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Melting behaviour of percolating solids

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Abstract. We consider the melting behaviour of randomly percolating solids and of porous solids in three dimensions. It is argued that the melting temperature T_m reaches zero ($T_m(p_c) = 0$) at the percolation point (p_c) and varies near p_c as $T_m \sim (p - p_c)^\tau$, where $\tau \approx 4.0$ is the elastic exponent. Similar behaviour is also predicted for melting in two dimensions. It is further proposed that the transition (for dimension $d > 2$) becomes continuous at p_c and the amount of discontinuity (e.g. in entropy ΔS_m) decreases monotonically to zero at p_c where, asymptotically close to p_c , a mean-field-type argument indicates that $\Delta S_m \sim \exp[-A/(p - p_c)^{\tau - \beta}]$, where $\beta (\approx 0.4$ in three dimensions) is the percolation order-parameter exponent.

Extensive studies have been made for cooperative (second order or continuous) transitions, like magnetism, on percolating lattices (see e.g. [1]). Detailed studies have also been made on mechanical properties (e.g. on elastic or non-linear response or transport properties (see e.g. [2]) of percolating or porous solids.

The melting transition of a solid (or freezing of a liquid) is a very common cooperative transition which is basically discontinuous (or first order) in nature [3]. Although not unanimously accepted it seems that this transition becomes continuous in lower dimensions (e.g. in two dimensions [4]). The melting properties of (low dimensional) fractals, like colloidal aggregates, are thus quite interesting and have been studied recently [5, 6].

In view of the above mentioned extensive studies on normal critical phenomena and on the mechanical properties of percolating solids, the melting behaviour (or the question of thermodynamic stability at finite temperature) of percolating solids is expected to be quite intriguing, especially near the percolation point where the dimensionality crossover takes place. Studies on discontinuous transitions of binary fluids in porous gels [7] might be a typical situation where such melting studies of percolating solids would be relevant. Molecular dynamic simulation [8, 9] of melting of an initially dilute (percolating) solid would be another example.

In the absence of a satisfactory thermodynamic theory of melting (in three dimensions) let us consider, following Peierls [10] and Mermin and Wagner [11], the stability of a percolating solid against lattice fluctuations at a finite temperature T . In passing, we note here that a similar Peierls-type argument was also employed by Harowell and

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Fixman [12] for studying shear-induced melting in colloidal systems (though the dimensional effects in the phase-space integral have not been treated carefully by them). For an effective harmonic system, applying the equipartition law to each independent lattice (phonon) mode of wavevector q we obtain

$$\omega_q^2 \langle |u_q^2| \rangle \sim k_B T$$

or

$$\langle u_q^2 \rangle \sim k_B T \int_{q_L}^{q_U} q^{d-1} / \omega_q^2 dq \tag{1}$$

where d denotes the dimension of the solid and q_L and q_U denote the lower and the upper cut-off wavevectors respectively. As one approaches the percolation point, the modulus of elasticity Y decreases as $(p - p_c)^\tau$ with $\tau \approx 4.0$ for dimension $d = 3$ (see Sahimi [2] and references therein), giving $\omega_q \sim (p - p_c)^\tau \omega_q^0$, $\omega_q^0 \sim q$ in the long-wavelength limit. It may be mentioned that the elastic percolation point coincides with the (normal) percolation point for systems with realistic bond-bending forces. For central force systems, the two points differ, although the exponent τ is believed to be the same [2]. It is obvious from equation (1) that the integrand becomes vulnerable near the lower cut-off ($q_L \sim 1/L$, and the system size $L \rightarrow \infty$), indicating the Peierls instability of the solid with respect to long-wavelength lattice fluctuations. The fluctuations remain bounded [10, 11] for $d > 2$; and for higher-dimensional systems the temperature (from (1)) above which the lattice density correlations are lost approaches zero near the elastic percolation point p_c as $(p - p_c)^\tau$.

This indicates that the percolating solid will melt at a lower temperature determined by the reduced elastic modulus and the melting temperature T_m reduces monotonically to zero with the elastic exponent τ :

$$\begin{aligned} T_m(p_c) &= 0 \\ T_m(p \geq p_c) &\sim (p - p_c)^\tau \quad \tau \approx 4.0, d = 3. \end{aligned} \tag{2}$$

In fact at p_c the dimensionalities cross over to the corresponding fractal values [13]. The dimensionality being reduced (at all wavelengths), the above mentioned Peierls instability, induced by the long-wavelength lattice fluctuations, becomes even more enhanced and the instability temperature drops. For a percolating fractal of size L (where $M \sim L^{d_f}$) the average lattice fluctuation at a temperature T is given by equation (1) as [5]

$$\langle u_i^2 \rangle \sim k_B T q_0^{d_f - 2z} \sim k_B T M^{(2 - d_s)/d_s} \tag{3}$$

where d_f and d_s denote respectively the fractal and the spectral dimensionality of the percolation cluster and $z (= d_f/d_s)$ denotes the dynamical exponent for diffusive modes (e.g. for phonons $\omega_q \sim q^z$) on the percolation cluster [13]. Unlike Euclidean objects, for which the lattice correlations are spontaneously broken [10] for dimension $d < 2$, fractals lose their correlations at any finite temperature if the spectral dimensionality d_s (and not the fractal dimensionality d_f) is less than two [5, 6]. Since for percolating fractals d_s is much less than two [13] ($d_s \approx \frac{3}{4}$), any infinite percolation cluster ($L \rightarrow \infty$) would have unbounded lattice fluctuations at any finite temperature (from equation (3)) and thus the melting temperature at p_c is expected to be zero.

Qualitatively speaking, the percolating fractal structure at $p = p_c$ being marginally stable, it is not expected that $T_m(p = p_c^+)$ is finite and that $T_m(p)$ approaches zero

discontinuously. Also, on the grounds that the structure is elastically stable at $p > p_c$, and hence requires a finite amount of mechanical energy to be destabilized, one can argue that the same structure would not melt (unless the dimensions are insufficient to arrest the growth of fluctuations) until a finite amount of thermal energy is provided. Since the lattice instabilities are induced by the longest-wavelength lattice fluctuations and the dimensionality reduces (to its fractal value) at p_c only (for the longest length scales), one expects that $T_m > 0$ for $p > p_c$. All of this suggests that $T_m(p_c) = 0$ and that T_m approaches zero monotonically as $p (> p_c)$ approaches p_c . If effective harmonic modes become destabilized at the melting point of a solid, as in the self-consistent phonon approximation [14], then the melting point T_m is related linearly to the elastic modulus, and again gives $T_m(p \gtrsim p_c) \sim (p - p_c)^{\tau}$. However, irreducible anharmonic terms may play an important role particularly near the melting point and the exponent for T_m may be slightly modified.

The same kind of picture holds for melting of dilute lattices in two dimensions as well. In the Kosterlitz–Thouless–Halperin–Nelson–Young (KTHNY) picture (for a review, see Strandburg [4]) melting in two dimensions is a two-stage process—the first one is a dislocation unbinding transition from a solid to a hexatic phase and the second one is a disclination unbinding transition from a hexatic to an isotropic liquid phase—and the whole process is continuous. On the other hand, recent computer simulations [4] suggest that melting in 2D may be either first order or continuous depending on the magnitude of the core energy of the defects. Recent results of experimental studies on melting in 2D systems (e.g. that of Armstrong *et al* [15] on monodisperse colloidal suspensions) are also equally ambiguous regarding the order of the transition. Whatever the order of this transition, the defect pairs are held together by some sort of elastic forces. For the second stage (hexatic to liquid), the elastic constants involved are the Frank elastic constants and at the melting point, the renormalized coupling (characterized by these Frank constants) between the defect pairs goes to zero. De Ville *et al* [16] found that the elastic response of a system of electrons on the surface of liquid helium goes to zero at the predicted dislocation-pair-unbinding temperature T_m as predicted by KTHNY theory. We argue that with dilution this aspect of the elasticity of the lattice breaks down much more easily and this would lead to a drop of the melting temperature with dilution.

The variation of the amount of discontinuity (for $d > 2$), for example in the latent heat (or the entropy discontinuity ΔS_m) at the melting point, with lattice dilution cannot be estimated using the above methods. For this, we use the Lennard-Jones and Devonshire (LJD) model of melting transition in this mean-field approximation [17], where the entropy is calculated from the disorder introduced into the system by the disappearance of a particle from a previously occupied lattice site and the simultaneous occupation of a previously unoccupied nearest neighbour interstitial (a higher-energy state). In the Bragg–Williams picture for the transition, total disorder (liquid phase) prevails when the fraction r of the occupied lattice sites equals $\frac{1}{2}$, assuming for simplicity that the lattice is such that the total number of interstitials is equal to the total number of lattice sites. It may be noted from the outset that the existence of a critical point is a necessary artefact for this model of melting transition, looked at as an order–disorder transition. Nevertheless, we argue that this artefact does not qualitatively affect our results since we do not approach criticality except at $p = p_c$.

Let us consider a dilute lattice (quenched disorder) at $T = 0$ with a fraction $p (> p_c)$ of its sites occupied. In this case, the interstitials are completely unoccupied. Our

argument below rests on the fact that only the infinite cluster, occupying a fraction [13] $(p - p_c)^\beta$ of all the sites ($\beta \approx 0.4$ when $d = 3$), takes part in the cooperative phenomena in this lattice. Now, as thermal energy is supplied by raising the temperature, a fraction r of the particles present in the infinite cluster jump into nearby interstitial sites. If each of these jumps uses an extra amount of energy w , we can write the configurational free energy per particle of the infinite cluster at temperature T as [17]

$$F_c = z'r\delta(\delta - r\delta)w + 2k_B T[r\delta \ln r\delta + (\delta - r\delta) \ln(\delta - r\delta)] \quad (4)$$

where $\delta = (p - p_c)^\beta$ and z' is the coordination number. The equilibrium value of r is calculated from the following equation obtained by minimizing the free energy with respect to r :

$$[1/(2r - 1)] \ln[r/(1 - r)] = z'w\delta/(2k_B T). \quad (5)$$

For a fully occupied lattice $\delta = 1$ and the above equation has only one solution $r = \frac{1}{2}$ corresponding to the liquid state when $4k_B T/(z'w) > 1$. When $4k_B T/(z'w) < 1$, there is another solution $\frac{1}{2} < r < 1$ which corresponds to the solid phase in this model. Obviously, the critical melting transition occurs at a temperature $T_c = z'w/(4k_B)$ for $p = 1$. However, we argue that for a given p ($> p_c$) the melting transition takes place at a temperature $T = T_m < T_c(p)$, where the degree of ordering in the coexisting liquid phase must be less than $\frac{1}{2}$ and in fact tends to zero as one approaches the percolation threshold. This is because the percolating solid at p_c is highly tenuous and has quite a few weak links (singly connected links), where a single excitation of a site into an interstitial cuts the single bond and breaks the infinite cluster into more than one finite cluster and we say the lattice melts. This picture is also consistent with our previous argument that $T_m(p_c) = 0$, in the sense that the lattice is elastically so unstable (since it is at the breakdown point) that the slightest amount of thermal excitation causes it to fall apart. Thus the coexistence value of r at p_c must be zero. If we now consider a dilution p asymptotically close to p_c (but greater), then both the coexistence, r , and T_m are much less than 1. In this limit the solution of equation (5) is

$$r = \exp[-z'w\delta/(2k_B T_m)]. \quad (6)$$

The discontinuity in entropy per particle on melting is given by

$$\Delta S_m \sim 2\delta[r \ln r + (1 - r) \ln(1 - r)]. \quad (7)$$

Clearly then in this asymptotic limit ($p \rightarrow p_c$ from above)

$$\Delta S_m \sim \exp[-z'w\delta/(2k_B T_m)] \sim \exp[-A/(p - p_c)^{\tau - \beta}] \quad (8)$$

using our previous argument for the variation of T_m with p . ΔS_m thus goes to zero as p tends to p_c ($\tau \gg \beta$). Hence, melting should be continuous at the percolation threshold. In fact, for compressible Ising systems, annealed disorder drives the continuous transition (of a pure Ising system) to a first-order transition [18]. However, the presence of quenched dilution drives the transition back to a continuous one because of the dominance of quenched fluctuation (of the order of $\varepsilon^{1/2}$ where $\varepsilon = 4 - d$) over the annealed fluctuation (of the order of ε when $\varepsilon < 1$) and this in fact has also been observed in Monte Carlo simulations [19]. Although the nature of the fluctuation-induced first-order transition in compressible Ising systems is quite different from the melting transition,

the general trend of the quenched disorder on a first-order transition may be expected to be the same, i.e. to reduce the amount of discontinuity.

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