

Tiling, Prime Numbers, and the Glass Transition

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BACKGROUND

Thermal motions in high-temperature liquids permit rapid and effective exploration of alternative molecular packings. But such exploration becomes increasingly sluggish if the liquid is supercooled, and it largely ceases if further cooling passes through a glass transition. This paper proposes and studies a new type of statistical mechanical model that is intended to explain such phenomena. These models possess several conceptual ingredients that seem not to have been considered before in the extensive theoretical literature devoted to supercooling and glass formation.¹⁻⁶ Although many of their features have yet to be worked out in quantitative detail, the early results reported here indicate success in describing qualitatively both static structure and relaxation behavior in real glasses. Furthermore, as discussed below, these models can in principle also be used to discuss the kinetics of crystal-phase nucleation from the supercooled liquid or vitreous solid states.

The inverse of the shear viscosity $\eta(T)$ provides a rough but convenient measure at absolute temperature T of the mean rate at which a liquid undergoes spontaneous structural change at the molecular level. For many substances the Tammann-Vogel-Fulcher (TVF) equation⁷

$$\eta(T) = A \exp [B/(T - T_0)] \quad (1)$$

provides a satisfactory fit to viscosity measurements, with positive constants A , B , and T_0 . The apparent activation enthalpy ΔH^\ddagger and entropy ΔS^\ddagger can be formally extracted from the TVF equation:

$$\frac{\Delta H^\ddagger}{k_B T} = \frac{BT}{(T - T_0)^2} \quad (2)$$

$$\frac{\Delta S^\ddagger}{k_B} = \frac{BT}{(T - T_0)^2} - \frac{B}{T - T_0} - \ln A \quad (3)$$

Both of these quantities diverge as T decreases toward T_0 . This suggests in turn that as T decreases, geometrically larger and larger zones of activation must be involved to permit macroscopic shear flow to take place. Evidently particles constituting the system manage to become well packed in domains of increasing size, so that flow and other relaxation processes require "unbundling" of these larger domains in order to permit repacking in an alternative way.

This point of view focuses attention on the temperature-variable mean size of

well-packed domains as a relevant physical parameter, an attribute not explicitly clear in other models for glasses.

From this perspective we can now state several fundamental concepts upon which our new family of models will be based: 1) Any molecular configuration of the material system of interest can be resolved into particle domains that are well packed but spatially nonrepetitive. These domains have variable size, and in principle could encompass the entire system. 2) The set of possible domains may include a crystalline fragment, but in view of the nonrepetitiveness constraint only a few unit cells could be involved. Large well-packed domains of necessity then are amorphous. 3) Walls between contiguous domains usually will have positive misfit energy; that is, they are locations of poor packing. The exception to this rule would be the properly registered contacts between pairs of the small crystalline domains, which together then would form a larger crystal fragment. The perfect macroscopic crystal formally will be regarded as a periodic array consisting just of the special crystal fragment domains. 4) Transitions occur as thermal motion spontaneously unbundles and repacks particles into different domain patterns.

TILING MODELS

We will now convert the four informal statements written above into a precise statistical mechanical model. For simplicity of exposition and of visualization we will confine attention to two dimensions, although the extension to the more realistic case of three dimensions is quite straightforward.

Let the region occupied by the system be covered by a square lattice of N sites with unit spacing. We will suppose that the "well-packed but spatially nonrepetitive" particle domains are squares with integer sides ($1 \times 1, 2 \times 2, \dots$), and that these must tile the lattice, that is, cover it without gaps or overlaps. For some positive integer a we will also suppose that any $a \times a$ square in the tiling represents a crystalline fragment but that all other square sizes represent well-packed amorphous domains. The allowed system configurations are all the distinct tilings of the given lattice. Periodic boundary conditions will apply.

The potential energy for any configuration will be assigned the form ($\lambda, \mu \geq 0$)

$$\Phi = 2\lambda \sum_{j=1} j n_j - a\mu N_{aa} \quad (4)$$

Here n_j is the number of $j \times j$ squares, and N_{aa} is the number of pairs of $a \times a$ squares that are in full contact along a common side. The coupling constant λ represents mismatch energy per unit length of boundary between pairs of amorphous domains, between an amorphous and a crystalline domain, or between a pair of misregistered crystalline domains. The other coupling constant μ is present to favor crystallization, and indeed if

$$\mu > \lambda > 0 \quad (5)$$

the ground-state configuration for Φ consists of a periodic registered array just of $a \times a$ squares filling the entire macroscopic lattice. FIGURES 1A & 1B show the crystalline and typical amorphous domain patterns, respectively.

Static thermodynamic properties of the tiling model can be obtained from the canonical partition function ($\beta = 1/k_B T$). Thus

$$Z(\beta) = \sum_{\text{tilings}} \exp(-\beta\Phi) \quad (6)$$

provided that the system is ergodic and that sufficient time is available for equilibration to have occurred at the prevailing temperature. If the inequality shown in equation 5 is satisfied, Z would reflect the existence of a melting transition at some temperature T_m .

In view of primary interest in the glass transition, we elect to suppress crystallization altogether by setting μ equal to zero. Consequently

$$Z(\beta) = \sum_{\{n_i\}} \Omega(n_1, n_2, \dots) \exp[-\beta\Phi(n_1, n_2, \dots)] \quad (7)$$

where Ω is the number of tilings possible with the given numbers n_1, n_2, \dots of squares of various sizes.

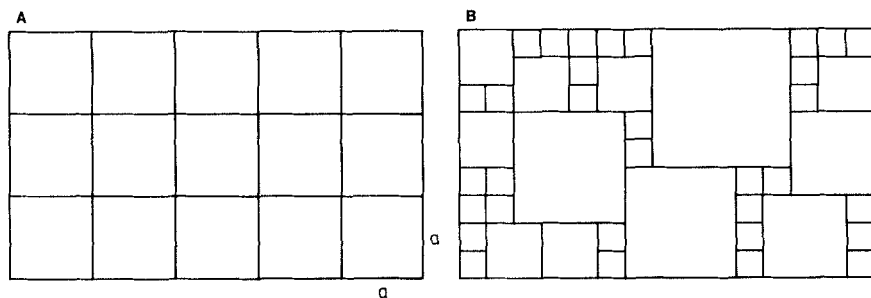


FIGURE 1. (A) A registered periodic arrangement of $a \times a$ squares representing the perfect macroscopic crystal. (B) A typical pattern of domains in the amorphous state.

Next we must specify the transitions allowed between configurations, and their respective rates. These will be selected according to a principle of parsimony, namely that they be a minimal set of transitions that assures ergodicity (any configuration can be reached from any other). Squares will be permitted both to fragment into smaller squares, and to aggregate into larger squares. The specific rules are given below.

Fragmentation: $(pq) \times (pq)$ can fragment into $p^2 q \times q$'s if and only if p is a smallest prime factor of pq . (The rate for this transition will be denoted by $r_f(pq)$.) Thus a 6×6 can transform into four 3×3 's by a single fragmentation transition, but not into nine 2×2 's. Squares of prime-number size such as 7×7 can only fragment fully into 1×1 's.

Aggregation: $p^2 q \times q$'s in a square arrangement can eliminate a common boundary to form $(pq) \times (pq)$ if and only if p is a smallest prime factor of pq . (The rate will be denoted by $r_a(pq)$.) This is obviously the reverse of the above fragmentation process.

Any tiling can be converted to the "vacuum state" consisting entirely of 1×1 's simply by implementing a series of fragmentations. Likewise, any other tiling can be created out of the vacuum by a suitable sequence of aggregations. This guarantees ergodicity.

The aggregation rates will be assigned the generic form

$$r_a(pq) = \nu_0 \alpha^{2pq(p-1)} \quad (8)$$

where

$$0 < \alpha < 1 \quad (9)$$

and ν_0 is a fundamental attempt frequency. The parameter α represents the probability that any given unit length of boundary is suitable for aggregation, and its exponent in equation 8 is the total length of boundary that would be annihilated by the aggregation.

Rates must satisfy detailed balance, of course. Consequently we have

$$r_f(pq) = \nu_0 \alpha^{2pq(p-1)} \exp(-\beta \Delta\Phi) \quad (10)$$

where $\Delta\Phi$ is the potential energy increment incurred by the fragmentation transition

$$\Delta\Phi = 2\lambda pq(p-1) \quad (11)$$

At high temperature the system will typically be tiled by a mixture of squares mostly of small size. As temperature declines, larger squares become more prominent, but equations 8 and 10 show that transition rates are then substantially slowed. It is the blocking of structural change by large squares, particularly those with prime-number sizes, that make the present model attractive for describing glass transitions.

PARTITION FUNCTION EVALUATION

The combinatorial factor Ω required for evaluation of the partition function can be obtained by a sequential filling process for the lattice, placing squares in the system one at a time in random order. Suppose that a fraction ξ of the system's area has been covered at some intermediate stage, with use of the same fraction of each of the available numbers n_j of squares of various sizes. Suppose the next square to be added has size $l \times l$, and let $E_l(\xi)$ denote the expected number of ways it could be fitted onto the partially filled lattice without overlap. Then Ω can be obtained as the product of such factors for the entire filling sequence.

The Flory or mean field approximation⁹ sets

$$E_l(\xi) \approx (1 - \xi)^{l^2} N \quad (12)$$

which assumes that a common attrition factor $1 - \xi$ is applicable for each unit of area to be covered by the $l \times l$ square. This leads to the estimate

$$\ln \Omega \approx N \left\{ \sum_{j=1}^{\infty} (n_j/N) [\ln(N/n_j) + 1] - 1 \right\} \quad (\text{mean field}) \quad (13)$$

In the spirit of the scaled particle theory¹⁰ it would seem reasonable that the $l \times l$

square's boundary length (linear in l) as well as its area (quadratic in l) should appear as exponents in an accurate $E_l(\xi)$ expression. Consequently we consider the following generalization of equation 12

$$E_l(\xi) \approx [F(\xi)]^{l^2} [G(\xi)]^l N \tag{14}$$

Two relations are available to determine F and G . The first is that equation 12 is actually an *exact* expression for $l = 1$. The second emerges in the large- l limit, where successful placement requires that all other squares be confined to a reduced macroscopic area, and thereby compressed to a higher effective filling fraction. One finds

$$F(\xi) = (1 - \xi) [1 - (1 - \mu_1)\xi]^{-(1-\mu_0)/(1-\mu_1)} \tag{15}$$

and

$$G(\xi) = [1 - (1 - \mu_1)\xi]^{(1-\mu_0)/(1-\mu_1)} \tag{16}$$

TABLE 1. Predicted Values of $N^{-1}\ln\Omega$ for Uniform Tiling with $l \times l$ Squares

l	Mean Field ^a	Improved ^b
1	0.000	0.000
2	-0.403	-0.173
3	-0.645	-0.244
4	-0.764	-0.260
5	-0.831	-0.258
6	-0.873	-0.249
7	-0.900	-0.238
8	-0.919	-0.227
9	-0.933	-0.217
10	-0.944	-0.207
100	-0.999	-0.046
1000	-1.000	-0.007

^a $N^{-1}\ln\Omega = (2/l^2)\ln l + 1/l^2 - 1$.

^b $N^{-1}\ln\Omega = [(1 - l)/l^2]\ln l$.

where the μ_k are moments of the size distribution for squares

$$\mu_k = \sum_{l \geq 1} l^k (n_l/N) \tag{17}$$

This improved combinatorial argument subsequently yields

$$\ln\Omega \approx N \left\{ \sum_{j \geq 1} (n_j/N) \ln(N/n_j) + [(1 - \mu_0)/(1 - \mu_1)] \mu_1 \ln \mu_1 \right\} \text{ (improved) } \tag{18}$$

That use of the improved combinatorics versus the mean field approximation may be important for our tiling model is illustrated by TABLE 1. It shows the respective mean field and improved values for $N^{-1}\ln\Omega$ in the event that the system were being tiled uniformly with $l \times l$ squares. In the large-system limit that is of primary concern, this quantity should be identically zero for all l . Although both approximations give

zero for $l = 1$, both also drift to negative values for larger l . This imprecision is clearly worse for the mean field case, especially for large squares that ought to be significant for the tiling model at low temperature. The improved combinatorics at least has the feature that it approaches the correct result in the large- l limit, in contrast to the mean field approximation.

When the Ω expression equation 18 is placed in the partition function equation 7, the equilibrium state at given β may be identified by locating the maximum term. This results in the following expression for the equilibrium mean concentrations of the squares

$$\langle n_l(\beta) \rangle / N = \exp [\Lambda_2(\beta)l^2 + \Lambda_1(\beta)l + \Lambda_0(\beta)] \quad (19)$$

Consequently

$$\Lambda_0(\beta) = -\frac{\mu_1 \ln \mu_1}{1 - \mu_1} - 1 \quad (20)$$

and

$$\Lambda_1(\beta) = \left(\frac{1 - \mu_0}{1 - \mu_1} \right) \left(\frac{\ln \mu_1}{1 - \mu_1} + 1 \right) - 2\beta\lambda \quad (21)$$

and $\Lambda_2(\beta)$ must be determined by the fixed total area condition $\mu_2 = 1$.

In view of the fact that the moments μ_0 and μ_1 depend on the concentrations, and that at the same time the concentrations depend on these moments, self-consistent numerical solutions must be sought at each temperature. TABLE 2 provides some results so obtained.

In the high-temperature regime for which

$$\beta\lambda < \beta_c\lambda = 0.323\ 106\ 608\ 8\ \dots \quad (22)$$

each of Λ_0 , Λ_1 , and Λ_2 is negative. Equation 19 then shows that the concentrations decrease monotonically with increasing l . TABLE 2, however, demonstrates that as β increases from zero to β_c , $\Lambda_2(\beta)$ drifts continuously upward to zero. Continuation past β_c would cause Λ_2 to become positive; the concentrations in equation 19 would no longer be monotonically decreasing with l , but would manifest a sudden appearance of squares near the maximum possible size (edge length proportional to $N^{1/2}$). Hence β_c is a condensation point at which the system in principle becomes macroscopically unstable with respect to the elimination of misfit boundary.

TABLE 2. Self-consistent Numerical Solutions

$\beta\lambda$	Λ_2	Λ_1	Λ_0	μ_1	μ_0
0.00	-0.37501	-0.27591	-0.16875	0.69843	0.56246
0.05	-0.31065	-0.39962	-0.18259	0.67668	0.53417
0.10	-0.24844	-0.52538	-0.19763	0.65357	0.50491
0.15	-0.18848	-0.65374	-0.21415	0.62874	0.47447
0.20	-0.13090	-0.78553	-0.23264	0.60163	0.44248
0.25	-0.07582	-0.92229	-0.25399	0.57122	0.40826
0.30	-0.02337	-1.06728	-0.28015	0.53527	0.37026
0.323 1066	0.00000	-1.13941	-0.29526	0.51514	0.35029

TABLE 3. Equilibrium Concentrations $\langle n_l(\beta) \rangle / N$ for Squares with $l \leq 10$

l	$\langle n_l(0) \rangle / N$	$\langle n_l(\beta_c) \rangle / N$
1	4.406×10^{-1}	2.382×10^{-1}
2	1.085×10^{-1}	7.622×10^{-2}
3	1.263×10^{-2}	2.439×10^{-2}
4	6.943×10^{-4}	7.806×10^{-3}
5	1.803×10^{-5}	2.498×10^{-3}
6	2.211×10^{-7}	7.994×10^{-4}
7	1.281×10^{-9}	2.558×10^{-4}
8	3.506×10^{-12}	8.186×10^{-5}
9	4.532×10^{-15}	2.620×10^{-5}
10	2.767×10^{-18}	8.383×10^{-6}

TABLE 3 shows equilibrium concentrations of squares computed from equation 19, with $l \leq 10$, at $\beta = 0$ and β_c . The effect of temperature reduction on large squares is particularly noticeable.

It should be mentioned in passing that the Flory or mean field approximation also leads to a condensation point, but at a substantially lower temperature

$$\beta_c \lambda = 0.628\ 028\ 3600 \text{ (mean field)} \quad (23)$$

To the extent that TABLE 1 suggests that the improved combinatorics has not entirely rectified the error in the mean field approximation, we might expect an exact solution for the model to display a condensation point at a temperature even higher (smaller $\beta \lambda$) than that given by equation 22.

The moment quantity μ_1 substantially gives the mean energy, and heat capacity follows from β differentiation. FIGURE 2 shows a plot of this heat capacity for temperatures above the condensation point ($0 \leq \beta \leq \beta_c$).

CONDENSED STATE

Although the preceding analysis appears to predict correctly the occurrence of the transition point, it is not reliable for indicating the structure of the condensed state itself. The reason is that one macroscopic square (or a small number of order unity of such squares) occupying a substantial fraction of the entire system area cannot be part of an essentially continuous filling operation. Yet precisely such continuous filling forms the basis of both the mean field and the improved estimates for the combinatorial quantity Ω . It is necessary to place macroscopic squares in the system first, then use the preceding continuous filling procedure as before to tile the remaining multiply connected region.

The end result of this generalization is that if the system shape is itself square, the condensed state consists just of the single tile of maximum size $N^{1/2} \times N^{1/2}$. With periodic boundary conditions this has degeneracy N because the corner of the tile can be located at any one of the N lattice sites. As the temperature decreases through the condensation point the system would (if equilibrium were obtained) discontinuously transform into a single well-packed amorphous domain. The mean energy on a per-site basis would drop discontinuously from 1.0303λ just above the transition temperature

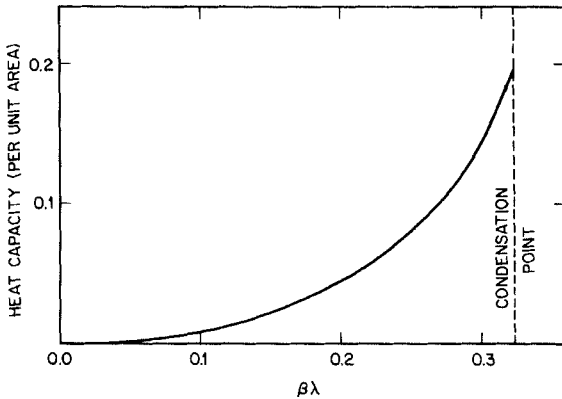


FIGURE 2. Heat capacity per unit area for $\beta \leq \beta_c$.

to zero below. This transition is unequivocally first order, with an entropy change $\Delta S/Nk_B = 0.3329$.

In the event that the system shape is not square, the condensed state may exhibit two or more macroscopic tiles, and the degeneracy of the corresponding ground state may be larger than N . A particularly interesting case arises when the system is rectangular, with a rational side ratio close to the irrational "golden mean," $\theta = (5^{1/2} + 1)/2$. The ground-state tiling then requires a hierarchy of square sizes, descending from the largest possible size down to the microscopic regime. One possible arrangement is shown in FIGURE 3. There are N places for the largest square, $(N/\theta)^{1/2}$ for the next largest, and two choices for each succeeding level in the size descent. The overall degeneracy of the ground state will be proportional to N^q , where

$$q = \frac{3}{2} + \frac{\ln 2}{2 \ln \theta} = 2.2202 \dots \quad (24)$$

Although this degeneracy is substantially larger than that for the square-shaped system, it does not alter the conclusion that in the infinite system limit the configurational entropy per particle of the condensed state is zero.

GLASS TRANSITION

Although the preceding has assumed thermal equilibration, the tiling model is useful precisely because it cannot equilibrate below the condensation temperature. A high-temperature configuration containing only microscopic squares could in principle reach the ground (condensed) state by allowed transitions, and this might be possible via many different sequences of intermediate configurations. Equations 8 and 10, however, show that impossibly small rates would be involved, with the pure number $0 < \alpha < 1$ raised at least to a power comparable to $N^{1/2}$.

Therefore, as temperature declines toward and through the condensation point the texture of the tiling will coarsen, but kinetic arrest will certainly prevent the appearance of macroscopically large squares. The condensation point would never be observed as such, but would be inferred (for example) from positions of maxima in apparent heat capacities for slower and slower cooling rates. It is natural to expect that with a slow, finite cooling rate, the properties of the model would manifest a reasonably sharp "glass transition" in the neighborhood of the true condensation point.

A typical glassy configuration would be kinetically strangled by large squares, but should still contain a few small inclusions of the type shown in FIGURE 4. The 2×2 square at the left in this structure can fragment into 1×1 's, then another 2×2 can form at the right, and then this sequence could reverse, and so forth. Such local oscillation would still have a respectably high rate below the condensation temperature, but would be totally ineffective in producing overall structural relaxation. Instead, it represents for the tiling model a simple analogue to the "two-level" systems, which appear almost universally in low-temperature amorphous solids.^{11,12}

Side-by-side coexistence of rapidly oscillating inclusions and of larger, more sluggish features in the tiling model glassy state suggests that a broad spectrum of relaxation times should be present. This spectral breadth may lead to a "stretched exponential," or "KWW," form for relaxation functions.¹³

COMPUTER SIMULATION

In the near future, the most reliable source of information about kinetic properties of the tiling model is likely to be computer simulation. Consequently a Monte Carlo

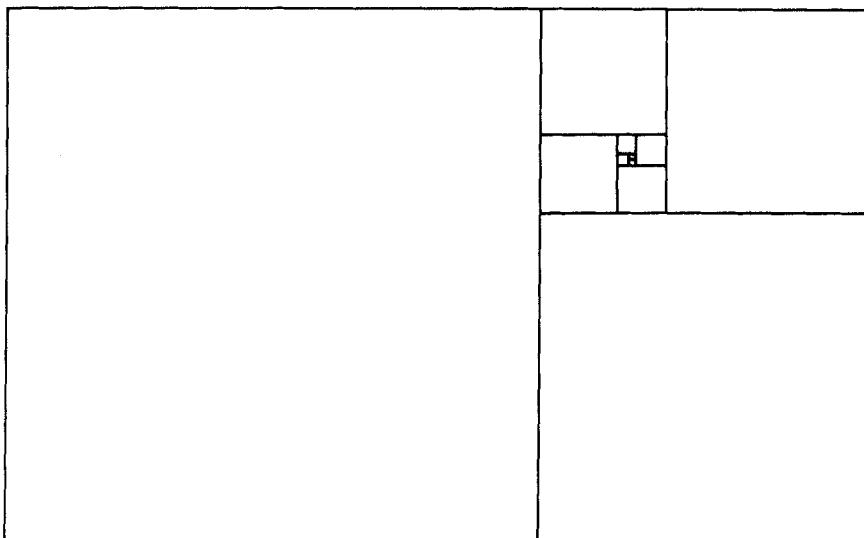


FIGURE 3. Condensed state tiling when the system shape is rectangular with the side ratio near the golden mean.

program for this purpose has been constructed and successfully tested. It embodies the transition rates shown in equations 8 and 10, and generates a stochastic sequence of tiling configurations appropriate to given initial conditions and the temperature of interest. At each Monte Carlo step it keeps full account of all possible transitions, and focuses on selecting the next configuration, while maintaining a record of the elapsed time.

Test runs with the Monte Carlo program (with $\alpha = 0.98$) have demonstrated the feasibility of simulating a two-dimensional system of size $N = 10^4$. This should be large enough to infer accurately properties for the infinite system limit. In particular we have carried out extended runs at $\beta\lambda = 0.15$ to assess the validity of the improved combinatorial method discussed above, and to verify that indeed it is superior to the mean field approximation.

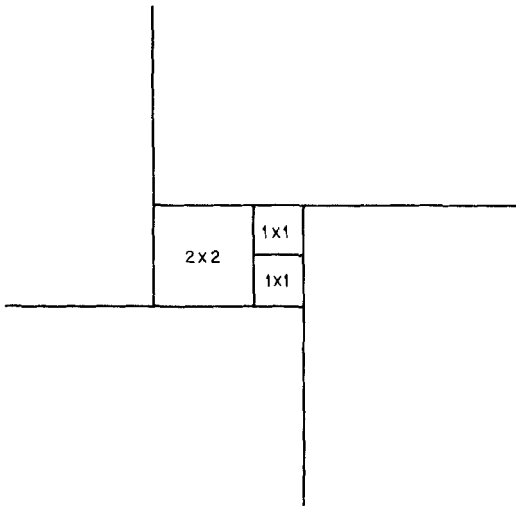


FIGURE 4. Randomly oscillating "two-state" inclusions expected in the low-temperature glass.

Further simulation calculations will be directed to establishing the following: 1) equilibrium square concentrations and the heat capacity over the entire high-temperature range; 2) the location of the underlying condensation point; 3) the cooling rate dependence of the glass transition and of the properties of the glass state itself; and 4) the time dependence of various linear and nonlinear relaxation functions, and how these vary with temperature near the condensation point.

Finally, it appears feasible both to include the crystallization-inducing interactions shown in equation 4 and to simulate three-dimensional models.

SUMMMARY

As a liquid is supercooled toward and through a glass transition, the constituent molecules collectively experience increasing difficulty in executing rearrangements that lower the overall interaction energy. A conceptually simple lattice model is

introduced to represent this phenomenon. In its two-dimensional version the plane is tiled by squares with integer sides. Each tile represents a well-packed but nonrepetitive domain of molecules, and domain walls have positive mismatch energy. Subdivisions and aggregations of squares are kinetically allowed if and only if the smallest prime factors of square sides are involved. At equilibrium, cooling coarsens the texture of squares until a first-order transition point is reached, at which macroscopic squares appear. This transition, however, is totally inhibited kinetically, yielding instead an amorphous "glass" of microscopic but relatively large squares. Exploratory calculations have been carried out that demonstrate the feasibility of using computer simulation to study kinetic properties of the model.

REFERENCES

1. O'REILLY, J. M. & M. GOLDSTEIN, EDS. 1981. *Ann. N.Y. Acad. Sci.* **371**.
2. MACKENZIE, J. D. 1960. *Modern Aspects of the Vitreous State*. Butterworths. Washington, DC.
3. PHILLIPS, J. C. 1979. *J. Non-Cryst. Solids* **34**: 153.
4. NELSON, D. R. 1983. *Phys. Rev. B* **28**: 5515.
5. PALMER, R. G., D. L. STEIN, E. ABRAHAMS & P. W. ANDERSON. 1984. *Phys. Rev. Lett.* **53**: 958.
6. LEUTHEUSSER, E. 1984. *Phys. Rev. A* **29**: 2765.
7. UBBELOHDE, A. R. 1978. *The Molten State of Matter*: 414. John Wiley & Sons. NY.
8. HILL, T. L. 1956. *Statistical Mechanics*. McGraw-Hill. New York, NY.
9. FLORY, P. J. 1953. *Principles of Polymer Chemistry*: 497-503. Cornell University Press. Ithaca, NY.
10. REISS, H., H. L. FRISCH & J. L. LEBOWITZ. 1959. *J. Chem. Phys.* **31**: 369.
11. ANDERSON, P. W., B. I. HALPERIN & C. M. VARMA. 1972. *Philos. Mag.* **25**: 1.
12. PHILLIPS, W. A. 1972. *J. Low Temp. Phys.* **7**: 351.
13. NGAI, K. L. 1979. *Comments Solid State Phys.* **9**: 127, 141.

DISCUSSION OF THE PAPER

R. G. PALMER (*Duke University, Durham, NC*): My guess is that the glassy behavior of your model comes from the limited transitions allowed: the system is highly constrained dynamically. Would you see the thermodynamic phase transition if you allowed more types of transition?

STILLINGER: Glassy behavior in the tiling model arises from a combination of three attributes: the sparse set of allowed transitions, the intrinsic slowness of those transitions that create or destroy large domains, and the restriction to domains with only square shapes. By relaxing the first two of these the opportunity for observing a vestige of the thermodynamic phase transition (at least on cooling from high temperature) would certainly be enhanced. In particular if the parameter α in equations 8 and 10 were set equal to unity, aggregation processes would be greatly facilitated. The system, however, still has the problem that most tilings with large squares will have those squares juxtaposed in ways inconsistent with further aggregation. Unless a new set of transitions is allowed that involves restructuring domains inside nonsquare boundaries of arbitrary size, the system will still be kinetically unable to achieve the fully condensed state.

J. T. BENDLER (*General Electric Research and Development Center, Schenectady, NY*): Dr. Stillinger, can you say how the entropy factor, α , was assigned in the simulations and how sensitive the stretched exponential is to it?

STILLINGER: The parameter α was set equal to 0.98 in the simulation studies thus far carried out. It is not obvious how the stretched exponential relaxation behavior should depend on α , so further simulation studies are warranted.

P. C. HOHENBERG (*AT&T Bell Laboratories, Murray Hill, NJ*): You indicated that there is a static transition in your model, from an approximate analytical calculation. How is this transition temperature related to the dynamic slowing-down transition?

STILLINGER: Computer simulation reproducibly achieves thermal equilibrium at temperatures greater than or equal to the condensation temperature T_c . Cooling below T_c eventually causes glassy behavior to emerge, the temperature range for which depends on the cooling rate. To the extent that a glass transition temperature T_g can be identified, $T_c > T_g$.

HOHENBERG: I understood your answer to be $T_{\text{dynamic}} < T_{\text{static}}$. Is this right?

STILLINGER: Yes.

J. C. PHILLIPS (*AT&T Bell Laboratories, Murray Hill, NJ*): Can you expect that this model contains a T_g as well as T_0 ? Will the specific heat exhibit the asymmetry usually observed in DTA experiments: S-shaped on cooling, peaked on heating?

STILLINGER: Under the condition of a constant cooling rate, the tiling model exhibits a smooth continuation of mean energy versus temperature through the transition point T_c . But especially with very slow cooling, this metastable continuation eventually halts when the prevailing arrangement of squares is blocked from further aggregation at any perceptible rate. At this point (" T_g ") the mean energy remains nearly constant as further cooling proceeds.

Simulation on the tiling model has not yet been turned to the task of examining asymmetry in apparent heat capacity under cooling and heating conditions, respectively. There are some basic elements present, however, that might create such asymmetry. Upon cooling, aggregation requires neighboring squares to be in registry (in full contact along a shared side), whereas fragmentation has no analogous precondition. In addition, unfavorable Boltzmann factors are present only in fragmentation rates, not in aggregation rates. There is no reason to suppose that the time-dependent populations of squares of different sizes that appear on cooling would be identically mirrored upon heating at the same rate. Any difference would affect the corresponding heat capacities.

M. WEINBERG (*Jet Propulsion Laboratory, Pasadena, CA*): If different geometrical units were used in the model, would there be qualitative changes in the results?

STILLINGER: Some changes in the allowed shapes of domains should have little effect on qualitative properties. For example, replacing the underlying square grid with a triangular lattice would permit tiling with equilateral triangles, and if least prime factors of side lengths were again used to define permissible transitions, no substantial change in either equilibrium behavior or kinetic behavior would ensue. But if very complicated domain shapes were allowed (such as elongated, nonconvex, and multiply connected shapes), with some selection of transitions to assure ergodicity, drastic changes would no doubt be possible, including elimination of the first-order condensation point.