Glass Transitions and Frustrated Tiling Models

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"Tiling models" were originally introduced in an effort to explain low-temperature behavior of glass-forming materials. These models have now been extended by inclusion of "frustration" interactions that limit tile sizes, motivated by observed temperature dependence of supercooled liquid viscosities. The fundamental combinatorial problem presented by tiling-model equilibrium statistical mechanics is discussed in detail, and a simple approximate solution is proposed. The corresponding phase transition behavior is examined, with emphasis on essential singularities at first-order condensation points. Results from numerical calculations in the presence of frustration exhibit low-temperature heat capacity maxima (in accord with observations on "fragile" glasses) but provide no support for the presence of "ideal glass transitions".

I. Introduction

Understanding the nature of glass transitions remains one of the most fascinating and challenging problems in condensed matter physics. In particular, the striking characteristics of the so-called "fragile" glass formers (large liquid-phase heat capacity, non-Arrhenius temperature variation of shear viscosity) have elicited special attention and have stimulated various theoretical concepts. One of these theoretical concepts, the positive-temperature ideal glass transition at Kauzmann's point of vanishing liquid-phase glass kinetic behavior are examined. Depending on the parameters selected, the tiling models are capable of displaying a wide range of behavior in both equilibrium and nonequilibrium regimes.

Section III presents several exact relations that are important in solving the combinatorial problem presented by the canonical partition functions for the tiling models. On the basis of these exact relations an approximate combinatorial solution is offered in section IV, which also contains some results on the analytic nature of first-order phase transitions in the tiling models subject to this approximation. Section V contains some numerical results in the same approximation that exhibit the kind of heat capacity anomalies associated with fragile glass formers.

The paper concludes with section VI in which some aspects of glass kinetic behavior are examined.

II. Generalized Tiling Models

The motivation behind the tiling models is the desire to describe and to partially classify particle arrangements which occur in the amorphous liquid and solid states. The viewpoint adopted is that these arrangements can be resolved at the atomic level into domain patterns, where the interior of each domain consists of a well-packed (and thus rather strongly cohering) cluster of particles. Walls between neighboring domains then would normally be locations of weakened bonding.

If such a viewpoint has merit, then surely the expected domain sizes and shapes would be diverse and complicated. In order to keep the statistics manageable, the D-dimensional tiling model assumes that the domains (tiles) are all D-dimensional "cubes" (squares for D = 2, cubes for D = 3, etc.) whose edge lengths are integer multiples of some fundamental molecular-scale unit distance. Furthermore, these tiles are required to fit together without gaps or overlaps with vertices residing on the nodes of a D-dimensional "cubic" lattice. The distinct configurations permitted in the tiling models are all such tilings (domain patterns) satisfying this description.

The definition of equilibrium aspects of the tiling model is completed by specifying the potential energy Φ for any tiling. Three kinds of contributions to Φ will be distinguished. The first represents the energy penalty associated with the presence of domain walls (tile boundaries) and is conveyed by a positive coupling constant λ that stands for energy per unit of domain wall. The second contribution is a "frustration" energy with positive coupling constant θ that limits the size of the tiles, whose relevance is suggested by the observed shear viscosity of fragile glasses. The third contribution provides a driving force for crystallization and has a coupling constant µ.

The generic form of Φ is the following:

$$\Phi = D \sum_{i \in \mathbb{Z}} (\lambda |p_i| + \theta \delta n_i - \mu a^{\delta-1} N_{ss})$$

(2.1)

Here ni represents the number of tiles with linear size i, and the exponent f occurring in the frustration term must exceed D in order to limit tile sizes. It has been assumed that tiles of linear size a have a special status, namely that they contain a crystalline arrangement of particles; it is favorable for pairs of such size-a tiles to be in full contact along a shared boundary, and Nss counts the number of such full-contact pairs.

If N is the number of sites in the underlying lattice, then the ni are subject to the constraint of complete filling:

$$\sum_{i \in \mathbb{Z}} i^n_i = N$$

(2.2)

Furthermore we must have

$$N_{ss} \leq Dn_{ss}$$

(2.3)

We will suppose that

$$\lambda, \theta, \mu \geq 0$$

(2.4)

in the following. It is clear that the ground state of the tiling model will be a periodic array of fully registered size-a tiles (a macroscopic crystal) if µ is sufficiently large. An elementary calculation
shows that this will be the case if
\[ \mu > \lambda + \theta \sigma^{j^{D+1}} \]  
(2.5)

Since \( \lambda, \theta, \) and \( \mu \) are independent coupling constants in the tiling models it is possible to vary \( \mu \) at will to drive for nucleation and crystal growth. Indeed if (2.5) is not satisfied the ground state will be noncrystalline.

For the remainder of this paper the emphasis is on the amorphous state alone, and for that reason we will now suppose that \( \mu = 0 \). Consequently the ground state will be determined by a competition between the tile boundary \( (\lambda) \) and frustration \( (\theta) \) terms in \( \Phi \). It is straightforward to verify that if, for some integer \( j \geq 1, \lambda \) and \( \theta \) are such that
\[ j(j - 1)[j^{D} - (j - 1)^{D}] < \lambda \theta < j(j + 1)[j + 1)^{D} - j^{D}] \]
(2.6)
then the ground state consists entirely of size-\( j \) tiles. This ground state is degenerate however, since rows of such tiles can slide relative to one another without energy penalty. In the large system limit such configurations are aperiodic with unit probability. Nevertheless, the degeneracy is not exponential in system size and so would not affect any intensive thermodynamic properties of the system.

If \( \lambda \theta \) happened to equal, say, the upper limit shown in (2.6), the ground state would display an indeterminate mixture of size-\( j \) and size-\( (j + 1) \) tiles. This special circumstance creates a positive residual entropy per unit area (or volume).

If both \( \mu \) and \( \theta \) vanish, the ground state consists of that tiling or set of tilings with the minimum possible boundary. This can be achieved with a single tile of linear dimension \( N^{1/D} \) if the system has the proper shape. Other system shapes require a combination of tiles, but for any reasonable system shape the boundary concentration on a per-lattice-site basis will be vanishingly small in the large system limit.\(^7\)

Time-dependent attributes of the tiling models stem from the selection of Markovian kinetic transition rates \( K(C \rightarrow C') \), which transform tiling configuration \( C \) to \( C' \) at inverse temperature \( \beta = (k_B T)^{-1} \). Any physically relevant case involves several basic requirements on the \( K \)'s. First, the system must be ergodic, i.e., a positive-rate pathway of successive transitions must be available between any two tiling configurations (though the direct transition rate may vanish). Second, detailed balance must be obeyed to assure that equilibrium is attainable:
\[ K(C \rightarrow C', \beta) \]
\[ K(C' \rightarrow C, \beta) = \exp[\beta(\Phi(C) - \Phi(C'))] \]  
(2.7)

Third, every \( K > 0 \) should be a nonincreasing function of \( \beta \). Finally, nonvanishing \( K \)'s should involve only pairs of tilings that differ locally, not globally, over the entire macroscopic system. Two distinct sets of \( K \)'s meeting these requirements have previously been investigated.\(^9\)

III. Exact Relations

The canonical partition function \( Z(\beta) \) for the tiling model at inverse temperature \( \beta = (k_B T)^{-1} \) is
\[ Z(\beta) = \sum \exp(-\beta \Phi) \]  
(3.1)
where the sum includes all distinguishable tilings of the underlying lattice. Because we limit present attention to the special case \( \mu = 0 \), eq 3.1 becomes
\[ Z(\beta) = \sum_{\Omega} \sum \exp[-\beta \Phi]\]  
(3.2)
where now the sum covers all sets of tile numbers \( \{n_i\} \) which satisfy the constraint eq 2.2, and where \( \Omega(\{n_i\}) \) represents the number of distinguishable tilings with the given set of tile numbers.

The combinatorial quantity \( \Omega \) is expected to rise exponentially with \( N \), the system size, in the large system limit.\(^{11}\) Consequently we can write
\[ \Omega(\{n_i\}) \approx \exp[N \sigma(\{\rho_i\})] \]  
(3.3)
Here the intensive quantity \( \sigma \) has been expressed as a function of tile concentrations; it is the per-site configurational entropy divided by \( k_B \). Evaluating equilibrium properties of the tiling model essentially reduces to determination of \( \sigma \).

The canonical partition function can be obtained for large \( N \) by the maximum term method. The equations locating the extremum are
\[ \frac{\partial \sigma}{\partial \rho_i} - D \beta (\lambda \rho^{D+1} + \theta \rho^D + \Delta(\beta) \rho^D) = 0 \]  
(3.4)
where \( \Delta(\beta) \) is a Lagrange multiplier associated with the complete filling constraint (2.2), or equivalently
\[ \sum_{i=1}^{\rho_i} \rho_i = 1 \]  
(3.5)
The set of concentrations \( \{\rho_i(\beta)\} \) which satisfy variational eq 3.4 at any \( \beta \) are the equilibrium values for that temperature.

In virtue of the fact that (aside from a factor \( k_B^{-1} \)) \( \sigma \) is an absolute entropy density, it cannot be negative:
\[ \sigma(\{\rho_i\}) \geq 0 \]  
(3.6)
Equality with the lower limit zero is achieved if all tiles have the same size, say \( n \):
\[ \sigma(\{\rho_i = l^{D} \delta_{ib}\}) = 0 \]  
(3.7)
a property mentioned in the previous section II.

\( \sigma \) obeys an exact scaling relation. Imagine expanding the extent of the underlying lattice by an integer factor \( b > 1 \) in all \( D \) directions, so that the new set of \( b^D \) sites. Also expand each tile by the same factor, so that every valid tiling of the original \( N \)-site system dilates into a valid tiling of the \( b^D N \)-site system. Under this operation the starting concentration set \( \{\rho_i\} \) transforms into the new set \( \{\rho_i(b)\} \):
\[ \rho_i(b) = b^{-D} \rho_i \]  
(3.8)
the only nonvanishing concentrations are those for which the size is a multiple of \( b \). As was the case before dilation, concentrations are still reckoned on a per-site basis.

While every tiling of the starting system maps into a distinct image tiling of the dilated system, not all dilated system tilings would be generated this way. This mapping specifically fails to produce all of the \( b^D \) translates that become possible or the occasional row translates (assuming periodic boundary conditions). However, these extra configurations are not sufficiently numerous to have any thermodynamic significance in the large system limit. Consequently we must have
\[ \sigma(\{\rho_i\}) = b^{-D} \sigma(\{\rho_i(b)\}) \]  
(3.9)
The factor \( b^D \) compensates for the fact that even after dilation the configurational entropy quantity \( \sigma \) is still computed on a per-site basis.

Enumeration of distinct tilings only requires considering tiles with \( l \geq 2 \). Once the larger tiles are in place only a single way remains to fill the untiled space with unit tiles. In particular this simplifies the enumeration task when the larger tiles form a dilute solution in nearly pure unit-tile solvent, for then the standard cluster techniques for dilute systems can be invoked.\(^{12}\) The leading terms in the dilute solution expansion can readily be obtained through pair cluster order, with the following explicit result:
\[ \sigma = \sum_{\rho_i} (1 - \ln \rho_i) - \frac{1}{2} \sum_{j \neq i} (j + 1)^{-1} \rho_j \rho_i + \ldots \]  
(3.10)
It is necessary to extend the formal definition of \( \sigma \) beyond the sets of concentrations obeying eq 3.5 to include independent \( \rho_i \).
variations, so that the variational equations (3.4) can be employed to locate the equilibrium concentrations $\rho_i(\beta)$. In this extended regime $\sigma$ must be a function of the $\rho_i$'s that is homogeneous of first degree:

$$\sigma(\rho \rho_i) = \sigma(\rho)$$  \hspace{2cm} (3.11)

A step-by-step demonstration of this property is too lengthy to include here. However, the key to such a demonstration lies in the behavior of $\rho_i(\beta)$ for $l \to \infty$. Very large tiles in effect provide internal macroscopic boundaries for the smaller tiles, reducing the effective system size, and so their occurrence probability is related to the system's energy density itself. Equation 3.11 assures that this internal consistency obtains.

IV. Approximate Solution

The next step involves introduction of a simple approximation to the configurational entropy quantity $\sigma$. The specific form to be utilized is

$$\sigma \approx - \sum_{l \geq 2} \rho_l \ln \left( \rho_l / \rho_0 \right)$$ \hspace{2cm} (4.1)

where $\rho_0$ is the zeroth moment of the size distribution:

$$\rho_0 = \sum_{l \geq 1} \rho_l$$ \hspace{2cm} (4.2)

Obviously expression 4.1 displays the first-degree homogeneity property (3.11) in the extended regime of independent $\rho_i$'s. In the physical regime for which constraint (3.5) is obeyed, it is straightforward to show that exact conditions (3.6), (3.7), and (3.9) are satisfied as well.

When the tiles of sizes $l \geq 2$ form a dilute solution in the $l = 1$ solvent, expression 4.1 can be expanded thus

$$\sigma = \sum_{l \geq 2} \rho_l \left( 1 - \ln \rho_l \right) - \rho_2 \left( \rho + 1 \right)$$ \hspace{2cm} (4.3)

Notice that this agrees with exact result (3.10) when $D = 1$. The reason is clear. Expression 4.1 is equal to the combinatorial entropy (divided by $k_B$) for a set of objects arranged along a line. Consequently, use of expression 4.1 is open to two interpretations. One is that expression 4.1 is equal to the combinatorial entropy (divided by $k_B$) for a set of objects arranged along a line. Consequently, expression 4.1 is open to two interpretations. The other is that expression 4.1 is equal to the combinatorial entropy (divided by $k_B$) for a set of objects arranged along a line. Consequently, expression 4.1 is open to two interpretations.

When (4.1) is substituted into the variational eq 3.4, one obtains the following expression for the tile concentrations:

$$\rho_i(\beta) = \mu_i(\beta) \exp(-D\beta(\lambda)^{l-1} + \theta) + \Lambda(\beta)$$ \hspace{2cm} (4.4)

Clearly we must have, from the definition of $\mu_0$

$$1 = \sum_{l \geq 1} \exp[-D\beta(\lambda)^{l-1} + \theta] + \Lambda(\beta)$$ \hspace{2cm} (4.5)

which determines the Lagrange multiplier $\Lambda(\beta)$. Also the preexponential factor $\mu_0$ in eq 4.4 must be selected to satisfy the complete filling condition (3.5), leading to

$$\mu_0 = \sum_{l \geq 1} \rho_i \exp[-D\beta(\lambda)^{l-1} + \theta] + \Lambda(\beta)$$ \hspace{2cm} (4.6)

The free energy per lattice site $F/N$ can be obtained from the logarithm of the maximum term of $Z(\beta)$, eq 3.2. Using eq 4.4 this yields the result:

$$-N^{-1} \ln Z(\beta) = N^{-1} \beta F(\beta) - \Lambda(\beta)$$ \hspace{2cm} (4.7)

This identification of the Lagrange multiplier $\Lambda$ with the free energy density (divided by $k_B T$) is not restricted to approximation 4.1 but is entirely general, and is connected to the homogeneity property of $\sigma$ expressed in eq 3.11 above.

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applied to this case indeed indicates that series 4.11 is divergent. Nevertheless it is Borel-summable, so we can write

$$\Lambda(\beta) = \int_0^\infty dt \exp(-t)L(yt) + M(y)$$  \hspace{1cm} (4.12)

$$L(x) = \sum_{n=1}^{\infty} (a_n/n!)x^n$$  \hspace{1cm} (4.13)

where $M(y)$ is a function which vanishes at $y = 0$ faster than any positive power of $y$, and which therefore cannot be revealed by asymptotic series 4.11.

The power series for the Borel transform $L(x)$, eq 4.13, has a positive radius of convergence determined by the presence of a simple pole at

$$x = x_0 \simeq 0.1801698$$  \hspace{1cm} (4.14)

whose location is indicated by the fact that coefficient ratios now approach the limit $x_0^{-1}$. Standard methods of analysis then show that the Borel integral in (4.12) indeed possesses an essential singularity at $\beta_c$ with an associated branch cut in the complex $\beta$ plane directed along the positive real axis. The leading-order (small $y$) imaginary part of $\Lambda(\beta)$ at this branch cut is found to be

$$\text{Im} \Lambda(\beta_c + y \pm i\epsilon) = \frac{1}{2}\text{Re}(\beta_0/a_1)^{-1/2} \exp[(-\beta_0/a_1) \times \frac{1}{2} \exp(-\beta_0^2/a_1)]$$  \hspace{1cm} (4.15)

and $a_1$ and $a_2$ are the leading coefficients in eq 4.11.

The Borel transform $L(x)$ is amenable to accurate approximation with Padé approximants, using the available $a_n$'s. Consequently the integral in eq 4.12 may be evaluated numerically. When this is done the result agrees to high precision with $\Lambda(\beta)$ obtained by direct numerical solution of eq 4.8. We conclude that $M(y)$ in eq 4.12 for $D = 2$ either vanishes or is undetectably small.

Formally it is possible to extend the preceding method for generating the $a_n$ to arbitrary real positive $D$. When this was done for $D$ in the range

$$1.75 \leq D \leq 3.00$$  \hspace{1cm} (4.16)

we found that ratios $a_{n+1}(D)/a_n(D)$ for large $n$ are proportional to $n^{(1/D-1)}$.

The calculations described in this section are similar (but not identical) with those required to describe Fisher's one-dimensional droplet model for condensation.

V. Numerical Results

We now return to the frustrated tiling models with $\theta > 0$. For the sake of definiteness we set

$$f = D + 1$$  \hspace{1cm} (5.1)

in the following. Equation 4.5 has been used to determine $\Lambda(\beta)$ numerically for closely spaced $\beta$ values, after which the other thermodynamic functions were evaluated. As a first example consider the case $D = 2, \theta = 0.001$. We continue to use $\lambda = 1$ in this section. Equation 2.6 implies that the ground state consists of tilings composed entirely of $32 \times 32$ tiles. Figures 2-5 respectively show computed values for $A$, mean energy, heat capacity, and entropy plotted versus $\beta$. It is clear that the first-order transition which occurs at $\beta = 1/2$ in 2 for $\theta = 0$ has been smeared out into a continuous variation for all
properties. Furthermore the results indicate a shift of the smeared transition to larger \( \beta \) (lower temperature): the heat capacity maximum in Figure 4 occurs at \( \beta \cong 0.416 \).

Figures 6 and 7 respectively present heat capacity and entropy curves versus \( \beta \) for another case, namely \( D = 3, \theta = 0.01 \). The qualitative pattern agrees with the preceding two-dimensional example, with the \( \theta = 0 \) sharp transition now smeared out and shifted to larger \( \beta \). The heat capacity maximum in this case occurs at \( \beta \cong 0.182 \).

The entropy curves in Figures 5 and 7 are relevant to the "ideal glass transition" controversy. Both display regions of rapid decline toward zero. If kinetic sluggishness at lower temperatures were to make observation of the remainder of the heat capacity curves impossible, it would seem natural to extrapolate the entropy curves to zero at a finite \( \beta \) (approximately 0.44 and 0.19 for \( D = 2 \) and \( D = 3 \)). However, we see that the entropy curves smoothly turn over and approach zero only as \( \beta \) approaches infinity. Consequently, tiling model behavior with frustration present seems to be inconsistent with the existence of an ideal glass transition. If these rates have a common Arrhenius form, then \( \tau \) in this very low temperature regime can be expected to adopt the Adam–Gibbs form (5.1) with appropriate \( T_0 \) and \( A \) values. At somewhat higher temperatures the mean tile size will be substantially smaller, and concentrations \( p_B \) and \( p_B^* \) will be negligibly small. Consequently a different set of basic transition rates \( K \) will be involved that in principle can be assigned independently. In particular these rates could be given Arrhenius form with a very different activation energy. If the result for \( \tau \) were forced into Adam–Gibbs form the constant \( A \) so obtained would differ from that appropriate to the very low temperature regime.

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### VI. Discussion

Time-dependent properties of the tiling models require specification of the basic transition rates between configurations. Even after accounting for the constraints on these rates mentioned in section II, it appears that a wide range of relaxation behaviors is possible for a given equilibrium behavior, since the rates are independently assigned.

A well-known relation due to Adam and Gibbs\(^{20} \) describes the temperature \( (T) \) dependence of average relaxation time \( (\tau) \) in glasses in terms of the configurational entropy \( S_c \):

\[
\ln(\tau) = r_0 \exp[A/T S_c(T)]
\]

(6.1)

Here \( r_0 \) and \( A \) are temperature-independent positive constants, which can be expected to vary from substance to substance. While the Adam–Gibbs relation appears to describe the glass-transition-region behavior of many substances quite satisfactorily,\(^{12} \) both experimental\(^{22} \) and theoretical\(^{16} \) exceptions have been noted.

In order to understand in principle how such exceptions could arise, it is worthwhile inquiring what circumstances in a kinetic tiling model should produce substantial violations of the Adam–Gibbs relation. One qualifying scenario has

\[
\lambda/\theta = j(j + 1)
\]

(6.2)

where \( j \) is a large integer, so that the ground state consists of a degenerate mixture of size-\( j \) and size-\( (j + 1) \) tiles. In this event

\[
\lim_{T \to 0} S_c(T) = 0
\]

(6.3)

as a result of the degeneracy. At very low (but positive) temperatures the system would be tiled almost exclusively with these two large sizes, and relaxation rates would be controlled just by the basic transition rates \( K(C \leftrightarrow C') \) within this special tiling set. If these rates have a common Arrhenius form, then \( \tau \) in this very low temperature regime can be expected to adopt the Adam–Gibbs form (5.1) with appropriate \( T_0 \) and \( A \) values. At somewhat higher temperatures the mean tile size will be substantially smaller, and concentrations \( p_B \) and \( p_B^* \) will be negligibly small. Consequently a different set of basic transition rates \( K \) will be involved that in principle can be assigned independently. In particular these rates could be given Arrhenius form with a very different activation energy. If the result for \( \tau \) were forced into Adam–Gibbs form the constant \( A \) so obtained would differ from that appropriate to the very low temperature regime.

### Shape Fluctuations in Ionic Micelles

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Molecular dynamics calculations are reported for a microscopic model of a sodium octanoate micelle in aqueous solution. The micelle, whose equilibrium structure is found to be a prolate spheroid, undergoes shape fluctuations with a characteristic time scale of order 30 ps. The results are discussed in the light of recent theoretical and experimental studies on related systems.

**Introduction**

The rich variety of phase behavior exhibited by ionic surfactant solutions\(^{1} \) can ultimately be traced back to the competing interactions between the constituent species: the repulsive interactions between polar head groups, the attractive interactions between the surfactant tails (hydrophobic effect), and the solvation forces associated with the hydrophilic head groups. Considerable theoretical progress has recently been made in understanding the overall behavior of micelles and related microemulsion systems in terms of mean-field theories and simplified or idealized models.\(^{2,12} \) However, the bulk of experimental and theoretical work

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