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Amorphous deposits with energies below the crystal energy

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A simple classical atomic liquid at equilibrium was simulated with constant-volume molecular dynamics. The homogeneous liquid was repeatedly quenched at constant volume for a range of densities near the triple-point density. The average energy of the resulting homogeneous amorphous deposits is for the first time observed to be lower than that of the lowest-energy homogeneous crystal. Both the crystal and the amorphous deposits are under tension at these densities. Tension-induced amorphization of the crystal (under perfect-wetting and constant-volume conditions) is also observed for the first time.

The inherent structure of a liquid consists of the configurations which correspond to local minima of the potential-energy hypersurface $\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ for the N classical particles.[1] The inherent structure has been extensively studied for simple atomic substances, and has been found to be substantially independent of the liquid temperature, even when moderately supercooled.[1,2] Previous studies have shown that the quenched configurations are amorphous and possess energies which are narrowly distributed about a mean energy much higher than the energy of the corresponding low-temperature crystal. For the circumstances described in this Brief Report, however, the potential energy of the inherent structure of the liquid lies below the lowest-energy crystal minimum. This Brief Report shows for the first time that dynamically stable amorphous structures possessing energies below that of the corresponding crystal can be found employing only simple (and traditional) models of the atomic interactions.

Molecular dynamics[3] using the fifth-order Gear-Nordsieck algorithm[4] was employed in order to simulate a classical homogeneous atomic liquid. The time increment was chosen to guarantee energy conservation to at least six decimal places. Periodic-boundary conditions were applied to 500 model atoms in a cube at constant density ρ. The potential energy was taken as $\Phi = \sum_{i<j} \phi(r_{ij})$, where r_{ij} is the distance between atoms i and j, and where ϕ is a well-tested[2] smoothly truncated version of the Lennard-Jones (12-6) model for noble gases and metals.[3] For reference, the Lennard-Jones critical[5] and triple points[6] are $T_{\text{cp}} = 1.36$, $\rho_{\text{cp}} = 0.36$ and $T_{\text{tp}} = 0.67$, $\rho_{\text{tp}} = 0.85$, respectively.

The liquid was equilibrated at $T \approx 3$ for selected densities in the range $0.760\,10 \le \rho \le 1.066\,27$. The pressures for this temperature interval are found in the range $8 < p < 31$, respectively. The density range here is a portion of the range for which, at zero temperature, the face-centered cubic (fcc) crystal possesses the lowest energy in comparison with the following crystals: diamond, simple cubic, body-centered cubic, simple hexagonal (with all c/a ratios considered), and hexagonal close packed. The zero-temperature fcc crystal is at zero pressure for $\rho = 1.066\,27$, and is the global minimum of Φ. For densities immediately below $\rho = 0.76$, the energy of the hexagonal close-packed crystal is lower than Φ_{fcc}.

For each of the selected densities, the inherent structure was determined from between 8 and 12 dynamically stable amorphous deposits quenched from the liquid at widely separated time intervals. The liquid was quenched by a sophisticated optimization procedure which finds the nearest local minimum on Φ via a steepest-descent path.[7] All 1500 eigenvalues of $\nabla\nabla\Phi$ were examined in order to verify that the quenched configuration was a true minimum and therefore dynamically stable. The per-particle energy u and enthalpy $h = u + p/\rho$ (at zero temperature) were collected from the averages of the energy and pressure, respectively, over the deposits in the inherent structure. Table I lists u, p, and h for both the fcc crystal and the inherent structure at the selected densities; Fig. 1 plots the resulting energy and pressure. Both the crystal and the inherent structure are under tension for these densities, although the tension is much less for inherent structure. The crystal enthalpy is always lower than that for the inherent structure. However, the

TABLE I. The energy u, pressure p, and enthalpy h at zero temperature for both the fcc crystal and the inherent structure for various densities ρ. The values are reported in reduced units. The uncertainty in u_q at $\rho = 0.760\,10$ is ± 0.05; at higher densities it is between ± 0.01 and ± 0.02.

ρ	u_{fcc}	p_{fcc}	h_{fcc}	u_q	p_q	h_q
0.760 10	−5.318	−5.763	−12.90	−6.01	−1.05	−7.39
0.832 72	−6.002	−6.037	−13.25	−6.15	−1.46	−7.90
0.855 00	−6.190	−5.980	−13.18	−6.18	−1.75	−8.28
0.911 60	−6.609	−5.463	−12.60	−6.30	−3.42	−10.1
0.960 00	−6.888	−4.500	−11.58	−6.46	−1.99	−8.53
1.002 20	−7.058	−3.156	−10.21	−6.52	−0.01	−6.53
1.066 27	−7.162	−0.000	−7.162	−6.43	−4.20	−2.49

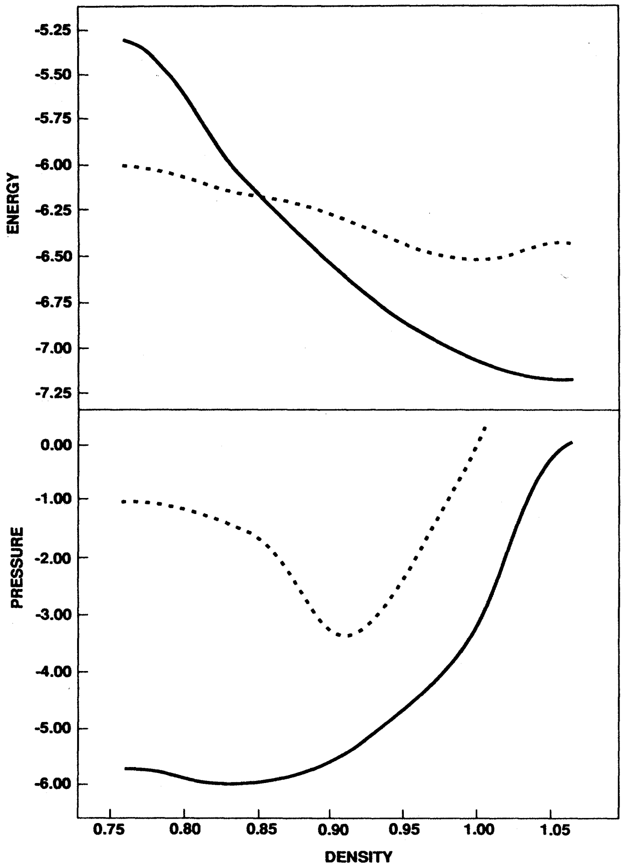

FIG. 1. The energy and pressure vs density (listed in Table I) for both the crystal and the inherent structure. In both panels the solid curve represents the results for the crystal and the dotted curve represents the results for the inherent structure. The results are interpolated with a cubic spline.

energy is lower for the inherent structure than for the crystal, for $\rho < 0.855$. As discussed below, this new result is directly connected with the constant-volume constraint.

The short-ranged order in the inherent structure is measured with the radial distribution function $g(r)$ averaged over the deposits in the inherent structure. Figure 2 shows $g(r)$ at the two extremes of the density range; both display the short-ranged order typical of simple atomic amorphous deposits.[1,2,8] The maximum of the first peak increases by just under 5% in going from the high- to the low-density example. The shift shows that the neighbors of an atom in the inherent structure are on average slightly farther apart at the lower densities, as expected. However, this shift in the mean nearest-neighbor distance is much less than the nearly 12% shift found for the nearest-neighbor distance in the close-packed crystal. This difference helps explain the energy difference between the crystal and the inherent structure for $\rho < 0.855$. The constant-volume constraint requires the crystal to occupy so much space that the atoms no longer are situated at the minimum of ϕ but instead begin to sample its rapidly increasing attractive "tail." On the other hand, the variety of arrangements available to the amorphous system permits relatively closer immediate neighbors, even at the expense of more distant second neighbors. This explanation also highlights the contribution of the short-ranged character of the attractions to this result.

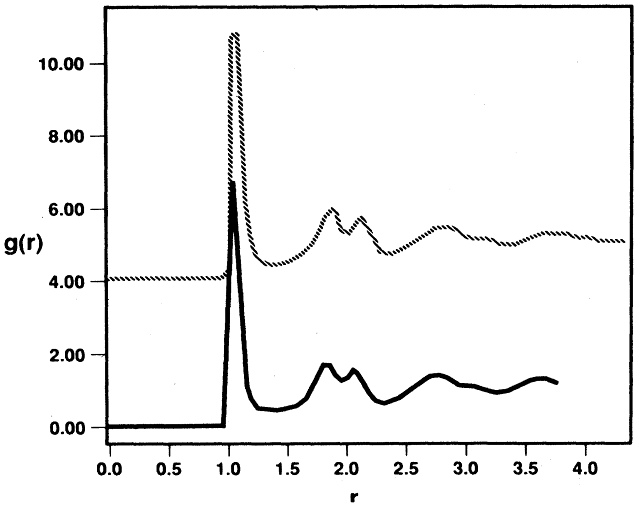

FIG. 2. The radial distribution function $g(r)$ of the inherent structure ($T=0$) at two different densities, for a bin width of $\Delta r = 0.05$. The results are interpolated with a straight line. The solid curve shows $g(r)$ for $\rho = 1.066\,27$. The dashed curve shows $g(r)+4$ for $\rho = 0.760\,10$. The distance is in reduced units.

The comparison in Fig. 2 between $g(r)$ at the two densities shows that no new order (i.e., new peaks or valleys) is introduced as the density varies in this range; all the differences are confined to mild shifts in the peaks and valleys. As discussed elsewhere,[8] the radial distribution function is neither the only nor the most sensitive diagnostic of local order in amorphous systems; studies employing alternate measures of order in the inherent structure at these densities might reveal important differences from their higher-density relatives.

In order to test the metastability of the low-density deposits at finite temperature, one of the deposits in the inherent structure at $\rho = 0.760\,10$ was heated by molecular dynamics at $T = 0.49$ (for which $p = -0.75$). At that temperature the average potential energy of the resulting supercooled liquid is $\langle \Phi \rangle / N = -4.8$, well above the crystal minimum at that density. Nevertheless, throughout the trajectory of length $t = 240$, neither the supercooled liquid nor the inherent structure showed any sign of either partial crystallization or fragmentation. Instead, repeated quenching of the supercooled liquid throughout the molecular-dynamics trajectory showed that inherent structure was the same as the one obtained from the high-temperature (and positive-pressure) liquid. On the other hand, the crystal at $\rho = 0.760\,10$ spontaneously "freezes" into the lower-energy (and lower-tension) amorphous state in much shorter time intervals when heated to temperatures as low as $T \approx 0.1$.

Whereas the complete discussion of these results is beyond the scope of this Brief Report and must be deferred to a future publication, the discussion is confined to the following brief comments. First, the claim that the fcc crystal represents the lowest-energy homogeneous crystal in this density range for the model employed here rests upon the comparison with a number of the most likely alternative structures. It may yet be that for this model some more exotic crystal (or quasicrystal) possesses a lower energy at zero temperature than the inherent structure. However, the failure so far of heated amorphous deposits to find lower minima, though not in itself conclusive, suggests that if such a lower-energy crystal were found, its unit cell would require a basis of hundreds of atoms. Second, the experimental realization of the foregoing computer "experiment" requires not only a rapid constant-volume quench, but also nearly perfect wetting between the liquid to be quenched and its container, without which the quenched liquid would probably peel away from the surface and fragment into crystallites. Periodic-boundary conditions provide perfect wetting in the calculations. The foregoing calculations show that on time scales which would be long enough to observe phase transitions in systems of this type, the inherent structure persists when subjected to moderate temperatures. Therefore the supercooled liquid and its inherent structure should be expected to persist for experimentally accessible time scales despite their thermodynamic instability at these densities. The centuries-old recipe for the preparation of "Prince Rupert's drops," well known to glass technologists,[9] provides an experimental example for which a glass which may persist under extreme tension after a constant-volume quench, and is related to conventional procedures employed for the preparation of "work-hardened" glass.

In conclusion, the energy of the amorphous inherent structure of a simple atomic liquid is for the first time observed to be lower than the lowest-energy crystal at zero temperature for densities just below the triple-point density. The amorphous deposits which constitute the inherent structure are dynamically stable at zero temperature and metastable at finite temperatures. The resulting tension-induced amorphization of the closely packed low-temperature crystal[10] provides a counterpart to the recently discovered[11] compression-induced amorphization of ice.

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