averages are calculated over N_{av} steps at the end of the simulations. The starting configuration, the number of the generated configurations, and the maximal translational and angular displacements (for the final N_{av} steps) are summarized in Table II.

The total potential energy per molecule, U, basal face structure factors, $S(\mathbf{k}_i)$, heat capacity, C_v, and pressure, P, are monitored in the simulations. The basal face structure factors are given by

$$S(\mathbf{k}_i)=(1/N)\left\langle \left| \sum_{j=1}^{N} \exp(i\mathbf{k}_i\cdot\mathbf{r}_j) \right|^2 \right\rangle , \quad (1)$$

where $\mathbf{k}_i$ is the ith reciprocal-lattice vector associated with the two-dimensional ice basal face lattice vector, $\mathbf{a}_i$, N is the number of molecules in the unit cell, and $\mathbf{r}_j$ is the position vector of the jth oxygen. The $\mathbf{a}_i$ are determined

TABLE II. Starting configurations and simulation data for the ice systems. For each temperature, T, the starting configuration is taken from the system at T_i after N_i million steps. N_{tot} is the total number of a million Monte Carlo steps for the system at temperature T in the present simulation. δr in Å and $\delta\theta$ in radians are the maximal translational and angular displacements, respectively, for the final configurations averaged over. The * indicates results of Deutsch *et al.*[5] The ** indicates that the system at $T_i=290$ K had density 1 g/cm^3; the starting configuration for 350 K at density 0.904 g/cm^3 was obtained by scaling the coordinates. The systems at 100, 150, and 280 K were studied for an additional initial configuration, marked *b*.

T (K)	N_i	T_i	N_{tot}	δr	$\delta\theta$
100 *b*	3.45	200	5.00	0.075	0.100
100	0	0*	7.00	0.075	0.100
150 *b*	3.45	200	4.00	0.075	0.100
150	7.00	100 *b*	3.50	0.075	0.100
200	3.75*	200*	3.45	0.075	0.100
240	3.45	200	4.00	0.075	0.100
260	5.61*	260*	3.74	0.085	0.100
280	5.61*	260*	16.00	0.105	0.125
280 *b*	13.74	290	5.00	0.105	0.125
290	5.03	280	23.65	0.175	0.150
295	6.00	290	23.55	0.200	0.200
300	5.61*	260*	21.15	0.105	0.15
305	14.94	300	16.00	0.105	0.15
310	16.00	305	12.00	0.105	0.15
320	12.00	310	26.00	0.105	0.15
350	17.99**	290**	19.06	0.225	0.225
370	8.00	350	21.00	0.250	0.250

from the initial ice unit cell where $|\mathbf{a}|=2^{2/3}R_0/3$ and $R_0=2.78$ Å.[5] The heat capacity, C_v, is given by

$$C_v=(\langle U^2\rangle-\langle U\rangle^2)/[NkT^2]+3k\ , \tag{2}$$

where k is the Boltzmann constant and $\langle\ \rangle$ denotes Monte Carlo averages. The second term in Eq. (2) represents the contribution to the specific heat from the kinetic energy. The pressure is calculated from[23]

$$P=(NkT/V)[1-(3NkT)^{-1}\langle\sum_{j=1}^{N}\mathbf{r}_j\cdot\nabla_j U\rangle]\ . \tag{3}$$

Since U in the above equation is subject to a cutoff, a contribution, δP, to the pressure from the cutoff "force" is present. We estimate δP from[24]

$$\delta P\approx\langle\delta U\rangle R/(3\,\delta R\ V)\ , \tag{4}$$

where $\delta R=0.5$ Å and $\langle\delta U\rangle$ is the average potential energy per molecule arising from interactions between molecules separated by r, where $R<r<R+\delta R$, and R is the cutoff.

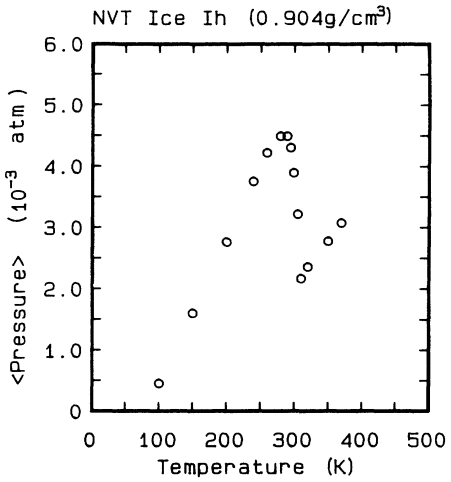

FIG. 2. Pressure$\times10^{-3}$(atm) vs temperature (K) for the bulk ice 0.904 g/cm^3 density sample from the *NVT* Monte Carlo simulations. The value of dP/dT near 300 K is ≈-140 atm/K.

III. RESULTS

In Table III are the fixed temperature, T, for each simulation, the number of final configurations averaged over, $N_{\rm av}$, the total average potential energy per molecule, $\langle U\rangle/N$, the pressure (in 10^3 atm), the total heat capacity, C_v, and the two basal face structure factors. The quoted pressures, $\langle P_{\rm tot}\rangle$, include the cutoff contribution, $\langle\delta P\rangle$.

Figure 2 shows the P-T results for this simulation. From 100 to 260 K P increases almost linearly with a slope of $\approx$24 atm/K. From 260 to 280 K the pressure increases less than 14 atm/K—suggesting the approach to liquid-solid coexistence. The simulations give the same pressure at 280 and 290 K and beyond 290 K the calculated pressure drops with a slope of ≈-140 atm/K to a value of 2160 atm at 310 K. This pressure behavior suggests that the onset of the liquid-solid coexistence region is between 280 and 290 K for the constant density (0.904 g/cm^3) model bulk ice-Ih system. As noted above, the pressure drop upon reaching the coexistence curve is characteristic of a substance which expands upon freezing and indicates that the RSL2 potentials with the rigid molecule condition reproduce this qualitative feature of water. We find some indication of nucleation hysteresis in a second system at 280 K (marked 280 *b*) whose simu-

TABLE III. Results for the average potential energy per molecule, $\langle U\rangle/N$ (in kcal/mole), the total average pressure, $\langle P_{\rm tot}\rangle=\langle P\rangle+\langle\delta P\rangle$ (in 10^3 atm), the average contribution to the pressure from the cutoff, $\langle\delta P\rangle$ (in 10^3 atm), the specific heat, C_v (in cal/g K), and the average structure factors for ice-Ih basal face reciprocal lattice vectors, $\langle S(\mathbf{k}_i)\rangle$; $N_{\rm av}$ is the number of a million final Monte Carlo configurations used to calculate system averages.

T (K)	$N_{\rm av}$	$\langle U\rangle/N$	$\langle P_{\rm tot}\rangle$	$\langle\delta P\rangle$	$\langle C_v\rangle$	$\langle S(\mathbf{k}_1)\rangle$	$\langle S(\mathbf{k}_2)\rangle$
100 *b*	2.00	−12.31	0.42	0.18	0.70	114.1	111.9
100	3.00	−12.32	0.45	0.21	0.71	115.8	112.2
150 *b*	2.00	−11.98	1.70	−0.37	0.67	119.6	113.4
150	2.50	−11.98	1.60	−0.53	0.67	111.4	110.6
200	2.35	−11.67	2.76	−0.79	0.70	106.9	105.7
240	2.00	−11.40	3.75	−1.10	0.72	107.8	106.7
260	2.50	−11.21	4.22	−1.10	0.71	106.1	94.3
280	7.00	−11.07	4.49	−1.27	0.71	96.9	99.9
280 *b*	3.00	−11.03	4.41	−1.11	0.75	78.1	82.0
290	9.00	−10.98	4.49	−1.18	0.72	78.9	81.0
295	2.95	−10.89	4.30	−1.26	0.75	70.8	75.3
300	3.50	−10.70	3.89	−1.14	0.78	60.3	50.2
305	9.00	−10.46	3.21	−1.33	0.94	36.5	38.8
310	5.00	−9.95	2.16	−1.04	0.95	4.6	5.3
320	6.00	−9.50	2.35	−1.13	1.03	1.9	1.5
350	6.00	−9.00	2.77	−1.18	1.03	1.7	1.4
370	6.00	−8.79	3.07	−1.22	1.05	1.2	1.4

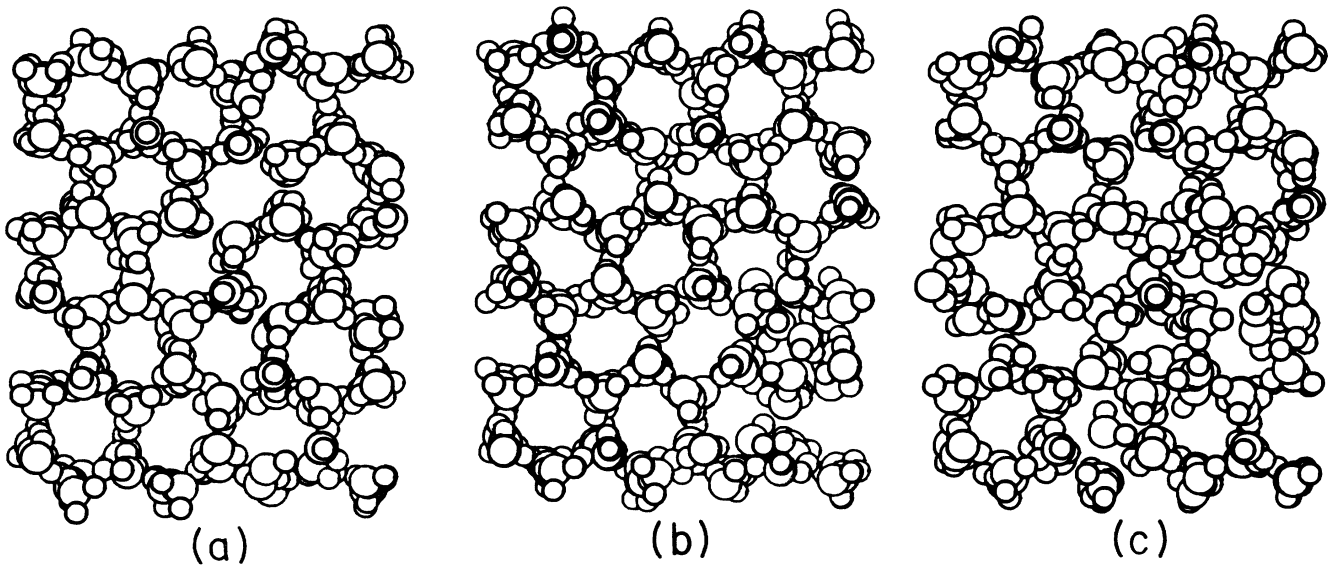

FIG. 3. Snapshots of the system projected onto xy (basal) plane after (a) 16 million steps at 280 K, (b) 23 million steps at 290 K, and (c) 21 million steps at 300 K.

lation starts with an equilibrated configuration at 290 K (see Tables II and III). It is interesting to compare dP/dT for the simulation data in the coexistence region with the experimental value, -133 atm/K.

For $T > 310$ K the pressure versus T slope reverses again, indicating departure from the liquid-solid coexistence region. The large positive dP/dT suggests a liquidlike property. However, whether the system is in a single liquid phase, or in the vapor-liquid coexistence region, cannot be determined from these results.

Figures 3(a)–3(c) show snapshots of the unit cell projected onto the xy (basal) plane for the 280-, 290-, and 300-K simulations after approximately 16, 23, and 21 million steps, respectively. The 290-K system snapshot shows some breakup of six-membered-ring structure at the bottom right corner—suggesting fluctuations which could give rise to a liquidlike cluster. The 300-K system snapshot shows a more widespread breakup of the structure in neighboring regions. These rather qualitative indications of the state of the system appear to persist over several million Monte Carlo steps.

In Fig. 4 is a plot of the average total potential energy per molecule versus temperature for the simulated system. There is a nearly linear increase in potential energy per molecule from 200 to 290 K; for $T > 290$ K the slope becomes steeper. In the liquidlike region ($T \geq 320$ K) the slope is smaller than in the transition region, but larger than in the low temperature solid phase region. This behavior of the potential energy is a natural consequence (except for a slight rounding near the onset melting temperature) of the NVT ensemble averaging for a system which exhibits a first-order phase transition. A similar behavior of the internal energy versus T has been observed in the melting of an ice microcrystallite.[11]

From the above results it is apparent that the potential energy is not as sensitive as the pressure to the onset of coexistence. Structure factors, however, are expected to be sensitive probes. In order to display the combined effects of the two basal face structure factors, an average structure factor, S_{av}, is calculated from

$$S_{av} = [\langle S(\mathbf{k}_1)\rangle + \langle S(\mathbf{k}_2)\rangle]/2 \ . \tag{5}$$

In Fig. 5 is plotted $\ln(S_{av})$ versus temperature. The latter quantity decreases linearly with temperature from 100 to 280 K and exhibits a noticeable drop for $T > 280$ K consistent with the P-T plot analysis. The values of S_{av} indicate that the system is partially structured in the coexistence region. It is not unexpected that (for a constant density coexistence region) some ice structure persists to

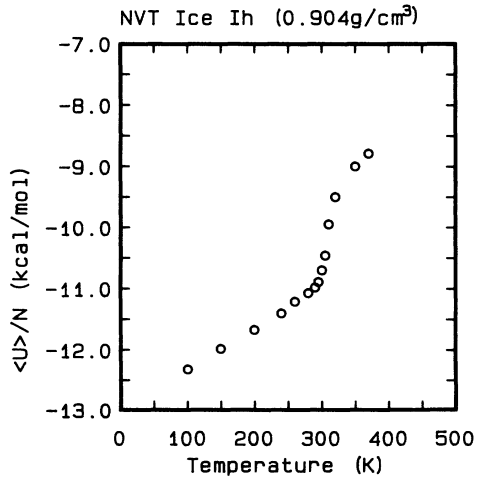

FIG. 4. Average potential energy per molecule in kcal/mole vs temperature (K) for the 0.904 g/cm^3 192 molecule ice sample from the NVT Monte Carlo simulations.

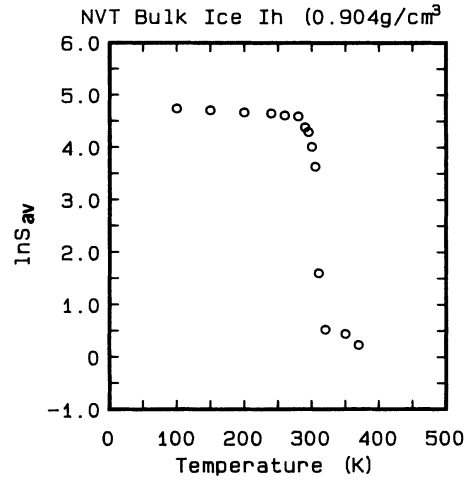

FIG. 5. The $\ln S_{av}$ vs T, where $S_{av}=[\langle S(\mathbf{k}_1)\rangle+\langle S(\mathbf{k}_2)\rangle]/2$, for the 0.904 g/cm^3 constant density ice sample from the *NVT* Monte Carlo simulations.

the triple point. For the "melted" systems at 320, 350, and 370 K the structure factors are small as expected for a disordered system.

In Fig. 6 the calculated constant volume heat capacity is shown to be near 0.7 cal/g K for the low temperature solidlike systems. It is interesting that a smaller value of 0.67 at $T=150$ K is obtained for both sample 150-K systems and appears to be stable. Near 290 K the specific heat increases as expected from the $\langle U\rangle$ versus T plot. This suggests that the simulated constant density ice system enters a two-phase (liquid-solid) coexistence region near 290 K.[25] However, the C_v data appears to be considerably less sensitive to onset of coexistence than the pressure or structure factor data. The values of the specific heat for $T\geq 300$ K (≈ 1 cal/g K) reflect a liquidlike property of the system.

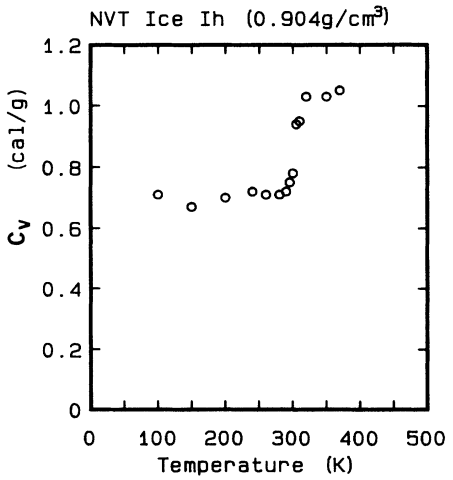

FIG. 6. The specific heat, C_v, in cal/g vs T for the 0.904 g/cm^3 constant density sample from the *NVT* Monte Carlo simulations.

IV. DISCUSSION AND CONCLUSIONS

In this study, an isochoric Monte Carlo simulation is used to study the *P-T* behavior of a model periodic unit cell of ice-Ih near "melting." The results of the simulations indicate (assuming minimal finite-size effects) an onset of the liquid-solid coexistence region between 280 and 290 K. In evaluating this result, we emphasize the parameters which define the ice model: the 0.904 g/cm^3 density; the 5-Å cutoff; the finite system size (192 molecules); the single hydrogen arrangement[5] at 0 K; and the internally rigid molecules with a 101° H—O—H angle. The model ice system expands with freezing and upon heating appears to enter the liquid-solid coexistence region at a temperature not far from the experimental triple point for water. The results for the specific heat, structure factors and energy support the *P-T* curve predictions. It is interesting that the *P-T* data and the structure factor data of this study show about equal sensitivity to onset of liquid-solid coexistence. We note that this *NVT* *P-T* plot technique for estimating the onset of melting is not particularly useful for substances which contract upon freezing. In the latter case the slope of the pressure does not reverse sign in the coexistence region and the point where the constant density system enters the coexistence region is more likely to be masked by finite size or nucleation hysteresis effects.

A comparison of the flexible molecular dynamics simulation of Kerr and Kiefer[18] and the present simulation suggests that the rigid molecule constraint does not dramatically alter the system's approach to liquid-solid coexistence. It is not known whether the cutoff alters the location of liquid-solid coexistence. However, the fact that the tetrahedral environment of the water molecule lies well within 5 Å suggests that cutoff effects on "melting" should be limited. Clearly, in future studies of the rigid molecule model a larger system size together with a larger cutoff or an Ewald summation should be considered. When Ewald sum data are available, the present work should be useful as a indicator of cutoff effects.

Finally, we note that the short-range part of the Stillinger-Rahman revised potentials (with intramolecular constraints) appears to do a credible job of supporting the model ice-Ih structure from 100 to about 280 K and of reproducing the expected shape of the *P-T* constant-volume behavior for the model ice-Ih system near 280 K. Since we assume rigid molecules, a cutoff on the potentials, and a particular hydrogen configuration at low temperatures, our "ice model" is an approximation to the average ice-Ih system supported by the general RSL2 potentials. However, the results are encouraging and should be useful in evaluating the effects of system size, hydrogen configuration, cutoff, and flexible molecules in future studies with these potentials. The present work also offers a point of comparison for studies using other water-water potentials[7–10] and more sophisticated techniques for extraction of the phase diagram.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation under Grants No. ATM83-10854 and No. ATM87-13827.

*Present address: Department of Chemistry, Purdue University, West Lafayette, IN 47907.

[1]R. C. Ward, J. M. Holdman, and B. N. Hale, J. Chem. Phys. **77**, 3189 (1982).

[2]R. C. Ward, B. N. Hale, and Sergio Terrazas, J. Chem. Phys. **78**, 420 (1983).

[3]J. Taylor and B. N. Hale (unpublished).

[4]F. H. Stillinger and A. Rahman, J. Chem. Phys. **68**, 666 (1978).

[5]P. W. Deutsch, B. N. Hale, R. C. Ward, and D. A. Reago, J. Chem. Phys. **78**, 5103 (1983).

[6]P. W. Deutsch, B. N. Hale, R. C. Ward, and D. A. Reago, J. Phys. Chem. **87**, 4309 (1983).

[7]W. L. Jorgenesen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983).

[8]W. L. Jorgensen and J. D. Madura, Mol. Phys. **56**, 1381 (1985).

[9]H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, and J. Hermans, in *Intermolecular Forces,* edited by B. Pullmann (Reidel, Dordrecht, 1981), p. 331.

[10]F. H. Stillinger and A. Rahman, J. Chem. Phys. **60**, 1545 (1974).

[11]T. A. Weber and F. H. Stillinger, J. Phys. Chem. **87**, 4277 (1983); J. Chem. Phys. **80**, 438 (1984).

[12]O. A. Karim and A. D. J. Haymet, Chem. Phys. Lett. **138**, 531 (1987).

[13]O. A. Karim and A. D. J. Haymet, J. Chem. Phys. **89**, 6889 (1988).

[14]O. A. Karim, P. A. Kay, and A. D. J. Haymet, J. Chem. Phys. **92**, 4634 (1990).

[15]W. L. Jorgensen and J. Gao, J. Phys. Chem. **90**, 2174 (1986).

[16]M. R. Reddy and M. Berkowitz, J. Chem. Phys. **87**, 6682 (1987).

[17]A. D. J. Haymet (private communication).

[18]J. A. Kerr and J. Kiefer, J. Chem. Phys. **89**, 4313 (1989).

[19]In Appendix A of Ref. 5 the numbering is clockwise, not counterclockwise.

[20]K. Han, Ph.D. thesis, University of Missouri-Rolla (1989).

[21]The simulations were done on an IBM 4381-P02 (taking ≈ 25 CPU hours per 10^6 steps) and on an Apollo DN3500 with floating-point accelerator (taking ≈ 36 CPU hours per 10^6 steps). A 6-Å cutoff increases this time about 44%.

[22]J. A. Barker and R. O. Watts, Chem. Phys. Lett. **3**, 144 (1969).

[23]J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 591 (1976).

[24]M. Mezei and D. L. Beveridge, J. Chem. Phys. **76**, 593 (1982).

[25]F. F. Abraham, in *Proceedings of the International Conference on Ordering in Two Dimensions,* edited by S. K. Sinha (North-Holland, New York, 1980), p. 155; *Melting, Localization, and Chaos,* edited by R. K. Kalia and P. Vashishta (North-Holland, New York, 1982), p. 75.