

## Crystal instability and melting

COTTERILL AND MADSEN<sup>1</sup> argue against an essential connection between thermodynamic melting and crystal instability. Their molecular dynamics simulation of a 336-particle Lennard-Jones (LJ) assembly revealed the existence of a dislocation-mediated mechanical instability in the superheated crystalline phase at a density ( $\rho_{\text{inst}} = 1.22$ ) lying just outside the melting interval ( $\rho_{\text{cryst}} = 1.38$ ,  $\rho_{\text{liq}} = 1.24$ ) determined by Hansen and Verlet<sup>2</sup> for the same isotherm. Moreover, with increasing temperature, the instability was progressively further removed from the melting interval. We suggest, however, that contrary to their hypothesis, these results add further to an already substantial weight of evidence for the essential connection between crystal instability and melting<sup>3,4</sup>.

Born<sup>5</sup> was among the first to propose that melting occurs as a mechanical instability when one of the crystal shear moduli falls to zero. Of course, experiment demonstrated that the shear moduli remained finite up to the melting point, but we have shown<sup>6,7</sup> that extrapolation of one of the shear moduli as a function of density beyond the melting point, reveals that it would fall to zero at the freezing density for a wide range of ionic, metallic and molecular crystals. We interpreted this as implying the universal existence of an instability concealed between the melting and freezing lines but lying close to the latter. This is confirmed by theoretical calculations for alkali halides<sup>4</sup> and, indeed, is what one would expect from a proper interpretation of Born's melting criterion. If the crystal were superheated to the critical density,  $\rho_c$ , of vanishing static shear modulus, the resultant localization of shear modes would contribute an additional amount,  $R \ln 2$ , to the entropy<sup>8</sup>, so that the system would be able thermodynamically to make an isothermal jump from a lower density,  $\rho_{\text{cryst}}$ , to the density,  $\rho_c$ . Thus the instability, in normal circumstances, would be concealed by the first-order transition, and to a first approximation  $\rho_c$  ( $= \rho_{\text{inst}}$ ) may be equated to  $\rho_{\text{liq}}$ .

The molecular dynamics result of Cotterill and Madsen seems to confirm our original interpretation of Born's melting criterion, since the freezing density and instability density are almost coincident. Both the suppression of long-wavelength phonons in their finite (336-particle) system and critical slowing would serve to delay the instability and thus it lies a little beyond the melting interval, and is displaced further away with increasing temperature.

Note also that the single-cell occupancy system simulated by Hansen and Verlet to obtain a reversible path between liquid and solid, probably has a first-order transition (L. V. Woodcock, personal communication) rather than the second-

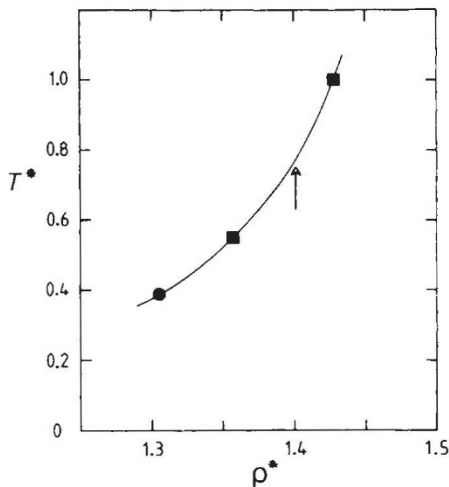


Fig. 1 LJ glass transition temperature ( $T^*$ ) as a function of density ( $\rho^*$ ). The expected transition temperature on Cotterill and Madsen's isotherm is indicated by the arrow.

order transition assumed by Hansen and Verlet. Their phase boundaries may not therefore be altogether reliable. We note that the actual freezing line for argon is displaced progressively away from the Hansen and Verlet line in the same manner as the instability line.

Finally, Cotterill and Madsen's location of the glass transition between the melting and freezing lines at  $\rho_g = 1.29$  seems incorrect. Their procedure of finding the intersection of extrapolated linear fits of the extremes of their isothermal pressure-density data ignores the fact that the isotherms are naturally curved in any one phase. Figure 1 shows LJ glass transition temperatures as a function of density reported by Abraham<sup>9</sup> (squares) and Damgaard-Kristensen<sup>10</sup> (circle) and this predicts a glass transition on Cotterill and Madsen's 0.77 isotherm at  $\rho_g = 1.401$ ; that is, well above their value  $\rho_g = 1.29$ , and outside the melting interval. That their glassy pair and bond angle distribution functions (pdf and adf, respectively) are actually evaluated for supercooled liquid is evidenced by the lack of a fully developed split-second peak in the pdf. Presumably the incipient splitting in their adf at 110° and 120° would be fully developed in a true glass.

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COTTERILL AND MADSEN REPLY—Tallon considers our instability density for  $T = 0.75$  to be indistinguishable from the freezing density, within computational error, and dismisses the disparate temperature dependencies with a reference to real argon, despite its differences from the pseudoinfinite Lennard-Jones matter studied by Hansen and Verlet<sup>1</sup> and ourselves<sup>2</sup>. Moreover, the discrepancy between the two materials is opposite to Tallon's claim. We cannot see why model-dependent stabilization, beyond the instability point, should be more effective at higher temperature. Melting is a reversible first-order transition, the location of which depends on the properties of both liquid and crystal. Instability theories attempt comprehensive treatment of the transition, including projections of liquid properties, using exclusively crystalline characteristics. Such unilateral approaches are inferior to those incorporating more realistic concepts of liquid structure.

Because the properties of all three condensed states are nevertheless determined by the same interatomic interactions, empirical correlations between properties are inevitable; the proximity of the instability and freezing densities<sup>2-4</sup> is thus hardly surprising. But vacancy<sup>5</sup> and dislocation<sup>6</sup> parameters both also correlate with the melting temperature, even though melting theories based on these two defects are mutually exclusive<sup>7</sup>. We show elsewhere<sup>8</sup> that the excess entropy of liquids over crystals is associated with fluidity, not disorder, and stems from conversion of transverse phonons to diffusive modes<sup>9</sup>. Tallon's rather nebulous analysis<sup>10</sup> fails through, amongst other things, neglecting the entropy associated with perfect crystal oscillatory modes. The location of the glass transition density is subject to a choice of convention, but a density of 1.4 for  $T = 0.77$  is irreconcilable with our findings; the pressure varies linearly with density in the range 1.35–1.45. Applying Abraham's convention<sup>11</sup> to our data, or vice versa, produces no contradiction.

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