

Vibrational melting and its possible relevance to amorphous silicon

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The conventional melting of “simple” substances involves configurational excitation from multi-dimensional potential energy basins surrounding crystalline structures to those surrounding amorphous structures. Vibrational anharmonicity changes relatively little in extent across such transitions. Motivated by observations of a sharp melting point for solid amorphous silicon well below that of the crystal, another possibility is proposed. This requires cooperative softening of vibrational modes with increasing mean amplitude. An exactly solvable model for this type of strong anharmonicity demonstrates that it can produce a first-order “intrabasin melting”, or a critical point with a symmetric heat capacity divergence.

1. Introduction

Understanding collective phenomena in many-particle systems often can be facilitated by identifying and classifying the “inherent structures”, i.e. the local minima of the potential energy function. In particular this approach has been useful for analyzing short-range order in liquids [1], for clarifying the nature of glass transitions [2], for identification of atomic motions in amorphous solids that produce low-temperature two-level systems [3], and for extending the Lindemann melting law to a conjugate freezing criterion [4].

The first-order melting transition for simple atomic and molecular substances receives a straightforward description in terms of the contributing inherent structures. Below the melting temperature T_m the relevant inherent structures (located by steepest-descent mapping of dynamical configurations) involve the stable crystal with an equilibrium defect concentration. Above T_m the liquid samples a distribution of amorphous particle packings as inherent structures. Detailed simulations for several simple models [1,5,6] reveal that this distribution of amorphous inherent structures is virtually independent of the temperature in the liquid from which it is generated (by the steepest-descent mapping to potential energy minima). Furthermore the dominant contribution to the heat of fusion is the difference in mean depths of the crystalline and the amorphous inherent structure basins; relatively little arises from the difference in vibrational free energies for these two classes of basins.

With these simple-liquid observations as background, it may seem strange that el-

emental silicon experimentally displays a metastable amorphous solid phase with its own distinct melting temperature T'_m , which is approximately 200 K lower than that of the stable crystalline solid ($T_m = 1684$ K) [7]. The latent heat for the former is estimated to be about 15 percent of the latter [8]. To the extent that a classical potential model can be invoked to explain this behavior, two possibilities appear. One is that inherent structures for the amorphous solid and for the liquid are distinctly different (thus posing an experimental challenge to characterize the difference). The other is that a strong and peculiar form of anharmonicity might be present which permits first-order intrabasin melting to occur. This latter option forms the subject of this paper.

2. Potential energy basins

Let $\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ denote the potential energy function for the N particle system. In the large system limit the number of distinct (non-permutationally related) Φ minima rises exponentially with N . The same is true if these minima are classified by their values of $\phi = \Phi/N$, so we write $\exp[N\sigma(\phi)]$ for the asymptotic density in ϕ of the distinct minima.

Each of these minima, the inherent structures, inhabits its own basin of attraction, say B_α for inherent structure α . B_α comprises all system configurations $\mathbf{r}_1, \dots, \mathbf{r}_N$ which map onto α by steepest descent on the Φ hypersurface. This mapping can be interpreted simply as removal of vibrational deformation from the system.

The vibrational free energy $Nf_{v\alpha}$ for basin B_α can be precisely defined as follows ($\beta = 1/k_B T$):

$$\exp(-N\beta f_{v\alpha}) = \int_{B_\alpha} d\mathbf{r}_1 \dots d\mathbf{r}_N \exp(-\beta \Delta\Phi), \quad (1)$$

where the multiple integral spans B_α , and $\Delta\Phi$ is the rise in Φ above the minimum. Considering the large number of degrees of freedom present, the $f_{v\alpha}$ for basins of depth ϕ will cluster closely around the mean, which will be denoted by $f_v(\phi)$. In the large N limit, the thermodynamic free energy is exactly given by [2]

$$\beta F/N = \ln \lambda_T^3 + \min_{(\phi)} [\beta\phi - \sigma(\phi) + \beta f_v(\phi)], \quad (2)$$

where λ_T is the mean thermal de Broglie wavelength. Melting of simple substances is associated with a discontinuous change in the minimizing depth ϕ in eq. (2) as T passes through T_m .

3. Anharmonic model

In the immediate vicinity of inherent structure α the potential will be harmonic, and has diagonal form in terms of normal mode amplitudes u_i :

$$\Delta\Phi = \frac{1}{2} \sum K_i u_i^2 + \mathcal{O}(u^3). \quad (3)$$

Rescaling each coordinate by $K_i^{1/2}$, $\Delta\Phi$ becomes locally isotropic:

$$\Delta\Phi = \frac{1}{2} S^2 + \dots, \quad (4)$$

where S is the $3N$ -dimensional hyper-radius. As an elementary model for typical amorphous structure basins we assume that the intrabasin vibrational partition function (1) can be expressed as a simple integral over S :

$$\begin{aligned} \exp(-N\beta f_v) &= \left(\prod K_i^{1/2} \right) [2\pi^{3N/2} / \Gamma(3N/2)] \\ &\times \int_0^\infty P(S) \exp[-\beta \Delta\Phi(S)] S^{3N-1} dS. \end{aligned} \quad (5)$$

Here $P(S)$ incorporates the truncating effects of the basin boundary: it is the probability that a randomly chosen point on the size- S hyperspherical surface lies within the basin. A reasonable choice is a Gaussian form:

$$P(S) = \exp(-c_0 S^2). \quad (6)$$

The low coordination number and high rigidity of silicon stem from the presence of strong directional bonds with tetrahedral angles. Any substantial deformation away from this ideal bond geometry disturbs the underlying electron orbital hybridization and weakens bonding. Large amplitude vibrations thus should weaken restoring forces on average. This motion can be incorporated in $\Delta\Phi(S)$ by postulating

$$\Delta\Phi(S) = \frac{1}{2} \left(\frac{1 + a_0 N^{-2} S^4}{1 + b_0 N^{-2} S^4} \right) S^2, \quad (7)$$

with $0 < a_0 < b_0$. The N^{-2} factors ensure that the cooperative weakening effect develops only when amplitudes at each atom are order unity. $\Delta\Phi$ must be monotonically increasing with S to be consistent with the basin definition, which thus requires $a_0 > \frac{1}{3} b_0$.

4. Basin partition function

Presence of the large parameter N in eq. (5) causes the integral to be dominated by

the neighborhood of the integrand maximum. Following the usual procedure we thus find

$$\beta f_v = \frac{3}{2} \left[\ln \left(\frac{3}{2\pi e} \right) - \langle \ln K_i \rangle \right] + F(w),$$

$$F(w) = -\frac{3}{2} \ln w + \frac{c_0 w}{b_0^{1/2}} + \frac{\beta w}{2b_0^{1/2}} \left(\frac{1 + (a_0/b_0)w^2}{1 + w^2} \right), \quad (8)$$

where

$$\langle \ln K_i \rangle = \frac{1}{3N} \sum \ln K_i, \quad (9)$$

and w is a positive real root of

$$\frac{b_0^{1/2}}{\beta} \left(\frac{3}{w} - \frac{2c_0}{b_0^{1/2}} \right) = \frac{1 + [(3a_0/b_0) - 1]w^2 + (a_0/b_0)w^4}{(1 + w^2)^2}, \quad (10)$$

which minimizes expression (8). The corresponding value of S^2 in eq. (5) is given by $Nwb_0^{-1/2}$.

Near the harmonic limit $a_0 = b_0$, the parameter w exhibits a smooth temperature variation from low to high temperature. However if a_0/b_0 is sufficiently small, the root w which minimizes βf_v at low temperature will suddenly be replaced by another at high temperature. This discontinuous shift heralds a first-order phase change, a vibrational melting transition. Fig. 1 illustrates this behavior for the case $a_0/b_0 = 0.15$, $c_0/b_0^{1/2} = 0.30$, with the vibrational melting point at

$$b_0^{1/2}/\beta \cong 0.0760. \quad (11)$$

The appropriate w value jumps from 0.254 (low temperature branch) to 2.246 (high temperature branch) at this point.

An intermediate case exists, displaying a higher order transition. With $a_0/b_0 = 0.15$ as above, this occurs when $c_0/b_0^{1/2} \cong 1.02671$, and the corresponding critical temperature is given by

$$b_0^{1/2}/\beta \cong 0.15548. \quad (12)$$

The vibrational heat capacity diverges at this critical point as $|\Delta T|^{-2/3}$, a behavior observed in some other phase transition models [9].

5. Conclusion

This paper explores the possibility that cooperative softening of restoring forces in a condensed phase can produce an intrabasin vibrational melting phenomenon. A specific model, eq. (7), is proposed for the required anharmonicity, and is shown to

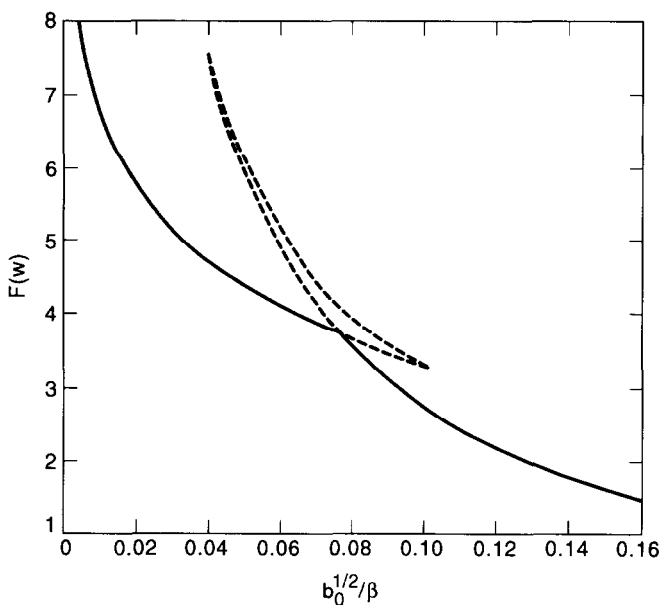


Fig. 1. Plot of $F(w)$ from eq. (8) versus the temperature variable $b_0^{1/2}/\beta$ for the case $a_0/b_0=0.15$, $c_0/b_0^{1/2}=0.30$. Dashed portions represent metastable and unstable branches.

produce either a first-order transition, a critical point, or no transition depending on the values of relevant parameters.

The model offered is intended only to represent a “typical” basin for amorphous inherent structures (potential energy minima) in the system, and does not imply that the system is dynamically confined to one such basin. Unless the system has been brought to very low temperature in a metastable amorphous state, transitions between neighboring basins (with associated particle diffusion) can be expected to occur.

It has been suggested that the vibrational melting phenomenon may be relevant to the behavior of amorphous silicon. Assessment of this proposition must await future discriminating experiments and/or simulation studies.

References

- [1] F.H. Stillinger and T.A. Weber, *J. Chem. Phys.* 80 (1984) 4434.
- [2] F.H. Stillinger, *J. Chem. Phys.* 88 (1988) 7818.
- [3] T.A. Weber and F.H. Stillinger, *Phys. Rev. B* 32 (1985) 5402.
- [4] R.A. LaViolette and F.H. Stillinger, *J. Chem. Phys.* 83 (1985) 4079.
- [5] F.H. Stillinger and T.A. Weber, *Science* 225 (1984) 983.
- [6] F.H. Stillinger and T.A. Weber, *J. Chem. Phys.* 88 (1988) 5123.
- [7] M.O. Thompson, G.J. Galvin, J.W. Mayer, P.S. Peercy, J.M. Poate, D.C. Jacobson, A.G. Cullis and N.G. Chew, *Phys. Rev. Lett.* 52 (1984) 2360.
- [8] M.H. Grabow and G.H. Gilmer, *Phys. Rev. B*, submitted.
- [9] F.H. Stillinger, *J. Chem. Phys.* 84 (1986) 945.