Molecular dynamics simulations of surface-initiated melting of nitromethane

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The melting of nitromethane initiated at solid-vacuum interfaces has been investigated using molecular dynamics MD simulations with a realistic force field [D. C. Sorescu et al., J. Phys. Chem. B 104, 8406 (2000)]. The calculated melting point (251±5 K) is in good agreement with experiment (244.73 K) and values obtained previously (~255.5 and 266.5±8 K) using other simulation methods [P. M. Agrawal et al., J. Chem. Phys. 119, 9617 (2003)]. Analyses of the molecular orientations and diffusion during the simulations as functions of the distance from the exposed surfaces show that the melting is a direct crystal-to-liquid transition, in which the molecules first gain rotational freedom, then mobility. There is a slight dependence of the melting temperature on the exposed crystallographic face. © 2006 American Institute of Physics.
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I. INTRODUCTION

We report here the results of molecular dynamics (MD) simulations of surface-induced melting of nitromethane. This work is a continuation of a series of theoretical studies of the physical properties of solid and liquid nitromethane that is based on a force field1 that is proving to be quite accurate.2–4 This work also fits into another series of studies in which we are using MD simulations to study melting of complex molecular and ionic solids,2–4,13–14 and nanoparticles.4,15,16 The objective of these studies is to develop models for predicting thermodynamic melting points given an accurate force field and a better understanding of the mechanisms of melting. The exact details of how melting occurs are not easily obtained experimentally; however, MD simulations can provide insights into the melting mechanisms at the molecular level. If a perfect crystal is heated, as can easily be done in a simulation but not in a laboratory, melting occurs well above the normal melting point because the system must overcome the free energy barrier to form a solid-liquid interface. In the laboratory melting begins at interfacial regions of the solids where the free energy barrier to form a solid-liquid interface is negligible. These interfaces may be voids, grain boundaries, exposed surfaces, or other disruptions of the crystal structure. Here we report the results of MD simulations of the melting of perfect crystalline nitromethane with surfaces exposed to vacuum.

It has been shown that there is crystal surface disorder at temperatures below the melting point (Tm,p).17 The degree of disorder ranges from a less-ordered crystalline or amorphous structure to a quasiliquid region, which is referred to as surface melting. Di Tolla et al.18 have presented a thorough and succinct discussion of the various classifications of incomplete melting and surface effects for various types of crystals. Surface roughing is probably the most appropriate term in the present case. The crystalline order of the surface layers ceases to exist. The temperature dependence of the formation and the nature of the quasiliquid region depend on the intermolecular forces. Theoretical derivations by Trayanov and Tosatti19 and by Mori et al.20 show that for long-range van der Waals interactions the thickness of the melted interfacial layer depends on temperature as (Tm,p−T)−α, with α as large as one-third. Pluis et al.21 have shown that for short-range metallic interactions the thickness grows logarithmically as |ln(Tm,p−T)|. These theoretical predictions are supported by experimental studies of surface melting of argon,22 which obeys the power law, and gallium,23 which obeys the logarithmic law; and molecular dynamics simulations of surface melting24–26 provide further support. We should note that while we refer to the transition temperature as the melting point, in fact, it actually corresponds to the triple point, although there is little difference.

Experiments show that melting points depend on the crystallographic face of the surface. As the orientation of the interface of crystal changes, the molecular configuration at the surface and the net interaction between the molecules at the surface vary. Thus, one may expect a different melting point for various interfaces. Studies of crystalline lead by Pluis et al.21 show that the (110) surface undergoes surface melting at temperatures lower than the melting point of bulk lead, while the (111) surface remains unchanged until the melting point is reached. The temperature at which surface melting starts can be as low as 0.66Tm,p27,28 and as T→Tm,p the thickness of the disordered surface layer increases, spreading throughout the entire crystal.

Most of the studies of surface disorder and surface melting have been simple atomic systems, e.g., metals and alloys,29–36 and Lennard-Jones systems;37,22 however, some have been done for materials comprising large molecules or polymers.38–42 Little is known about surface melting in molecular crystals. Agrawal et al.2 have reported the results of MD simulations of the melting of nitromethane for the same potential used here. They used two simulation methods: void-induced melting with constant heating (1.5×10−4 K/0.75 fs) and equilibration of solid and liquid

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in contact. In the former they calculated the melting point to be 266±8 K and in the latter to be ~255 K. The main difference in these two methods is how entropy is introduced into the system. The coexisting solid-liquid interface method gives a value for the melting point closer to the measured value of 244.73 K. Agrawal et al. speculated that the difference in the values of the computed melting point obtained by the two methods is due to hysteresis in the direct-heating approach.

We have performed nvt MD simulations of the melting of nitromethane with free surfaces. Our interest is the mechanisms of melting of molecular crystals at the atomic level, thus we have attempted to probe the details of how the transition occurs. We have investigated the dependence of the melting point on the crystal structure (100, 010, and 001) of the exposed face. Order parameters as functions of the distance from the surface show the evolution of disorder in nitromethane as it undergoes the solid to liquid transition.

II. METHODS

A. Simulations

The simulations were performed using the DL_POLY (v. 2.15) code, which uses a Verlet leapfrog integration algorithm. Simulations of the nvt ensemble using the Nosé-Hoover thermostat were carried out over the temperature range from 226 to 286 K. The trajectories were integrated for $6 \times 10^5$ steps with step size of 0.75 fs; the first $2 \times 10^5$ steps were for equilibration. The thermostat relaxation time was 2 ps. The cutoff range for the potential was set at 11 Å and the Verlet shell at 0.5 Å. Trajectory data were stored every 100 steps for analysis.

Simulations of crystalline nitromethane with two faces exposed to vacuum as illustrated in Fig. 1 were carried out. Two exposed surfaces are necessary because of the periodic boundary conditions that were applied in all directions. The length of the crystal is “infinite” in two directions and finite in the third. The density, order parameter, and diffusion coefficient were computed within rectangular fixed-volume slabs approximately one molecular size in width, as illustrated in Fig. 2, to analyze the evolution of the melting processes from the interface. Because of the symmetry of the simulation cell, the properties of the molecules in slabs n and n’ were combined to compute averages of quantities as functions of the distance from the exposed surface or the center of the simulated crystal. The melting was considered to be complete when the properties of the core, i.e., slabs 1 and 1’

in Fig. 2, indicated the liquid state. The nitromethane crystal structure was based on the neutron diffraction scattering data reported by Trevino and Rymes.

Simulations were performed for exposed faces (100), (010), and (001), which are shown in Fig. 3. The simulation supercell for the exposed (100) surface was constructed by defining an empty orthorhombic simulation cell of dimensions $a=78.66$ Å, $b=25.25$ Å, and $c=26.19$ Å, then placing a perfect $5 \times 4 \times 3$ crystal of nitromethane in it so that the center of mass of the crystal was located at the center of the orthorhombic cell with the [100] direction of the crystal parallel to edge a of the simulation cell. Thus, the actual crystal occupied the central one-third of the volume of the supercell, with the remaining two-thirds vacant. In the case of the exposed (010) surface a $5 \times 4 \times 3$ crystal was placed in the center of a simulation cell of dimensions $a=26.22$ Å, $b=75.84$ Å, and $c=26.19$ Å with the [010] direction of the crystal parallel to the b direction of the simulation cell. In the case of the (001) face, a $5 \times 4 \times 3$ crystal was placed at the center of a simulation cell of $a=26.22$ Å, $b=25.28$ Å, and $c=78.75$ Å with the [001] direction of the crystal parallel to the c direction of the simulation cell.

We also performed simulations for $5 \times 5 \times 5$ cells (with dimensions $a=78.66$ Å, $b=31.60$ Å, and $c=43.65$ Å) and for $10 \times 4 \times 3$ cells (with dimension $a=157.32$ Å, $b=25.28$ Å, and $c=26.19$ Å). These simulations were done only for the exposed (100) surface. The results for these larger supercells show that the $5 \times 4 \times 3$ supercell is of adequate size.

The state of the system was determined by computing the density, orientation order parameter, diffusion coefficient, and radial distribution function, all of which undergo abrupt changes at the melting point for a first-order transition. The orientational order was determined by calculating the ensemble average of the absolute value of the cosine of the angle between the direction of the C–N bond and the vector of the unit cell.
\( \langle \cos \theta \rangle = \frac{1}{N} \sum_i |\mathbf{e}_i \cdot \mathbf{k}|, \)

(1)

where \( \mathbf{e}_i \) is the unit vector along the C–N bond and \( \mathbf{k} \) is the unit vector along direction \( c \). The angle between the C–N bond and edge \( c \) is close to 0° and 180° in the crystal, thus \( \langle |\cos \theta| \rangle \cong 1 \) in the crystal and decreases as the crystalline order diminishes. The diffusion coefficient \( D \) was calculated using

\( \langle \Delta r^2 \rangle = 6Dt, \)

(2)

where \( r \) is the position vector of a molecule relative to the center of mass of the system and \( t \) is the time. The physical state of the system was confirmed by computing the radial distribution function (RDF):

\[ g(r) = \frac{1}{nN} \left( \sum_i \sum_j \delta(r - r_{ij}) \right), \]

(3)

where \( N \) is the total number of molecules in the slab, \( n \) is the number density, and \( r_{ij} \) is the distance between the centers of mass of the molecules within the slab.

**B. Force field**

The force field is based on the crystal model originally developed for cyclotrimethylene trinitramine (RDX) by Sorescu et al., but which has been shown to be applicable to a wide range of organic solids. It has been shown to accurately predict the solid- and liquid-state properties of nitromethane. It was used with minor modifications by Agrawal et al. to study melting of nitromethane, giving results in good agreement with experiment.

The intermolecular forces are described by the Buckingham (exp-6) potential plus Coulombic interactions with fixed partial charges. The intramolecular interactions are represented by a sum of Morse potentials for the bond stretches, harmonic oscillators for the bond angles, and cosine sum for the torsion angles. A description of the force field and the values of the parameters are given in Ref. 1.

**III. RESULTS AND DISCUSSION**

Constant volume-constant temperature (NVT) simulations of 5\( \times \)4\( \times \)3, 5\( \times \)5\( \times \)5, and 10\( \times \)4\( \times \)3 supercells with exposed (100) faces [see Fig. 3(a)] were carried out over the temperature range of 226–286 K. The simulation lengths for the 5\( \times \)5\( \times \)5, 10\( \times \)4\( \times \)3, and 5\( \times \)4\( \times \)3 supercells were, respectively, 7.5\( \times \)10\(^5\) steps (including 2\( \times \)10\(^4\) equilibration steps), 1.6\( \times \)10\(^6\) steps (including 2\( \times \)10\(^4\) equilibration steps), and 6\( \times \)10\(^5\) steps (including 2\( \times \)10\(^4\) equilibration steps), where each step is 0.75 fs. The RDFs for the molecules in the cores (labeled 1 and 1’ in Fig. 2) of the three supercells are shown for 246 and 251 K in frames (a) and (b), respectively, of Fig. 4. The RDFs were calculated by averaging over the last 5000 steps (3.75 ps) of the simulations. The multiple peaks in Fig. 4(a) are indicative of a solid and the structure of the curves in Fig. 4(b) are typical of a liquid. The computed values of the melting point are independent of the size of the simulation supercell. The predicted melting point agrees with experiment (244.73 K) and the values calculated by Agrawal et al. using the same force field. They used void-induced melting and solid-liquid equilibration simulations, obtaining, respectively, 266\( \pm \)8 and ~255.5 K for the melting point.

Complete melting was determined by computing properties in the core (labeled 1 and 1’ in Fig. 2) of the simulation supercell. The computed density, order parameter, and diffusion coefficient for the core of the 5\( \times \)4\( \times \)3 supercell as functions of temperature are shown in Fig. 5. The abrupt changes in these properties correspond to the solid-liquid phase transition between 246 and 251 K, which is in accord with the computed RDFs shown in Fig. 4. The simulations at 246, 248.5, and 251 K were 1.4\( \times \)10\(^6\) integration steps (0.75 fs/step) longer than those for the other temperatures, which were run for 4.6\( \times \)10\(^5\) steps. At temperatures near the melting point longer simulations are required for complete equilibration. The variation in temperature during a nvt simulation is typically \( \pm \)5 K.

The calculated orientational order parameter, density, and diffusion coefficient at the core of the simulated crystal at 251\( \pm \)5 K as functions of simulation time are shown in Fig. 6 for the 5\( \times \)4\( \times \)3 (green curve), 5\( \times \)5\( \times \)5 (red curve), and 10\( \times \)4\( \times \)3 (blue curve) supercells. For reference, the values of the liquid-state properties calculated for the same thermodynamic conditions (1 atm, 251 K) are indicated by

**FIG. 3. Illustration of the crystallographic orientations of the surfaces that were investigated: (a) 100, (b) 010, and (c) 001.**
arrows: the order parameter at 0.78, the density at 0.0114 Å⁻³, and the diffusion coefficient at 0.11 Å²/ps. The results show that the molecules gain orientational and translational freedom on roughly the same time scale; compare the red and green curves for the order parameter and diffusion coefficient. In general, one assumes that rotational freedom precedes translational freedom as a solid is heated to its melting point, and it seems reasonable to assume that the disordering of a perfect crystalline face would occur by this mechanism. The fact that it does not appear to be true for nitromethane may be due to its rather large dipole moment.

There is an intermediate stage in the loss of orientational order, which is seen most clearly in the results for the 10x4x3 simulation, shown by the blue curve in Fig. 6(a).

We see behavior more in line with the usual assumption about how disorder evolves in the conversion of a solid to a liquid at the surface of the crystal. The orientational order parameter, density, and diffusion coefficient at the surface of the crystal are defined by 5 and 5' in Fig. 2 as functions of time for the 5x4x3 crystal at 251 K are shown in Fig. 7; again the arrows indicate the values of the property in the liquid state. Complete orientational disorder is established at about 100 ps, but the diffusion coefficient does not reach the liquid-state value until after 200 ps. The diffusion coefficient rises above and the density drops below the liquid-state values because these quantities are for the molecules in contact with the vacuum.

The observation that orientational disordering precedes translational freedom is characteristic of molecules such as nitromethane and RDX.¹¹,¹² The melting mechanism differs from that for polymer chains in colloidal systems where the crystalline structure melts by a first-order transition to a nematic phase in which centers of mass of the molecules have no long-range order while the molecules still show orientational order.⁵⁰ The actual time differences we observe may be affected by the simulation parameters; however, we believe the qualitative conclusion is valid.

Because there is a time gap between the establishment of orientational disorder and translational freedom of the mol-
molecules, there is the possibility that the system passes through an amorphous state. The RDF of amorphous state looks like liquid RDF. The RDF calculated for the core defined by 1 and 1’ in Fig. 2 for the $5 \times 4 \times 3$ supercell. The values for the diffusion coefficient are averages over 3.75 ps intervals and those for the order parameter and density are averages over 0.075 ps intervals of the simulations. The arrows indicate the values for the liquid state: 0.78 for the order parameter, 0.0114 Å$^{-3}$ for the density, and 0.11 Å$^2$/ps for the diffusion coefficient.

The thickness of the disordered surface layer $l(T)$ of van der Waals solids is expected to increase according to the equation

\[
l(T) = \left( \frac{(T_{mp} - T) L}{2T_{mp} W \rho_l^2} \right)^{-1/3},
\]

where $T_{mp}$ is the melting temperature, $L$ is the latent heat of melting per atom, $W$ is the Hamaker constant, and $\rho_l$ is the density of the liquid. The Hamaker constant and density depend on the temperature; if it is assumed that the temperature

![FIG. 6.](image1) (a) Orientational order parameter, (b) density, and (c) diffusion coefficient as functions of the simulation time for the $5 \times 4 \times 3$ (green curve), $5 \times 5 \times 5$ (red curve), and $10 \times 4 \times 3$ (blue curve) supercells at 251 K. The quantities are calculated for the core of the simulation cells, as labeled as 1 and 1’ in Fig. 2 for the $5 \times 4 \times 3$ supercell. The values for the diffusion coefficient are averages over 3.75 ps intervals and those for the order parameter and density are averages over 0.075 ps intervals of the simulations. The arrows indicate the values for the liquid state: 0.78 for the order parameter, 0.0114 Å$^{-3}$ for the density, and 0.11 Å$^2$/ps for the diffusion coefficient.

![FIG. 7.](image2) (a) The orientational order parameter, (b) density, and (c) diffusion coefficient (the points are connected by solid lines) of the molecules at the surface ($5$ and $5'$ in Fig. 2) of the $5 \times 4 \times 3$ crystal at 251 K. The arrows, as in Fig. 6, indicate the values of the properties in the liquid state. Complete orientation disorder is established at about 100 ps, but the diffusion coefficient does not reach the liquid-state value until about 200 ps.

![FIG. 8.](image3) Radial distribution function (data points on the solid line) of the core of the nitromethane crystal calculated over the time period from 300 to 303.75 ps. The shape of the RDF is closer to crystalline pattern [Fig. 4(a)] than the liquid pattern [Fig. 4(b)] and thus it does not indicate existence of amorphous state during the process of melting of nitromethane crystal.
dependence is negligible, melting point can be estimated by fitting the thickness of the melted layer to the form of Eq. (4). The thickness of the molten surface was calculated by determining the number of layers as defined in Fig. 2, with liquid properties determined by the density, order parameter, diffusion coefficient, and RDF. The results are shown in Fig. 9. The computed results are accurately fitted by $l(T) = K(T_{mp} - T)^{-1/3}$, where $K$ and $T_{mp}$ are fitting parameters assumed to be temperature independent. The melting point obtained from this fit is $239 \pm 5$ K, which is in good agreement with the experimental value of $244.73$ K. This estimate of $T_{mp}$ is about 12 K lower than that predicted by the other method used here; this difference is slightly outside the estimated statistical error bars. This may be due to the assumption that the fitting parameters are independent of $T$ and to the arbitrariness in the definition of the thickness of the molten layer. The latter is likely the more serious approximation.

We investigated the dependence of the melting point on the crystallographic orientation of the exposed surface. The three faces, (100), (010), and (001), are illustrated in Fig. 3. The molecules at the surface of the (100) interface are almost normal to the page, while those at the (010) and (001) interfaces are almost parallel to the page. We carried out simulations of $5 \times 4 \times 3$ supercells for the three interfaces. The melting point for the (010) and (001) interfaces is $266.0 \pm 6.0$ K, compared to $251 \pm 5$ K for the (100) interface. The orientational order parameter, density, and diffusion coefficient of the surface layers of molecules (defined by 5 and 5' in Fig. 2) for the (100), (010), and (001) interfaces as functions of time at 266 K are shown in Fig. 10. The arrows indicate the liquid-state values for the properties. The time evolutions of the disorder, density, and diffusion coefficient are in accord with the computed melting points; that is, the evolution of orientational disorder, translational freedom, and change in density occurs more slowly for the crystals with (010) and (001) interfaces than in the case of the (100) interface. This behavior is obviously related to the surface tension of the interfaces. In the (010) and (001) cases the surfaces are polymerlike strings of the polar molecules, which resist disordering, while the (100) interface, which
exposes the tails of the molecules in the polymerlike chains, are less resistant to reorientation and mobility. Dependences of melting points on the structure of exposed faces of crystals have been observed in experiments for metallic systems and predicted by MD simulations.

Melting will begin at the solid surface (or defect) that has the lowest free energy to the formation of the solid-liquid interface. For exposed perfect crystallographic surfaces the lowest melting point is the one that would be closest to the measured melting point; however, it could be higher since defects in that crystallographic surface could serve to lower the free energy barrier. In the current study the calculated melting point of (100) surface (251.0±4.9 K) is determined to have the lowest melting point, and thus is one that we compare to the bulk melting point (244.73 K).

We compared the fluctuation in density within each molecular layer in our simulation with the theoretical value calculated using statistical mechanics. The fluctuations in density \( \sigma_\rho \) for a grand canonical ensemble (constant chemical potential \( \mu \), volume \( V \), and temperature \( T \)) is

\[
\sigma_\rho = \left( \frac{kT}{V} \right)^{1/2},
\]

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \kappa \) is the isothermal compressibility, \( V \) is the volume, and \( \rho \) is the density. The isothermal compression data for liquid nitromethane reported by Jones \( \kappa = 4.74 \times 10^{-5} \text{ atm}^{-1} \). Assuming free energy and temperature are distributed evenly throughout a molten slab (as defined in Fig. 2), of volume 1736 Å\(^3\) at temperature close to calculated melting point (256 K), the fluctuation in density is \( \sigma_\rho = 0.0014 \text{ Å}^{-3} \), which is comparable to the fluctuations in the values of the density calculated in the simulations.

### IV. CONCLUSIONS

We have investigated the melting of nitromethane initiated at free surfaces of perfect crystals by using MD simulations with a force field that has been validated in several previous applications. The computed melting point is in good agreement with the values obtained in previous MD simulations using different methods and with the experimental value. The density, radial distribution function, diffusion coefficient, and orientational order parameter were calculated at the surface and the core of the simulated supercell. The melting point was shown to depend on the crystallographic orientation of the exposed interface. The melting point of crystals with a (100) free surface was calculated to be 251±5 K, while crystals with (010) and (001) exposed faces melted at 266.0±6.0 K.

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