# Thermodynamic properties of a three-dimensional defect system

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We analyze the recently proposed model of defect melting in three dimensions via high- and low-temperature expansions and compare the internal energy and specific heat with the result of Monte Carlo simulations. The transition is found to be strongly of first order with a Lindemann number $L > 112$ and a transition entropy $\Delta s \approx 1.2$, thus very much resembling a crystalline melting process.

Recently, a simple model has been proposed[1] to study the process of crystal melting from the point of view of defect proliferation. This point of view has been advanced as early as 1952 by Shockley[2] but because of the complexities of defect systems and their long-range interactions it has been very difficult to test this idea quantitatively. This obstacle is overcome by the model[1] which combines both, elastic and defect degrees of freedom, in the simplest possible way, namely, via the Gaussian partition function

$$Z=\prod_{\mathbf{x},i}\int_{-\pi}^{\pi}\frac{du_i}{2\pi}\sum_{\substack{\{n_{ij}(\mathbf{x})\}\\(i\le j)}}\exp\left\{-\frac{\beta}{2}\left[\sum_{\substack{\mathbf{x},i,j\\(i<j)}}(\nabla_i u_j+\nabla_j u_i-4\pi n_{ij})^2+2\xi\sum_{\mathbf{x},i}(\nabla_i u_i-2\pi n_{ii})^2\right.\right.$$
$$\left.\left.+\frac{\lambda}{\mu}\sum_{\mathbf{x}}\left[\sum_i\left[\nabla_i u_i(\mathbf{x}-\mathbf{i})-2\pi n_{ii}(\mathbf{x}-\mathbf{i})\right]\right]^2\right]\right\}. \tag{1}$$

[There also exists a version of the model involving the cosines of the strains, $\cos(\nabla_i u_j+\nabla_j u_i)$. This has been studied elsewhere; see the last reference in Ref. 1.] Here $u_i(\mathbf{x})$ is the displacement field, rescaled to a lattice spacing of $2\pi$, $\mathbf{x}$ runs over all $N$ sites of a simple cubic lattice, the labels $i,j$ refer to the link vectors, $\nabla_i u_j(\mathbf{x})=u_j(\mathbf{x}+\mathbf{i})-u_j(\mathbf{x})$ are lattice derivatives, $\mu,\xi,\lambda$ are elastic constants,

$$\mu=C_{44},\quad \lambda=C_{12},\quad \xi=\frac{C_{11}-C_{12}}{2C_{44}},$$

and $\beta=\mu a^3/(2\pi)^2 T$ is the inverse temperature in reduced units ($\mu$ times the cell volume $a^3$). The sum over $n_{ij}(\mathbf{x})$ (which is equal to an integer for $i=j$, to a half-integer for $i\neq j$) accounts for jumps of $u_i(\mathbf{x})$ across Volterra sheets. They are the integer versions of the well-known plastic strains $u_{ij}^p$ in material science.[3] This integer nature accounts for the discreteness of the defects. They are *gauge fields* of defects[4] with the gauge transformations $u_i\to u_i+2\pi N_i$, $n_{ij}\to n_{ij}+\frac{1}{2}(\nabla_i N_j+\nabla_j N_i)$, ensuring the irrelevance of the shape of the Volterra sheets. The boundaries of these sheets are the defects. The gauge-invariant defect tensor

$$\eta_{ij}(\mathbf{x})=\epsilon_{ikl}\epsilon_{jmn}\nabla_k\nabla_m n_{ln}(\mathbf{x}+\mathbf{i}+\mathbf{j})$$

is the source of stress.

Notice that, structurally, the model lies halfway between the Villain model of superfluidity, in which there is only one $u(\mathbf{x})$ field instead of three, and the Villain form of $U(1)$ lattice gauge theory, which involves the antisymmetric combination $\nabla_i u_j-\nabla_j u_i$ instead of the symmetric one $\nabla_i u_j+\nabla_j u_i$.[5]

By a standard duality transformation,[1] the model can be rewritten in two different forms.

(1) The stress representation, convergent for small $\beta$,

$$Z=\left[\frac{1}{2\pi\beta}\right]^{3N/2}\left[\frac{1}{2\pi 2\beta\xi}\right]^{3N/2}\left[1-3\frac{\xi}{\gamma}\right]^{N/2}\sum_{\substack{\{\sigma_{ij}\}\\(i\le j)}}\prod_{\mathbf{x},j}\delta_{\nabla_i\sigma_{ij},0}\exp\left\{-\frac{1}{2\beta}\left[\sum_{\substack{\mathbf{x},i,j\\(i<j)}}\sigma_{ij}^2+\frac{1}{2\xi}\sum_{\mathbf{x},i}\sigma_{ii}^2\right.\right.$$
$$\left.\left.-\frac{1}{2\gamma}\sum_{\mathbf{x}}\left[\sum_i\sigma_{ii}(\mathbf{x}-\mathbf{i})\right]^2\right]\right\}, \tag{2}$$

 

where $\gamma \equiv 3\xi + (2\mu\xi^2/\lambda)$ and the sum over $\sigma_{ij}$ covers all integer-valued stress field configurations with vanishing lattice divergence, $\bar{\nabla}_i \sigma_{ij}(\mathbf{x}) \equiv \nabla_i \sigma_{ij}(\mathbf{x}-\mathbf{i}) = 0$. In the general dimension $D$, the prefactors become

$$\left[\frac{1}{2\pi\beta}\right]^{(N/2)D(D-1)/2} \left[\frac{1}{2\pi 2\beta\xi}\right]^{(N/2)D} \left[1 - D\frac{\xi}{\gamma}\right]^{N/2}$$

with $\gamma \equiv D\xi + 2\mu\xi^2/\lambda$.

(2) The defect representation, convergent for large $\beta$,

$$Z = \left[\frac{1}{2\pi\beta}\right]^{3N/2} \left[\frac{1}{2}\right]^{N/2} e^{-(3N/2)l(\xi,\lambda/\mu)} \sum_{\substack{\{\eta_{ij}\} \\ (i \le j)}} \prod_{\mathbf{x},j} \delta_{\bar{\nabla}_i \eta_{ij},0} \times \exp\left[-4\pi^2\beta \sum_{\mathbf{x},\mathbf{x}'} \eta_{ij}(\mathbf{x}) V_{ijkl}(\mathbf{x}-\mathbf{x}') \eta_{kl}(\mathbf{x}')\right], \tag{3}$$

where in the isotropic case $\xi = 1$, the exponential is simply

$$\exp\left[-4\pi^2\beta \sum_{\mathbf{x},\mathbf{x}'} \left[\eta_{ij}(\mathbf{x})\eta_{ij}(\mathbf{x}') + \frac{\nu}{1-\nu}\eta_{ii}(\mathbf{x})\eta_{jj}(\mathbf{x}')\right] v_4(\mathbf{x}-\mathbf{x}')\right] \tag{4}$$

with

$$v_4(\mathbf{z}) = \int_{-\pi}^{\pi} \frac{d^3k}{(2\pi)^3} \frac{e^{i\mathbf{k}\cdot\mathbf{z}}}{\left[\sum_{i=1}^{3} \bar{K}_i K_i\right]^2},$$

$$K_i = -i(e^{ik_i} - 1), \quad \bar{K}_i = -i(1 - e^{ik_i}), \quad \bar{K}_i K_i = 2 - 2\cos k_i,$$

and $\nu \equiv 1/(\gamma - 1)$. The exponent $l(\xi,\lambda/\mu)$ in the prefactor is the anisotropic version of the phonon fluctuation integral

$$\int_{-\pi}^{\pi} \frac{d^3k}{(2\pi)^3} \ln\left[\sum_{i=1}^{3} \bar{K}_i K_i\right] = 1.67339,$$

namely

$$l(\xi,\lambda/\mu) \equiv \tfrac{1}{3} \int_{-\pi}^{\pi} \frac{d^3k}{(2\pi)^3} \ln\left\{\left[A_1A_2A_3 + \left[1 + \frac{\lambda}{\mu}\right] \sum_{\substack{i,j,k \\ \text{cyclic}}} \bar{K}_i K_i A_j A_k\right] \Big/ 2\right\} \tag{5}$$

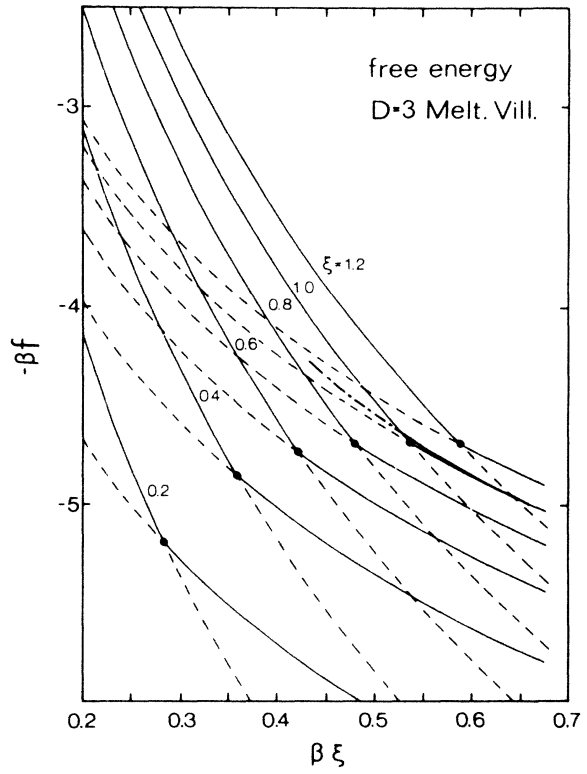


FIG. 1. Free energy of the $D=3$ melting model (Villain type) for various $\xi = 0.2, \ldots, 1.2$. The stress corrections are so small that they are practically invisible on this figure. The defect correction is shown explicitly for $\xi = 1$.

with

$$A_i = (2\xi - 1)\bar{K}_i K_i + \bar{K}_j K_j + \bar{K}_k K_k \quad (i,j,k = \text{cyclic}).$$

The lowest contribution to the stress representation (2) is

$$Z = \left[\frac{1}{2\pi\beta}\right]^{3N/2} \left[\frac{1}{2\pi 2\beta\xi}\right]^{3N/2} \left[1 - 3\frac{\xi}{\gamma}\right]^{N/2} \times (1 + 6Ne^{-(1/\beta)(2+3/\xi-5/\gamma)} + \cdots) \tag{6}$$

coming from

TABLE I. Transition points and entropy jumps of defect melting for $\lambda/\mu = 0$. •The zeroth-order approximation is given by

$$\beta_m^{(0)} = \frac{1}{2\pi} \frac{1}{4^{1/3}} \frac{1}{\xi} \frac{1}{\left[1 + \frac{1}{\xi}\frac{3\lambda}{2\mu}\right]^{1/3}} e^{l(\xi,\lambda/\mu)}$$

with $l(\xi,\lambda/\mu)$ defined in Eq. (5), and $\beta_m^{(1)}$ can be seen in Fig. 1.

| $\xi$ | $\beta_m^{(0)}$ | $\beta_m^{(1)}$ | $\beta_m^{MC}$ | $\Delta s^{MC}$ |
|---|---|---|---|---|
| 0.2 | 1.41 | | 1.40 ±0.05 | 1.47 |
| 0.4 | 0.89 | | 0.888 ±0.005 | 1.40 |
| 0.6 | 0.70 | | 0.6875±0.0025 | 1.33 |
| 0.8 | 0.60 | | 0.5875±0.0025 | 1.27 |
| 1.0 | 0.53 | 0.524 | 0.5175±0.0025 | 1.21 |
| 1.2 | 0.49 | | 0.4690±0.0025 | 1.15 |

$$\sigma_{11}(0)=1,\ \sigma_{11}(2)=-2,\ \sigma_{11}(2+2)=1,$$
$$\sigma_{22}(0)=1,\ \sigma_{22}(1)=-2,\ \sigma_{22}(1+1)=1,$$
$$\sigma_{12}(0)=1,\ \sigma_{12}(1)=-1,$$
$$\sigma_{12}(1+2)=1,\ \sigma_{12}(2)=-1$$

(for graphical techniques see Ref. 6). For the defect representation we find for $\xi=1$

$$Z=\left[\frac{1}{2\pi\beta}\right]^{3N/2}\left[\frac{1}{2}\right]^{N/2}e^{-(3N/2)l(1,\lambda/\mu)}$$
$$\times(1+6Ne^{-\beta 8\pi^2\{(1/12+[2/(1-\nu)]0.02106\}}+\cdots). \quad (7)$$

The prefactor reflects the Dulong-Petit law ($1/2\beta$ in the internal energy $U$ and $\frac{1}{2}$ in the specific heat $C$ per potential degree of freedom; the kinetic terms would have to be added separately).

From the intersection of the free energies we find the transition point for $\xi=1$, $\lambda/\mu=0$, at

$$\beta_m^{(1)}=0.524\,. \quad (8)$$

Without stress and defect corrections we would have found ($\xi=1$)

$$\beta_m^{(0)}=\left[\frac{1-\nu}{1+\nu}\right]^{1/3}\frac{1}{2\pi}\frac{1}{4^{1/3}}e^{1.67339}\underset{\nu=0}{=}0.534\,.$$

The free energy $-\beta f=\ln Z/N$, the internal energy $u=-(\partial/\partial\beta)(-\beta f)$, and the specific heat $c=-\beta(\partial/\partial\beta)u$ are plotted in Figs. 1, 2(a), and 2(b). In Fig. 1 the stress graphs are so small that they can be ignored. The effect of the defect graph is shown only for the isotropic case $\xi=1$. The transition points are listed in Table I.

In order to obtain more precise results we have performed a Monte Carlo (MC) simulation on $8^3$ and $16^3$ lat-

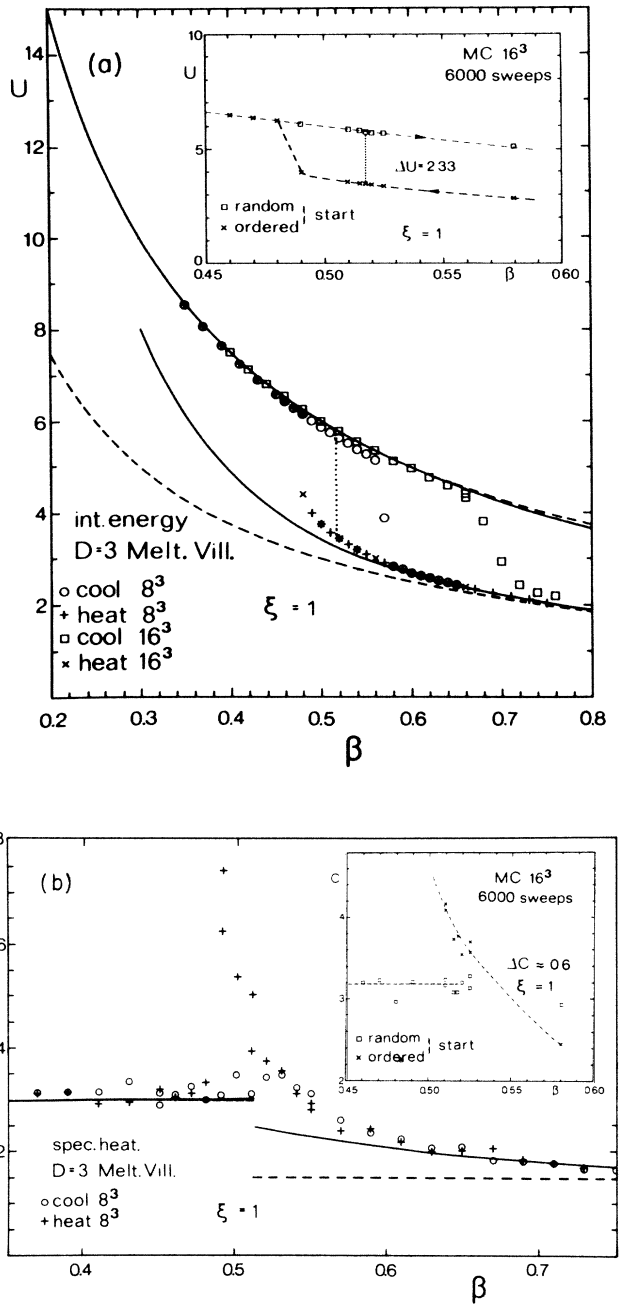


FIG. 2. (a) Internal energy and (b) the specific heat of defect melting for $\xi=1$ showing the contribution of the first defect and stress correction. The Monte Carlo data are taken on $8^3$ ($16^3$) lattices with 500 (50) sweeps for equilibrium and 1000 (100) for measurement. In the inset of each figure we have given a blow-up of the transition region.

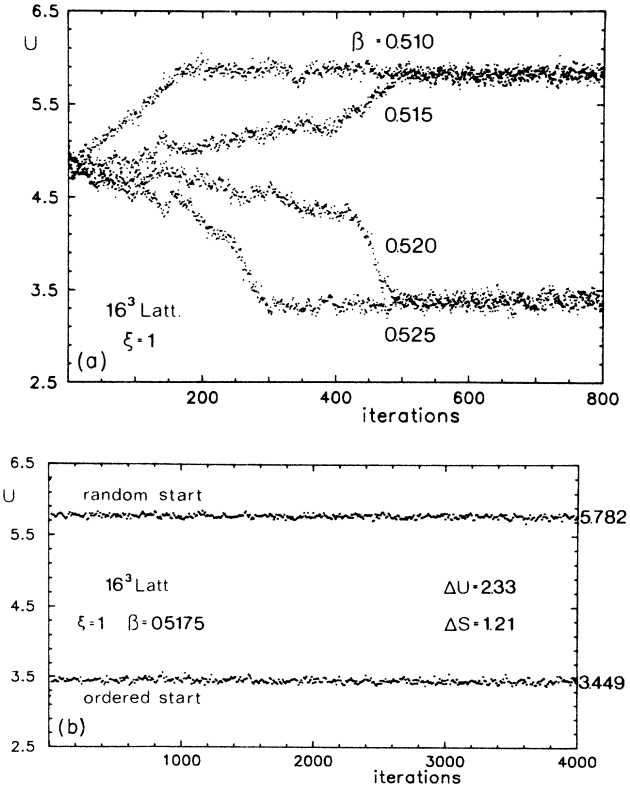


FIG. 3. (a) Equilibration of the internal energy of a mixed initial state (half solid, half liquid) near the melting point $\beta_m\approx 0.5175$ ($\xi=1$) and (b) the stability of the solid and liquid initial states at the melting point $\beta_m=0.5175$ ($\xi=1$).

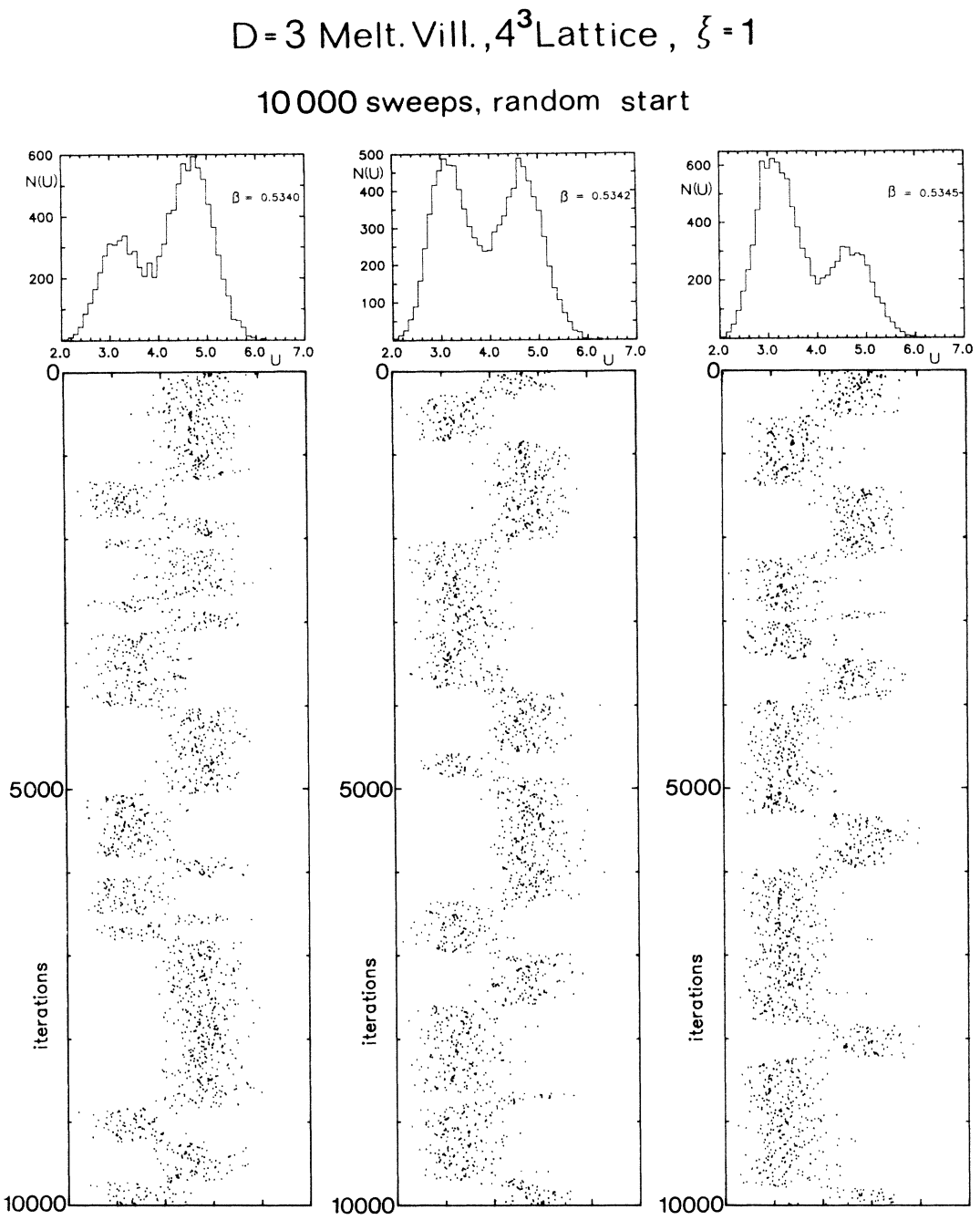


FIG. 4. Development of the internal energy (from a liquid initial state) over 10000 iterations on a $4^3$ lattice and histograms of their distributions for $\xi=1$. The melting point lies where the double peak is symmetric, i.e., at $\beta_m=0.5342$. The peak-to-peak distance gives $\Delta u \approx 1.5$ and $\Delta s \approx 0.8$ ($\xi=1$).

tices with periodic boundary conditions. To save computer time, the variables $u_i(\mathbf{x}) \in (-\pi,\pi)$ are discretized to $(2\pi/N)n$ with $N=16$ or 32. The results for $\beta \lesssim 1$ turn out to be insensitive to the choice of $N$. For the particular case $\xi=1$, the internal energy and specific heat are shown in Figs. 2(a) and 2(b), respectively. Notice that $c$ drops as the system melts. Experimentally, this is usually the opposite. We have therefore studied the $\xi$ dependence of $\Delta c$ and found that it is very sensitive on $\xi$ and becomes, indeed, negative for $\xi \lesssim 0.7$ [see Fig. 5(c)]. (Experimentally, $\xi=0.14$ for K, 0.25 for Pb, 0.3 for Cu, Ag, and Au, and 0.82 for Al.)

In order to obtain the transition temperature and entropy, we have placed the system into a mixed initial state (half solid, half liquid) and observed the development of the internal energy over many iterations. The model turns out to equilibrate quite fast and even in the neighborhood of the melting point it relaxes quite rapidly into one state [see Fig. 3(a) for the case $\xi=1$]. There is no critical slowing down since the transition is of first order, as predicted

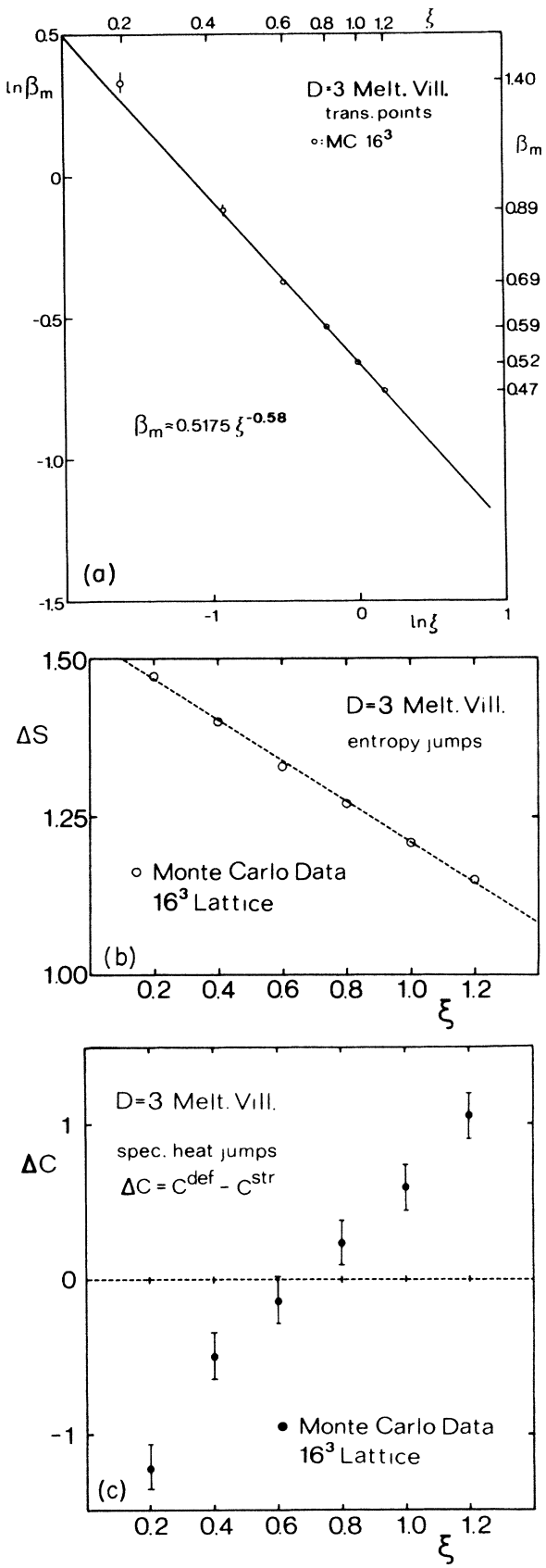


FIG. 5. The $\xi$ dependence of (a) $\beta_m$ and (b) $\Delta s$. We see that $\beta_m = 0.5175\xi^{-0.58}$ and $\Delta s \approx 1.53 - 0.32\xi$. (c) Difference of the specific heat between the solid and liquid phase as a function of the anisotropy parameter $\xi$.

on qualitative grounds.[7] The precise value of the transition temperatures, $\beta_m$, was confirmed by placing the system once in the solid state and once in the liquid state and watching the stability over many iterations [see Fig. 3(b) for the case $\xi = 1$]. The distance between the energies gives $\Delta u$ and $\Delta s = \beta_m \Delta u$ (for $\xi = 1$, $\beta_m = 0.5175$ $\Delta u \approx 2.33$, $\Delta s \approx 1.21$).

Another way of seeing the first-order nature is by taking a smaller system ($4^3$) and now watching the probability of the internal energy being in the solid or liquid state, as shown in Fig. 4, for $\xi = 1$, in particular, in the histograms. At $\beta_m$ (which on a $4^3$ lattice is shifted to $\beta_m \approx 0.534$) the two states have equal probability. The distance between the peaks gives again $\Delta u$ (for $\xi = 1$, $\Delta u \approx 1.5$) and $\Delta s$ (for $\xi = 1$, $\Delta s \approx 0.8$). By going through the same procedure for various values of $\xi$, we determine the $\xi$ dependence of $\beta_m$, of the transition entropy and of the specific-heat jump at $\beta_m$ [see Figs. 5(a)–5(c)]. Plotting $\beta_m$ logarithmically we see that there is an excellent fit:

$$\beta_m = 0.5175\xi^{-0.58} . \tag{9}$$

This corresponds to a Lindemann number[8]

$$L = 143 \left[ \frac{3+2\xi}{5} \beta_m \right]^{1/2} [1 - \tfrac{1}{3}(1-r)]^{-1/3}$$

$$\approx 112\xi^{-0.58/2} , \tag{10}$$

where

$$r \equiv \frac{c_T^3}{c_L^3} = \left[ \frac{\bar{\mu}}{2\bar{\mu} + \bar{\lambda}} \right]^{3/2}$$

with $\bar{\mu}$ and $\bar{\lambda}$ being the averaged elastic constants $\mu(3 + 2\xi)/5$ and $\lambda - \frac{2}{5}\mu(1-\xi)$, respectively. For small $\bar{\lambda}$, $r \approx 1/2^{3/2}$. The result (10) implies that $\beta_m$ of the model (1) agrees with the experimental findings in most atomic crystals.[9] For $\Delta s$ there is a rough fit around $\xi = 1$

$$\Delta s \approx 1.53 - 0.32\xi . \tag{11}$$

This number also agrees with experiment.[8]

In conclusion, we see that the simple model involving elastic and plastic fluctuations can easily be studied analytically in high- and low-temperature regions and that computer simulations display a first-order transition which looks just like crystal melting. Both the Lindemann number and the transition entropy have the magnitude observed in many materials. Finally, it may be worth mentioning that in our model the defect formation is related to the Debye temperature in accordance with Mukherjee's relation.[10]

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