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Glass transition, competing energy, and the tiling model

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The glass-transition point of the square-tiling model is shown not to be an isolated point but a point of confluence of a large number of higher-order phase transition lines. This multiphase nature of the glass-transition point is a consequence of the competition of the internal energy with the domain-wall energy that drives the glass transition in the model.

What is the nature of the glass transition that occurs when a liquid is cooled?[1-5] This is a question that has been haunting physicists for decades ever since Kauzmann pointed out the thermodynamic necessity of a glass transition to prevent a negative entropy disaster.[6] At present the question is hotly debated and many alternatives have been suggested.[7] In such a situation, it helps to study simple model systems to gain a better understanding of the phenomena. It is in this spirit that the square-tiling model is studied in this paper.

The square-tiling model as a model for glass transition has been studied numerically,[8-10] and by rigorous methods.[11] The physics that goes into the model building is that any amorphous structure obtained by cooling a liquid can be divided into domains of various sizes, the interiors of which contain only well-packed particles.[8,9] Restructuring of these domains as the temperature changes is taken to be the important process for the glass transition. In the model, the set of domains are represented by square tiles of all sizes and the geometric packing problem is to tile a square lattice by these tiles without any overlap or gap. (See Fig. 1.) For a particular configuration, the energy is taken as[12]

$$E=2\lambda\sum_j (j+\theta j^{\alpha})n_j\,, \qquad (1)$$

where n_j is the number of $j\times j$ tiles (also called j-tiles). The first term on the right-hand side represents the domain-wall energy, $\lambda/2$ being the energy per unit length of the perimeter of each tile. Periodic boundary conditions will be assumed. The second term assigns internal energy to the tiles according to their sizes. This term is important because domains with different geometrical structures are expected to have different energies. θ is the relative strength of the internal energy. The exponent α needs to be greater than 2 in two dimensions for the θ term to compete with the domain-wall term.[13] For simplicity, we consider $\alpha=3$. Generalization to arbitrary α is straightforward.

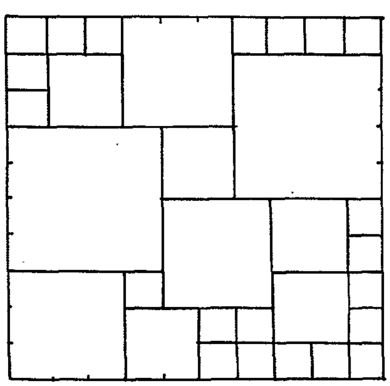

FIG. 1. Tiling of a 10×10 lattice. The energy for this particular configuration with periodic boundary condition is $2\lambda(48+270\theta)$.

In the previous studies,[8-11] the domain-wall energy was taken to be the only relevant quantity and so the θ term was not considered. The existence of the thermodynamic limit for the $\theta=0$ case was proved by Bhattacharjee and Helfand.[11] A first-order transition was found at $\tilde{T}_c=k_BT_c/\lambda=3.7$ from extrapolation of a sequence of rigorous bounds on T_c.[11] A finite-width strip transfer matrix was used to obtain these bounds which were shown to have T_c as the limit point. The above estimate agrees well with Monte Carlo results[9,10] which, furthermore, show the glassy behavior of the system near T_c. For $T<T_c$, with $\theta=0$, the system is frozen in its ground state where the lattice is covered by a macroscopic tile of size $N\times N$ ($N\rightarrow\infty$). Our purpose is to study the nature of this glass-transition point when θ is not equal to zero.

The competing nature of the two terms in Eq. (1) follows from the fact that the domain-wall energy is minimized by reducing the number of walls, thereby going over to larger tiles, whereas the internal energy is lowered by choosing smaller tiles. The compromise, in the $N\rightarrow\infty$ thermodynamic limit, is a ground state that consists of j-tiles (see below) if

$$[(j+1)j]^{-1}<\theta<[j(j-1)]^{-1}\,. \qquad (2)$$

This means that for $\theta>\frac{1}{2}$, there are only 1×1 tiles whereas only 2×2 tiles if $\theta\in[\frac{1}{6},\frac{1}{2}]$, and so on. See Fig. 2.

The stability of the assumed uniform j-tiled structure for the ground state in Eq. (2) against any aperiodic fragmentation can be proved by comparing the energy E_j of a j-tile with θ satisfying Eq. (2) with the energy E_j' of an arbitrary tiling of a $j\times j$ lattice. The difference is

$$\Delta E\equiv E_j'-E_j=2\lambda\left[\left(\sum_k kn_k-j\right)+\theta\left(\sum_k k^3n_k-j^3\right)\right], \qquad (3)$$

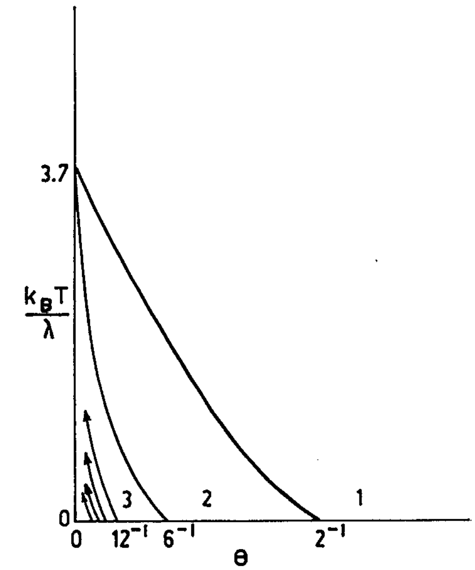

FIG. 2. Proposed phase diagram in $\hat{T}=k_BT/\lambda$ plane. The glass transition is at $\hat{T}_c=3.7\ldots$ for $\theta=0$. The numbers 1, 2, 3, . . . (not all shown) represent the ground-state structure at $\hat{T}=0$. For example, 2 represents a ground state with all 2×2 tiles.

where k goes from 1 to $j-1$. Using the perfect tiling constraint $\sum n_k k^2=j^2$, ΔE can be written as

$$\Delta E=2\lambda\sum_{k=1}^{j-1}\left[\frac{1}{kj}-\theta\right]k^2 n_k\,,$$

which is strictly positive if θ satisfies Eq. (2) as an inequality. ΔE is zero only at the boundaries of Eq. (2), and, in fact, at these special values there is a large degeneracy.

The energy per lattice site for the tiling with the j-tiles is $\mathcal{E}=2\lambda(j^{-1}+\theta j)$. There is a discontinuity in the slope of $\mathcal{E}$ (=free energy at $T=0$) with θ at each of the transition points $\theta=[j(j+1)]^{-1}$, $j=1,2,\ldots$, indicating a sequence of first-order transitions at $T=0$ at these special values, the last one being at $\theta=\frac{1}{2}$ beyond which we have only 1×1 tiles, and no further fragmentation is possible.

To study the behavior for $\hat{T}=k_BT/\lambda\neq0$, let us first concentrate on the region θ close to $\frac{1}{2}$ and $\hat{T}=0$. At very low temperatures ($\hat{T}\to0$) with $\theta=\frac{1}{2}+\varepsilon$, an expansion of the free energy involves excitations above the 1-tiled structure which are obtained by replacing n 1-tiles by one n-tile. The relevant expansion is ($\beta=1/k_BT$)

$$\beta f=2\lambda\beta(1+\theta)-xx^{-2\theta}+\tfrac{9}{2}x^2x^{-4\theta}-\tfrac{97}{3}x^3x^{-6\theta}-x^3x^{-9\theta}+\cdots\,, \qquad (4)$$

where $x=\exp(4\beta\lambda)$, and f is the free energy per lattice site.[14] The low-temperature limit $x\to\infty$ with fixed $z=x^{-2\varepsilon}$ removes all but the 2×2 excitations. For example, the last term $x^3x^{-9\theta}$ in Eq. (4) that originates from 3×3 tiles goes to zero. Hence, in the low-temperature limit, the free energy, apart from a trivial constant, is equivalent to a hard-square lattice gas (HSG) problem with both nearest-neighbor and next-nearest-neighbor exclusion, i.e., the problem of placing 2×2 squares on a square lattice with fugacity z.[15–19] Equation (4) in terms of z is

$$\beta f=2\beta\lambda(1+\theta)-z+\tfrac{9}{2}z^2-\tfrac{97}{3}z^3+\cdots\,,$$

which agrees with the corresponding expansion of Bellemans and Nigam for the hard-square problem.[15]

The hard-square lattice gas problem,[15–19] after a long debate, has been resolved in favor of a higher-order, nonuniversal transition at $\ln z=4.7$. This value has been found by phenomenological renormalization-group method[18] and agrees well with the independent interfacial method,[19] but slightly higher than the estimate from direct transfer matrix approach.[16] Incidentally, this is a problem that has been resolved very easily by the renormalization-group method, for which even the existence of a phase transition was in doubt.[15,16]

A phase transition (PT) in the HSG implies a PT for the tiling model at very low temperatures ($\hat{T}\neq0$). The phase boundary in the $\hat{T}$ vs θ plane near $\theta=\frac{1}{2}$ and $\hat{T}=0$ is given by $\hat{T}=0.85\,(1-2\theta)$, using $z=x^{-2\varepsilon}$. The negative slope of the phase boundary (see Fig. 2) forbids any reentrant PT. Since the 1-tiled structure (degeneracy = 1) is not connected by any symmetry to the 2-tiled structure of infinite degeneracy, a symmetry argument *à la* Landau tells us that the phase boundary cannot terminate unless it hits a special point in the phase diagram or its boundary. The line cannot extend to infinity like the ordinary solid-liquid line because at high temperatures $\hat{T}\gg\hat{T}_c$, the state with $\theta\neq0$ should be similar to $\theta=0$. The only possibility is the termination at the glass-transition point on the $\theta=0$ axis. Bending over to $\hat{T}=0$ is ruled out by the presence of a narrow window of N-tiled phase close to $\theta=0$. The thermodynamic equivalence of the 1-tiled structure for $\theta>\frac{1}{2}$ and $\hat{T}=0$ to the high-temperature phase for $\theta=0$ should not come as a surprise because a similar equivalence was shown in Ref. 9 by considering $\lambda<0$.

What happens at the other values of θ where first-order transitions take place at $\hat{T}=0$? Low-temperature expansions of the free energy around these special values can be done as for $\theta=\frac{1}{2}$. For example, around $\theta=[j(j-i)]^{-1}$, $j>1$, the relevant excitations are $(j+1)$-tiles on a lattice covered with j-tiles. Since the j-tiled lattice has a large degeneracy, an averaging over the degenerate states has to be done as, e.g., for fcc Ising antiferromagnet.[20] However, the corresponding lattice gas problems, though similar to the two-dimensional physisorbtion problems (commensurate phase transitions[21]) remain unexplored. Weak transitions are expected to occur at nonzero $\hat{T}$.

A transition from j-tiles to $(j+1)$-tiles can take place only if the $(j+1)$-tiles form an infinite network or percolate on the j-tiled lattice. The critical density of the $(j+1)$-tiles should be bounded below by this percolation threshold. Thresholds for such correlated percolation problems are, in general, not known. However, for $\theta=\frac{1}{6}$, an estimate would be $p=p_c/9$ where $p_c=0.59$ is the threshold for a square lattice. Since, for a lattice gas, the transition takes place when $\mu n\sim k_BT$, where μ is the chemical potential and n the density, an upper bound for the slope for the transition line around $\theta=\frac{1}{6}$ can be obtained as $|d\hat{T}/d\theta|=1.08$, following the procedure for $\theta=\frac{1}{2}$ case. The bound obtained is crude, no doubt, but at least gives an idea of the phase boundary. Symmetry argument can again be invoked to conclude that all these lines meet at the glass-transition point as shown in Fig. 2. The glass-transition point, therefore, appears as a multiphase point in the extended $\hat{T}$ vs θ phase diagram.

A further justification of the phase diagram of Fig. 2 comes from finite-size effects observed in Ref. 11. For $\lambda > 0$, if we change the sign of θ, the energy in Eq. (1) is minimized by going over to the largest tile. Because of the infinitely large cost in energy, smaller tiles will not be allowed no matter how small $\theta(<0)$ is. Since the texture changes drastically as the $\theta = 0$ line is crossed on the high-temperature side $(\hat{T} > \hat{T}_c)$, this part of the temperature axis is a singular line in the phase diagram.[22] At singular or critical points, various thermodynamic quantities approach the bulk limit algebraically with the size of the system.[23] Such an algebraic approach is, therefore, expected for $\hat{T} > \hat{T}_c$ with $\theta = 0$. In contrast, for $\hat{T} < \hat{T}_c$, if the proposed phase diagram of Fig. 2 is correct, the $\theta = 0$ line is surrounded by the largest tile phase on both sides and nothing special happens when the line is crossed. For such cases exponential approach to the bulk limit with the size of the system should be observed. This difference in behavior has, indeed, been seen in Ref. 11 where only the $\theta = 0$ case was considered.

In summary, we propose that the glass-transition point observed in the square tiling model without the competing internal energy [$\theta = 0$ in Eq. (1)] is a multiphase point where an infinitely large number of higher-order phase-transition lines meet, even though it looks like a first-order transition for $\theta = 0$.[24] The whole high-temperature phase for $\theta = 0$ is a singular phase in the extended $\hat{T}$ vs θ phase diagram of Fig. 2, which is supported by the observed[11] finite-size effect. Since the phase boundaries for $\theta \neq 0$ are of higher order (>2) they will be rather elusive[15,16] with signatures only in derivatives higher than 2. Specific heat, for example, will not show any divergence.

Further analytical and numerical studies are necessary to obtain the full phase diagram and to understand the significance of the multiphase nature of the glass-transition point. It is necessary to know if a richer phase diagram than Fig. 2 is possible. A renormalization-group approach, currently under investigation, will shed light on these issues, and will, in particular, put to the test a recent conjecture[4] on the fixed-point structure for the glass transition.

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[22]The nature of the singularity can be discussed by considering the tiling model of Eq. (1) but without the perfect tiling constraint. This will be discussed elsewhere.

[23]See, e.g., M. Barber, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8.

[24]The importance of infinitely many states near the glass-transition point has recently been pointed out by Kirkpatrick and Wolynes in their studies on the Potts glass [T. T. Kirkpatrick and P. G. Wolynes, Phys. Rev. B **36**, 8552 (1987)]. However, the connection between the Potts glass and the tiling model is not clear at this point, though it should be mentioned that the four-state Potts model provides a lower bound to the free energy of the tiling model with $\theta = 0$. See Ref. 11.