Crystallization of Molecular Liquids in Computer Simulations: Carbon Dioxide

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(Received 25 April 1995)

Using molecular dynamics simulations we investigate the process of homogeneous crystallization of a typical nonpolar molecular liquid, carbon dioxide. A time-temperature-transformation plot is displayed, with the nucleation times being in the range of a few hundreds of picoseconds to a few nonoseconds. Directional anisotropy in the local molecular diffusion is found to be an important feature of the nucleation process.

PACS numbers: 61.25.Em, 61.20.Ja, 64.60.Qb, 64.70.Dv

The crystallization of liquid is a widespread phenomenon, yet our understanding of this process at the microscopic level is rather fragmented. Over the past two decades computer simulations have provided us with a detailed picture of the crystallization of simple monatomic liquids [1–4] by directly probing the microscopic dynamics of this phase transition. However, rather limited success has been reported for molecular systems [4]. The crystallization of a molecular liquid, in contrast to a melting of a molecular solid [5], has not been readily observable in computer simulations [1]. The galssy states which emerge upon reducing the temperature have, within the time scale of a typical simulation, effectively prevented a spontaneous nucleation of a molecular heterophase. It is not surprising then that, although the crystallization of a simple Lennard-Jones fluid was first studied almost 20 years ago [6], only recently has the crystallization of a molecular fluid, water, been observed in a computer simulation [7].

In the molecular dynamics (MD) simulations reported in Ref. [7] the crystallization of supercooled liquid water was induced with a homogeneous static electric field; the resulting polar crystal forming under constant density conditions had the structure of cubic ice I. In the present study we investigate the process of the homogeneous crystallization of a typical nonpolar *molecular* liquid in the absence of any externally applied field. We have carried out a series of extensive MD simulations of carbon dioxide (CO_2) and have observed the spontaneous formation of a fcc (face-centered cubic) crystal from a supercooled liquid on time scales of 10^{-10} to 10^{-9} s over a narrow range of temperatures. We are aware of no other simulation study in which the transformation of an isotropic molecular liquid into a crystalline solid has been observed in the absence of external perturbations [8].

Our MD simulations were performed with samples of 108, 256, and 500 molecules at a constant density of 1.4 g/cm^3 and employed the three-site Murthy-Singer-McDonald potential [9], as modified by Geiger, Ladanyi, and Chapin [10]. In the present study Ewald sums (and spherical cutoff for the larger systems) were utilized in cubic periodic boundary conditions to calculate the electrostatic interactions [11,12]. Gaussian isokinetic equations of motion [13] were integrated using a fourth-order Gear algorithm [12] with a time step of 2.0 fs.

A 108 particle sample of supercooled liquid carbon dioxide was prepared at 180 K by first cooling (wihin 100 ps) a well-equilibrated liquid configuration at 300 K, a temperature well above the estimated mechanical melting point of 240 K [14], followed by a further equilibration for 200 ps. The resulting configuration of supercooled liquid CO_2 at 180 K served as the starting point in a series of MD simulations in which the temperature was further reduced at a rate of 30 deg/ps from 180 K to the desired final value where it was fixed. These deeply quenched liquid samples were then allowed to evolve. The crystallization of carbon dioxide with the density of 1.4 g/cm^3 was observed on time scales of hundreds of picoseconds to a few nanoseconds at temperatures between 70 and 90 K. Samples quenched to temperatures of 65 and 95 K did not crystallize within 2 ns, nor did they give any indications that such a transformation would occur (see below). We remark that the short-range interactions in the condensed phases of our model carbon dioxide account for approximately 75% of the total configurational energy, which may explain its susceptibility to crystal formation upon simple quenching.

Figure 1 displays the average total configurational energy and the pressure, as a function of time, for the 108 particle carbon dioxide sample quenched to a temperature of 85 K. In Fig. 1 $t = 0$ corresponds to the moment when this temperature was established. Both the energy and the pressure clearly indicate the nucleation event [15] at approximately 750 ps (0.75 ns). Similar time dependences in the energy and the pressure were obtained for other samples that eventually undergo crystallization.

A critical question to address at this point is what microscopic changes accompany the liquid to solid phase transition in this molecular system. We have calculated the carbon-carbon radial distribution functions (RDF) $g(r)$ and the projections $h^{220}(r)$ of the full pair-correlation function [16] (which are useful for examining the average orientational order in the system). We have also determined values for the mean self-diffusion coefficient D

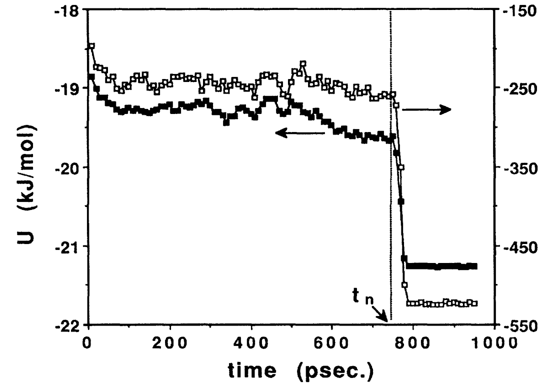

FIG. 1. The time dependence of the total configurational energy and the pressure for the carbon dioxide sample quenched to a temperature of 85 K. Each point represents a block average taken over 19.0 ps. The nucleation time t_n is approximately 750 ps.

and its two principal components $D_\perp$ and $D_\parallel$, characterizing the translational motion of linear CO_2 molecules in directions perpendicular and parallel to their principal axes [11]. These results were accumulated (as averages taken over 30 ps) at various points along the system's trajectory at 85 K and are displayed in Table I and in Fig. 2.

We find that the average local structure in the system does not appear to exhibit significant changes until virtually the moment when the nucleation begins at approximately 750 ps. The RDF $g(r)$ and the projection $h^{220}(r)$ recorded at 10, 200, 400, and 600 ps after quenching are essentially identical; only a small change in these functions is detectalbe at $t = 700$ ps (see Fig. 2). Representative molecular configurations for this carbon dioxide sample generated at $t = 700$ ps and at the completion of the simulation run are shown, respectively, in Figs. 3(a) and 3(b). Figure 3(a) illustrates the formation of disordered molecular layers as early precursors of the crystallined heterophase. More detailed analysis of molecular configurations generated in the proximity of the phase transition suggests that both the translational order and the rotational order of the CO_2 crystal emerge simultaneously. While the RDF and the projection $h^{220}(r)$ appear rather insensitive to the microscopic changes taking place in the system up to the moment of the phase transition, it is the self-diffusion coefficients that exhibit a more pronounced response. In the transforming liquid the translational motions of CO_2 molecules perpendicular to their axes "freeze" more rapidly than the motions parallel to their axes (compare $D_\perp$ and $D_\parallel$ in Table I) [17]. As a result, the anisotropy in the self-diffusion coefficient as measured by the relative difference of the orthogonal components $(D_\perp - D_\parallel)/D$ increases threefold between 400 and 700 ps (see Table I). We note that the mean self-diffusion coefficient $D = \frac{1}{3}(2D_\perp + D_\parallel)$ decreases almost fivefold during the same time period. Clearly, the development of directional anisotropy in the local molecular diffusion is crucial in the nucleation process.

TABLE I. The mean self-diffusion coefficient D and its two principal components $D_\perp$ and $D_\parallel$, obtained during the evolution of a CO_2 system at 85 K. Nucleation occurs at approximately 750 ps. The statistical uncertainty is estimated at (10–15)%.

Time (ps)	D (10^6 cm^2/s)	$D_\parallel$ (10^6 cm^2/s)	$D_\perp$ (10^6 cm^2/s)	$(D_\perp - D_\parallel)/D$
10	1.7	1.9	1.6	0.18
200	1.5	1.7	1.4	0.2
400	1.5	1.7	1.4	0.2
600	0.52	0.64	0.42	0.04
700	0.33	0.47	0.26	0.6

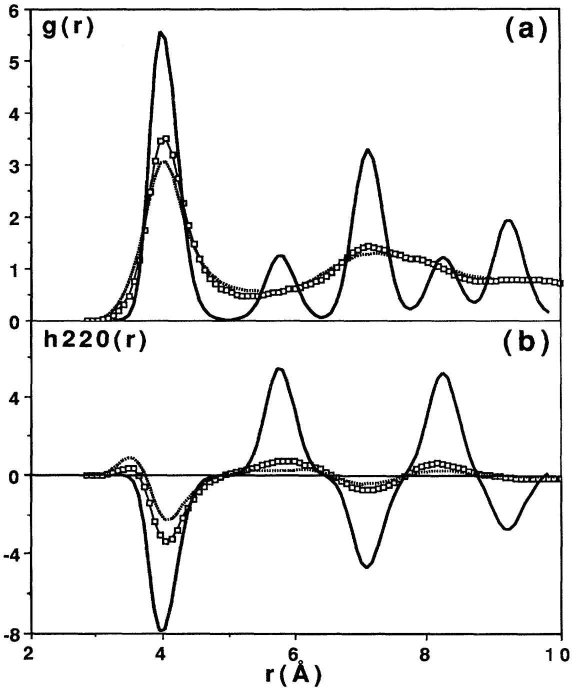

FIG. 2. The local structure in the carbon dioxide sample quenched to a temperature of 85 K at different stages of its liquid to crystalline-solid transition. (a) The carbon-carbon RDF $g(r)$; (b) the orientational distribution functions $h^{220}(r)$. The dotted and heavy solid lines portray, respectively, the local structure in the supercooled liquid at the beginning of the simulation run (at $t = 10$ ps) and in the resulting crystalline solid. The solid line marked with open squares represents the local structure just prior to crystallization at $t = 700$ ps.

We have performed a second series of 108 particle simulations starting from a different supercooled liquid configuration at 180 K. Again quenching resulted in the crystallization of the samples at temperatures between 70 and 90 K. Nucleation times obtained in all our simulation runs with $N = 108$ are plotted versus final temperature in Fig. 4(a), a so-called time-temperature-

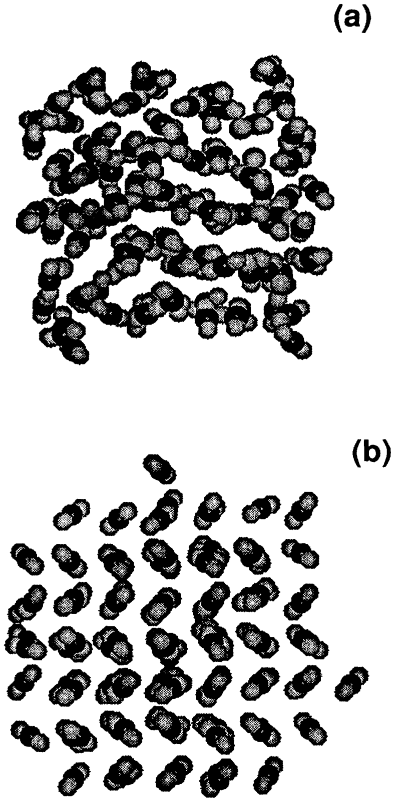

FIG. 3. Molecular configurations, depicted as projections into 2D, of carbon dioxide at 85 K (a) at $t = 700$ ps after quenching and (b) at the completion of the simulation run. The black spheres are the carbon atoms and the gray spheres are the oxygen atoms of CO_2 molecules.

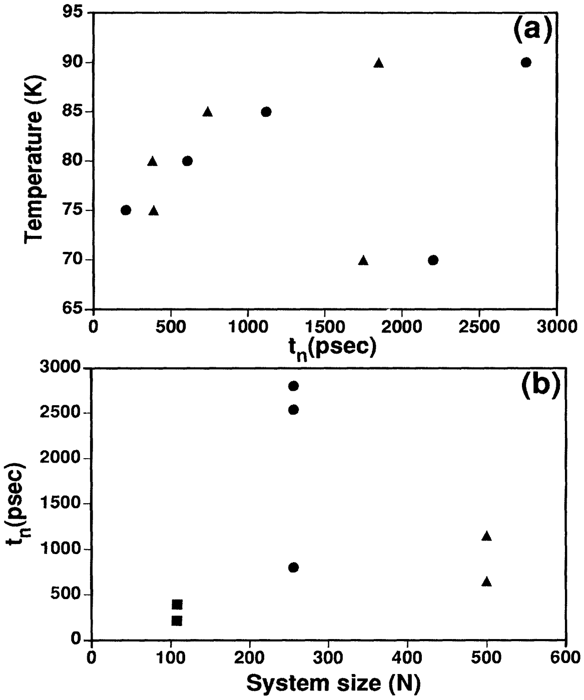

FIG. 4. (a) The nucleation times t_n for 108 particle samples of carbon dioxide at a density of 1.4 g/cm^3. In this TTT plot the triangles and circles are results obtained in two independent series of simulations. (b) The system size effects in the nucleation times. The squares, circles, and triangles are values observed for 108, 256, and 500 particle samples, respectively, of carbon dioxide at a density of 1.4 g/cm^3 quenched to a temperature of 75 K.

transformation (TTT) plot. These results indicate the existence of a minimum in the time for crystal formation at a specific temperature, in our case near 75 K. It is interesting to note that this extremal shape of the TTT plot obtained in our simulations with a relatively small molecular system ($N = 108$) is qualitatively in accord with the predictions of the classical nucleation theory as described in Ref. [18].

Several simulations have been carried out with systems of 256 and 500 molecules to examine the influence of the sample size; the nucleation times obtained at 75 K are plotted versus N in Fig. 4(b). Following the same preparatory procedure, rapid quenching of three independently equilibrated 256 particle samples from 180 to 75 K resulted in their crystallization at 0.8, 2.54, and 2.8 ns, respectively, respresenting approximately a fivefold increase in the mean nucleation time when compared with our 108 particle samples. It is worthwhile noting that similar sample size effects have been previously observed by Honeycutt and Andersen in their MD simulation study of simple Lennard-Jones systems [19]. Finally, two 500 particle simulations of liquid carbon dioxide quenched to the temperature of 75 K were performed. Spontaneous crystallization was observed at 0.65 and 1.15 ns, respectively. These times are somewhat smaller than those obtained for $N = 256$ suggesting that with a 500 particle CO_2 sample the process of the catastrophic crystal growth from the metastable liquid is already becoming less biased by the periodic boundary conditions [20].

The crystals of carbon dioxide obtained in our simulations feature the same regular fcc packing of carbon atoms found experimentally [5], as can be seen in Fig. 3(b). They occasionally exhibit some rotational defects (but obviously not the rotational disorder found in plastic crystals), in accord with experimental observatins which indicate the presence of some rotational defects in real CO_2 crystals [20]. A rotational phase transition into a plastic crystal [21] before (translational) melting has been found, for instance, in solid N_2, making it an interesting candidate for computer simulations.

Given the success of this initial study a more in-depth investigation of CO_2 as well as an extension to other molecular systems is clearly warranted. We would predict that simulation methodology exploiting deep quenching should be applicable to the study of crystallization in such simple molecular systems as liquid oxygen, nitrogen, carbon tetrachloride, carbon monoxide, etc. For highly polar liquids, such as water and aqueous solutions, where the highly directional electrostatic forces play a more prominent role, the nucleation-promoting effect of an electric field [7] is worth exploring in computer simulations. The important effects of boundary conditions and sample size upon the nucleation times and their incorporation into existing theories of crystallization [4,18] should be further investigated.

We are grateful for the financial support of the Natural Sciences and Engineering Research Council of Canada. We also wish to thank P.H. Poole for many stimulating discussions.

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[14] A perfectly ordered fcc lattice of a solid CO_2 with the density of 1.4 g/cm^3 was equilibrated at a temperature of 100 K, and then was slowly heated. At regular 10-deg intervals the temperature was fixed and the system was allowed to evolve for at least 50 ps. If no melting was observed during this period, as detected by a simple visual inspection of configurations, the heating was resumed. In this manner we determined a mechanical melting point of 240 ± 10 K fo rour model CO_2 crystal.

[15] We associate "nucleation" with onset of the catastrophic growth of the crystalline heterophase as evident in the energy and the pressure curves. Our "nucleation time" refers to the point along the system's trajectory beyond which the energy and the pressure sharply decrease (see Fig. 1). The energy and the pressure data are averages accumulated over 19 ps blocks; this time interval is representative of the uncertainty in our determination of nucleation times.

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