Structural Equilibration in Condensed Phases

Frank H. Stillinger

AT&T Bell Laboratories, Murray Hill, New Jersey 07974 (Received: June 4, 1984)

This paper examines several aspects of the natural packing structures for molecules in condensed phases, i.e., the collection of local minima in the many-body potential energy function. Thermal equilibrium at different temperatures populates regions surrounding these minima differently. Kinetic processes occur via transitions through saddle point neighborhoods that connect neighboring minima. General properties of this representation suggest an approximate mapping of minima and feasible transitions respectively onto the vertices and edges of a hypercube. For the purposes of specific calculation this latter picture has been projected onto a two-dimensional order-parameter space with an appropriate model potential energy function. The resulting statistical-mechanical construct exhibits distinct "crystal" and "liquid" phases, with a first-order melting transition as well as metastability. A Fokker–Planck equation has been derived for the model to describe relaxation in the order-parameter space.

I. Introduction

To a large extent materials science studies geometric patterns of atoms and molecules in space, and the kinetics of transition between those patterns. Theory is obliged to specify the underlying interactions, and then show how they produce the local order that obtains under given conditions of temperature, pressure, and thermal history.

It is useful for understanding a condensed-phase material to identify the "natural structures" it can exhibit, namely the me-chanically stable arrangements of its constituent atoms or molecules. These are configurations corresponding to local minima of Φ, the total interaction potential. This function generally will include intramolecular, intermolecular, and wall forces. These natural structures or particle packings provide a fiducial set against which any arbitrary configuration (not necessarily at mechanical equilibrium) can be gauged. It has been demonstrated previously[1]

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(1) Stillinger, F. H.; Weber, T. A. *Phys. Rev. A* **1982**, *25*, 978.

that such a strategy uniquely separates the equilibrium statistical-mechanical problem into a pure packing part, and a part attributable to anharmonic vibrations away from the Φ minima.

This paper continues the theoretical exploration of the natural structure formalism. Section II summarizes some of the earlier conclusions reached both from analytical studies and from computer simulation of selected (but diverse) classical many-body systems.[1-6] A master equation is then introduced in secion III to describe the approach to thermal equilibrium, particularly at low temperature; the "states" kinetically coupled by the master equation are precisely those defined by the Φ minima.

In order to confer a modest degree of concreteness on the formal theory, a simple solvable model is introduced in section IV. This model entails two order parameters and exhibits a first-order melting transition. It also illustrates the possibility of metastable states, specifically supercooled liquid and superheated solid. Section V discusses some aspects of kinetic behavior in this simple model, starting with the relevant master equation for transitions between its natural structures, and then deriving a Fokker–Planck equation for relaxation in the two-dimensional order-parameter space. Section VI discusses prospects for developing more realistic models and for relating them more closely to experimental studies of nucleation rates and of glass formation and relaxation.

II. Natural Structures

Suppose that the system of interest comprises N atoms whose respective positions and masses are r_j and m_j $(1 \leq j \leq N)$. The full configuration space therefore is $3N$-dimensional. Any point $r \equiv (r_1, r_2, ..., r_N)$ is this multidimensional space (with exceptions having no more than zero measure) can be mapped uniquely onto a local minimum of the potential energy function Φ. The mapping is generated by the solution to the set of equations $(s \geq 0)$:

$$m_j(dr_j(s)/ds) = -\nabla_j\Phi[r_1(s)...r_N(s)] \quad (2.1)$$

with the given r as initial condition. The solution $r(s)$ to eq 2.1 describes a mass-weighted descent on the Φ hypersurface in the multidimensional configuration space. In the limit that s approaches $+\infty$ it settles into the relevant Φ minimum onto which the initial configuration is thereby mapped.

The set of starting positions r all of which map onto a common minimum α define a connected region R_α surrounding that minimum. These regions exhaustively and without overlap divide the configuration space in a natural way into discrete cells. Whenever r is in R_α, we can simply say that the system possesses the natural structure α.

Let Ω denote the number of potential energy minima. General considerations[1] suggest that in the large system limit Ω has the following form:

$$\Omega \sim \Omega_p \exp(\theta N)$$

$$\theta > 0, \quad \Omega_p = N_1!N_2!...N_\nu! \quad (2.2)$$

where

$$N_1 + \cdots + N_\nu = N \quad (2.3)$$

are the numbers of distinguishable atomic species present. Ω_p in eq 2.2 accounts for the possibility of permuting identical atoms (this creates distinct but equivalent packings), while the exponential factor indicates how the number of *inequivalent* packings rises with system size. The vast majority of the minima correspond to amorphous packings; those with recognizable crystalline order are rarer and tend to be lower in energy than the average.

Classical dynamics specifies $r(t)$, the continuous temporal evolution of the system's $3N$-dimensional configuration vector. This

(2) Stillinger, F. H.; Weber, T. A. *Phys. Rev. A* **1983**, *28*, 2408.
(3) Stillinger, F. H.; Weber, T. A. *J. Phys. Chem.* **1983**, *87*, 2833.
(4) Weber, T. A.; Stillinger, F. H. *J. Chem. Phys.*, submitted for publication.
(5) Stillinger, F. H.; Weber, T. A. *J. Chem. Phys.*, submitted for publication.
(6) Weber, T. A.; Stillinger, F. H. *Phys. Rev. B*, submitted for publication.

vector passes through a sequence of regions R_α, slowly executing transitions at low total energy, but doing the same much more rapidly at high total energy. Previous studies utilizing the computer simulation technique[2,5,6] have established several general attributes of the transition sequence:

(1) The feasible transitions between contiguous regions occur strictly as a result of localized rearrangements of particles; i.e., most of the system remains virtually fixed in comparing the configurations of the two potential minima involved. A consequence of this feature is that the difference in potential energy between the minima is order unity, not order N, so that with each such fundamental transition the potential energy in a large system changes by a small fraction.

(2) The transition rate between successively visited regions is an *extensive* quantity. This follows from the localization property. The number (and thus the net rate) of feasible transitions out of a given packing region scales linearly with the system size.

(3) Only a very small fraction of the direct structural transitions occur between equivalent packings and thus merely involve permutations of identical particles. The great majority instead cause the system to shift from one packing structure to another inequivalent one which therefore differs in potential energy.

(4) The activation energy in the liquid phase for self-diffusion significantly exceeds that for structural transitions. The latter typically requires the system vector $r(t)$ to cross the boundary between neighboring packing regions in the vicinity of a Φ saddle point embedded in that boundary. Evidently self-diffusion is controlled by a relatively small but high set of potential barriers that act a bit as kinetic bottlenecks in the entire transition sequence.

These considerations lead to a qualitative picture of the natural packing structures and the kinetically feasible transitions connecting them which will be useful for justifying the simple model discussed in section IV. Equation 2.2 shows that a macroscopic material system possesses a huge number of alternative packing structures, even after discounting all possible permutations among identical particles. However, the feasible transitions connect any one packing structure only to a number of others of order N, a tiny fraction of the total. Using the language of graph theory[7] one would say that packing structures (vertices) are very sparsely connected by feasible structural transitions (edges connecting the vertices).

III. Master Equation

Consider a microcanonical ensemble of identically prepared systems, all with the same total energy E. The statistical state of this ensemble can in principle be described by the full $6N$-dimensional phase-space distribution function. But for present purposes it suffices to use a more economical coarse-grained description in terms of the probabilities $p_\alpha(t)$ that any member of the ensemble resides in packing region R_α at time t. The obvious normalization condition

$$\sum_\alpha p_\alpha(t) = 1 \quad (3.1)$$

applies for all t.

Time dependence of the regional probabilities $p_\alpha(t)$ can be described adequately for many circumstances by a master equation:

$$dp_\alpha(t)/dt = \sum_{\gamma(\neq\alpha)} [K_{\gamma\to\alpha}(E) p_\gamma(t) - K_{\alpha\to\gamma}(E) p_\alpha(t)] \quad (3.2)$$

The transition rates in this equation obviously must be nonnegative, and through the considerations mentioned in section II we know that most of them vanish.

Denote by $M_\alpha(E) \geq 0$ the phase-space measure for the system when configurationally it lies in packing region R_α. A formal expression for this measure is the following:

$$M_\alpha(E) = \int_{R_\alpha} dr \int dp \, \delta[E - \Phi(r) - \sum_{j=1}^{N}(p_j)^2/2m_j] \quad (3.3)$$

(7) Harary, F. "Graph Theory"; Addision-Wesley; Reading, MA, 1969.

where $\mathbf{p} \equiv (\mathbf{p}_1...\mathbf{p}_N)$ comprises all N particle momenta. At equilibrium the probabilities p_α must adopt time-independent values that are proportional to the respective M_α, and in order for this to hold the transition rates must obey conditions of detailed balance, namely

$$K_{\alpha \to \gamma}(E) = [M_\gamma(E)/M_\alpha(E)]^{1/2}A_{\alpha\gamma}(E) \qquad (3.4)$$

where $A_{\alpha\gamma}(E)$ is symmetric

$$A_{\alpha\gamma}(E) = A_{\gamma\alpha}(E) \qquad (3.5)$$

This form automatically preserves the normalization condition (3.1) at all times.

The relaxation spectrum for approach to equilibrium as described by the master equation (3.2) is determined by the linear eigenvalue problem

$$\mathbf{Ka} = \lambda\mathbf{a} \qquad (3.6)$$

where $\mathbf{K}$ is the $\Omega \times \Omega$ matrix whose elements are

$$(\mathbf{K})_{\alpha\gamma} = -K_{\gamma \to \alpha}(E) \qquad (\alpha \neq \gamma)$$

$$(\mathbf{K})_{\alpha\alpha} = \sum_{\gamma(\neq\alpha)} K_{\alpha \to \gamma}(E) \qquad (3.7)$$

Thermal equilibrium corresponds to the smallest eigenvalue (zero) and the related eigenvector $\mathbf{a}$ is just the equilibrium set of packing-region populations.

If the initial set of probabilities $\{p_\alpha(0)\}$ is symmetric under interchange of identical particles (that is, equivalent regions have equal probabilities), then the master equation causes the same to hold at all subsequent times. In this circumstance a contracted description is warranted which lumps together all Ω_p equivalent packings. Hence, we consider the probabilities $P_j(t)$ which refer to sums of the p_α over these equivalence classes [denoted by $C(j)$]:

$$P_j(t) = \sum_{\alpha \in C(j)} p_\alpha(t) \qquad (3.8)$$

The master equation (3.2) can easily be transformed into a kinetic equation for the $P_j(t)$:

$$dP_j/dt = \sum_{l(\neq j)} [L_{l \to j}(E)P_l(t) - L_{j \to l}(E) \; P_j(t)] \qquad (3.9)$$

where the L's simply comprise all of the previous rates K that act between the given equivalence classes. The conditions of detailed balance now read

$$L_{j \to l}(E) = [M_\gamma(E)/M_\alpha(E)]^{1/2}B_{jl}(E) \qquad (3.10)$$

where α and γ belong to $C(j)$ and $C(l)$, respectively, and where B_{jl} is symmetric.

The relaxation spectrum defined by the contracted master equation (3.9) is determined by the eigenvalue problem

$$\mathbf{LA} = \Lambda\mathbf{A} \qquad (3.11)$$

in the permutation-symmetric subspace of dimension $\Omega_0 = \Omega/\Omega_p$, where matrix $\mathbf{L}$ is defined by

$$(\mathbf{L})_{jl} = -L_{l \to j}(E) \qquad (j \neq l)$$

$$(\mathbf{L})_{jj} = \sum_{l(\neq j)} L_{j \to l}(E) \qquad (3.12)$$

The real eigenvalues Λ are a subset of the previous set of λ's, including zero of course.

For most properties of interest it suffices to use this contracted statistical description.

IV. Two-Order-Parameter Model

The next goal is to see how the general formalism developed above applies to a specific example. For that purpose we now introduce an artificial but solvable model for packing structures and their kinetic connections in the $3N$-dimensional configuration space. In some respects this model will prove to be too naive, but it does serve to illustrate some important basic aspects of the melting transition, of supercooling, and of glass formation.

We take advantage of the possibility to use the permutation-symmetric contracted description embodied in the probabilities P_j. The numbers of (contracted) packing states that must be considered initially is

$$\Omega_0 \sim \exp(\theta N) \qquad (4.1)$$

It follows from remarks contained in section II that this very large number of states is only sparsely connected by feasible kinetic transitions. Each state in fact can transform only to order N others, through the nonvanishing rates $L_{j \to l}(E)$ in the contracted master equation (3.9).

The vertices of a hypercube in D dimensions and its edges connecting those vertices in pairs offer a convenient geometric basis for the model. By selection of D according to

$$2^D = \exp(\theta N)$$

$$D = \theta N/\ln 2 \qquad (4.2)$$

the hypercube vertices will be equal in number to the distinguishable packing states for the problem in hand. Furthermore, each hypercube vertex has edge connections to exactly D others, which the second of eq 4.2 shows to have the correct order in N. Therefore, our simple model will be selected to involve transitions in the hypercube vertex–edge network.

Hypercube vertices in Cartesian D-space can be placed at the following vector locations:

$$\sigma = D^{-1/2}(\pm 1, \pm 1, ..., \pm 1) \qquad (4.3)$$

Edges connect vertices whose locations differ only by a single sign change among the D vector components. This representation makes it obvious that transitions are equivalent to flips of Ising spins.[8]

A second postulate for the model is that the packing regions for distinct structures are the same in shape near their respective minima, though they can differ in depth. This requires in turn that we commit to a specific form for the potential energy function at each of the distinct packings. We choose one that involves only two orthogonal axes in D space, say those defined by the following unit vectors:

$$\mathbf{u}_x = D^{-1/2}(1,1,...,1)$$

$$\mathbf{u}_y = D^{-1/2}(1,1,...,1,-1,-1,...,-1) \qquad (4.4)$$

Here we have assumed (without essential loss of generality) that D is even, and thus that the first $D/2$ components of $\mathbf{u}_y$ are positive and the rest are negative. These unit vectors point along hypercube diagonals, and for any of the vertices we calculate components x and y in the obvious way:

$$x = \sigma \cdot \mathbf{u}_x \qquad y = \sigma \cdot \mathbf{u}_y \qquad (4.5)$$

Potential energy Φ at the minima by assumption will be just a function of x and y, which can be interpreted as a pair of order parameters for the packings.

Let n be the number of $+1$'s that occur as components (eq 4.3) for a given σ, and let n_1 be the subset of $+1$'s that occur among the first $D/2$ components. Consequently we have

$$x = (2n/D) - 1$$

$$y = (4n_1 - 2n)/D \qquad (4.6)$$

or equivalently

$$n = \frac{1}{2}D(x + 1)$$

$$n_1 = \frac{1}{4}D(x + y + 1) \qquad (4.7)$$

The projections of the 2^D hypercube vertices onto the x,y plane fall within the square

$$|x + y| \leq 1 \qquad (4.8)$$

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(8) Hill, T. L. "Statistical Mechanics"; McGraw-Hill; New York, 1956; Chapter 7.
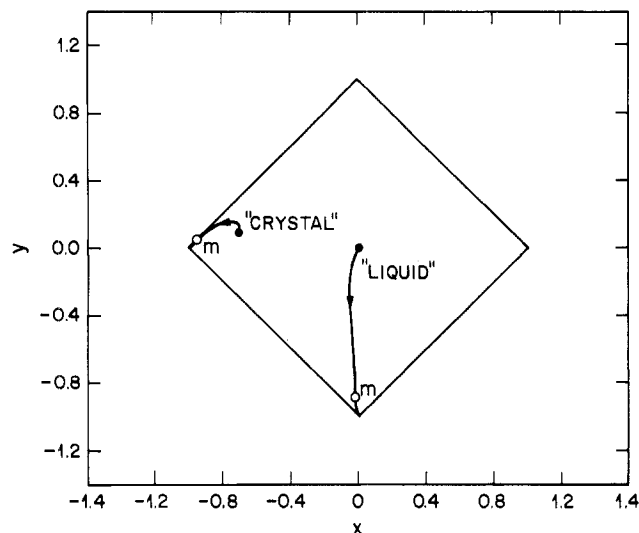
Figure 1. Paths in order-parameter space described by free energy maxima as temperature varies. The directions shown correspond to decreasing temperature (increasing β). Open circles labeled m are the positions at the melting point. The "liquid" curve starts at infinite temperature; the "crystal" curve begins when $\beta \cong 0.34$.

It is straightforward to evaluate $W(n,n_1)$, the number of vertices with given n and n_1:

$$W(n,n_1) = \frac{[(\tfrac{1}{2}D)!]^2}{n_1!(\tfrac{1}{2}D - n_1)!(n - n_1)!(\tfrac{1}{2}D - n + n_1)!} \quad (4.9)$$

Using Stirlings' approximation for factorials and then recasting the result in terms of x and y, this leads to the following expression valid for large D (or N):

$$\ln W \cong Dw(x,y) \quad (4.10)$$

$w(x,y) = \ln 2 - $
$\tfrac{1}{4}[(1 + x + y) \ln (1 + x + y) + (1 + x - y) \ln (1 + x - y) + (1 - x + y) \ln (1 - x + y) + (1 - x - y) \ln (1 - x - y)]$

The specific form selected for the potential at the minima is the following:

$$\Phi(x,y) = D\phi(x,y) \quad (4.11)$$

$$\phi(x,y) = x + y - (x - y + 0.2)^2 + 0.38(x - y + 0.2)^3$$

This function achieves its absolute minimum in the square defined by eq 4.8 at the vertex $x = -1$, $y = 0$:

$$\phi(-1,0) = -1.83456 \quad (4.12)$$

This vertex therefore represents the most ordered state of the system, namely a "defect-free crystal". Any movement away from this point to the interior of the square therefore would involve structural transitions that cause Φ to rise and thus introduce "defects" into the "crystal", and which in the extreme would produce amorphous packings. Two order parameters are needed to describe the packings not only because the number of defects can vary, but also because the way in which they are arranged can vary in respect to their mutual interaction. The algebraic expression 4.11 gives a reasonable concrete form to the interplay of these two independent variables.

Thermal equilibrium at $\beta = 1/k_B T$ involves the free energy maximum in the x,y square region, that is

$$w(x,y) - \beta\phi(x,y) = \text{maximum} \quad (4.13)$$

Locating this maximum for variable β is numerically an easy task. In the small-β regime the maximum is located near $x = 0$, $y = 0$, and as β increases (declining temperature) the position of this maximum moves continuously to the lowest vertex of the square (4.8), at $x = 0$, $y = -1$. However, a second local free energy maximum appears when $\beta > 0.34$; this is the one which continuously moves to the perfect-crystal vertex at $x = -1$, $y = 0$ in the
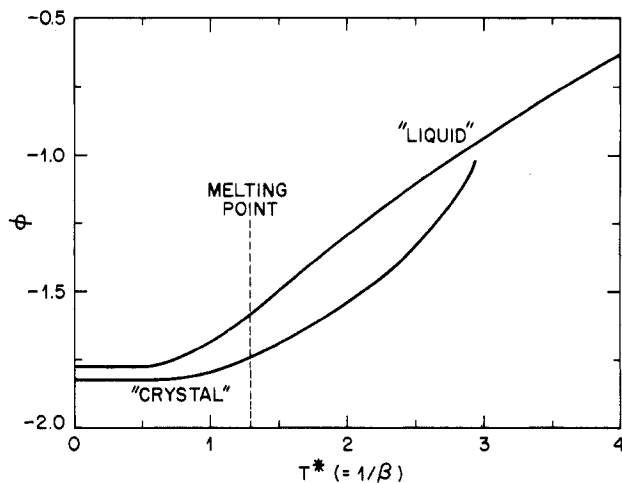

Figure 2. Packing potential energy per particle (ϕ) vs. $T^* = 1/\beta$ for the two free energy maxima.
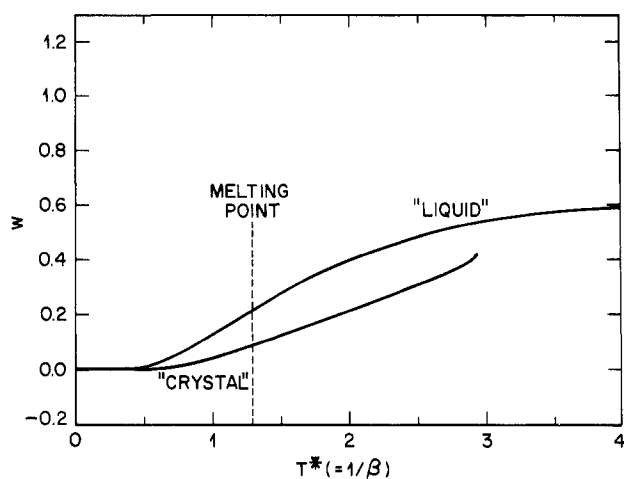

Figure 3. Combinatorial entropy per particle (w) vs. $T^* = 1/\beta$ for the two free energy maxima.

low-temperature limit and which therefore supplies the stable low-temperature phase. On the basis of the relative heights of the two maxima when both exist, it is possible to identify the thermodynamic melting point:

$$\beta_m = 0.773 \quad (4.14)$$

When $\beta < \beta_m$, the former ("liquid state") maximum dominates, but roles interchange when $\beta_m < \beta$.

Figure 1 shows the paths described by the two minima in the square (4.8) as β varies, and shows in particular where the maxima reside at β_m.

Evidently this simple model yields metastable states by following the separate maxima beyond their ranges of dominance. In this fashion both supercooled fluid and superheated crystal states can be identified. The former extends to absolute zero, while the latter disappears when $\beta < 0.34$. The packing potential energy per particle in the limiting low-temperature amorphous state is only slightly higher than that shown earlier (eq 4.12) for the perfect crystal:

$$\phi(0,-1) = -1.78336 \quad (4.15)$$

The ϕ values for the two branches are presented plotted against $T^* = \beta^{-1}$ in Figure 2, where both stable and metastable ranges are shown.

Figure 3 exhibits the combinational entropy quantity w for the two branches, as functions of $T^* = \beta^{-1}$. Both approach zero as T^* goes to zero. For the crystal phase this is no surprise since only one structure survives in that limit. The model predicts as well that the same is true for the low-temperature amorphous phase (local quasi-equilibrium in the x,y space is assumed). In
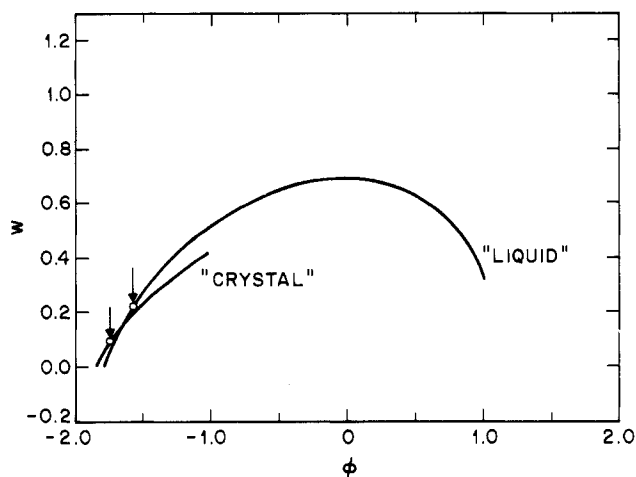
Figure 4. Combinatorial entropy per particle (w) vs. potential energy per particle (ϕ). Arrows locate the relevant coexisting positions at melting.

other words, for this model there is in principle just one optimal amorphous packing of lowest potential energy that survives as T^* approaches absolute zero. Such behavior is subject to continuing discussion in the theory of glasses.[9]

Figure 4 combines results in Figures 2 and 3, showing w vs. ϕ for the two branches. This type of "density of states" function plays a prominent role in the general equilibrium theory of natural packing structures,[1,3,5] and as has been observed before[2,4,5] it is skewed toward the low-ϕ side of its maximum.

V. Fokker–Planck Equation

Just as the potential energy function Φ has been assumed to depend only on the two order parameters x and y, we now add a corresponding postulate for the symmetric matrix $\mathbf{B}_{jl}$:

$$B_{jl}(E) = B(x_{jl}, y_{jl}, E) \qquad (5.1)$$

$$x_{jl} = \tfrac{1}{2}(x_j + x_l) \qquad y_{jl} = \tfrac{1}{2}(y_j + y_l)$$

Because transitions between pairs of states with slightly different x and y values are involved, we suppose simply that these coefficients depend on the mean values of those parameters for the two states.

It can readily be demonstrated that the detailed-balance expression 3.10 leads to

$$L_{j\rightarrow l}(E) = \exp[(\Phi_j - \Phi_l)/2k_B T(E)]B_{jl}(E) \qquad (5.2)$$

where Φ_j and Φ_l are the values of Φ at the respective minima. The temperature $T(E)$ appearing here is the one appropriate for total energy E at thermal equilibrium. The goal now is to use this expression to convert the contracted master equation (3.9) eventually into a kinetic equation in the two-dimensional x,y order-parameter space.

A given hypercube vertex at x,y or equivalently at n,n_1 (see eq 4.7) is connected to D others only of the types $(n-1,n_1-1)$, $(n-1,n_1)$, $(n+1,n_1+1)$, and $(n+1,n_1)$. After accounting for the respective numbers of each type, eq 3.9 simplifies to the following:

$$B^{-1}(dP(n,n_1)/dt) =$$
$$(\tfrac{1}{2}D - n_1)\{\exp[\tfrac{1}{2}\beta\Delta(1,1)]P(n+1,n_1+1) -$$
$$\exp[-\tfrac{1}{2}\beta\Delta(1,1)]P(n,n_1)\} + (\tfrac{1}{2}D - n +$$
$$n_1)\{\exp[\tfrac{1}{2}\beta\Delta(1,0)]P(n+1,n_1) - \exp[-\tfrac{1}{2}\beta\Delta(1,0)]P(n,n_1)\} +$$
$$n_1\{\exp[\tfrac{1}{2}\beta\Delta(-1,-1)]P(n-1,n_1-1) -$$
$$\exp[-\tfrac{1}{2}\beta\Delta(-1,-1)]P(n,n_1)\} +$$
$$(n - n_1)\{\exp[\tfrac{1}{2}\beta\Delta(-1,0)]P(n-1,n_1) - \exp[-\tfrac{1}{2}\beta\Delta(-1,0)]P(n,n_1)\}$$
$$(5.3)$$

This expression incorporates the potential energy increment symbol

$$\Delta(k,l) = \Phi(n+k,n_1+l) - \Phi(n,n_1) \qquad (5.4)$$

for the transitions. Its derivation also supposes that B can be taken as locally constant over the D edges emanating from the given vertex.

As it is written, eq 5.3 does not typographically distinguish between any of the W vertices with given n,n_1. Under the assumption that these are all indistinguishable and have equal probabilities it suffices to examine the set of quantities

$$Q(n,n_1) = W(n,n_1) \, P(n,n_1) \qquad (5.5)$$

which are the net probabilities that the system inhabits any one of the W vertices with fixed n and n_1. Equation 5.3 can then trivially be converted to a Q equation:

$$B^{-1}(dQ(n,n_1)/dt) = (n_1 + 1) \exp[\tfrac{1}{2}\beta\Delta(1,1)]Q(n+1,n_1+1) +$$
$$(n - n_1 + 1) \exp[\tfrac{1}{2}\beta\Delta(1,0)]Q(n+1,n_1) + (\tfrac{1}{2}D - n_1 + 1)$$
$$\exp[\tfrac{1}{2}\beta\Delta(-1,-1)]Q(n-1,n_1-1) + (\tfrac{1}{2}D - n + n_1 + 1)$$
$$\exp[\tfrac{1}{2}\beta\Delta(-1,0)]Q(n-1,n_1) - \{(\tfrac{1}{2}D - n_1) \exp[-\tfrac{1}{2}\beta\Delta(1,1)] +$$
$$(\tfrac{1}{2}D - n + n_1) \exp[-\tfrac{1}{2}\beta\Delta(1,0)] +$$
$$n_1 \exp[-\tfrac{1}{2}\beta\Delta(-1,-1)] + (n - n_1) \exp[-\tfrac{1}{2}\beta\Delta(-1,0)]\}Q(n,n_1)$$
$$(5.6)$$

The time-independent solution Q_{eq} to eq 5.6 will be essentially Gaussian and should vary slowly on the n,n_1 scale near its maximum. This follows from the expectation that fluctuations should be proportional to $D^{1/2}$ in magnitude. Under this circumstance it becomes legitimate to pass to a continuum representation in x and y, and the finite differences appearing in eq 5.6 can be handled by second-order Taylor's expansions. In this manner it is possible to show that eq 5.6 is satisfied by

$$Q_{eq}(x,y) = C \exp\{-D[E_{11}(\Delta x)^2 + E_{12}\Delta x\Delta y + E_{22}(\Delta y)^2]\}$$

$$\Delta x = x - x_m(\beta) \qquad \Delta y = y - y_m(\beta) \qquad (5.7)$$

where C is a normalizing constant, x_m and y_m are the β-dependent solutions of the free energy maximum equation (4.13), and where

$$E_{11} = \frac{1}{4}\left[\frac{1}{1 - (x_m + y_m)^2} + \frac{1}{1 - (x_m - y_m)^2}\right] + \tfrac{1}{2}\beta\phi_{xx}$$

$$E_{12} = \frac{1}{2}\left[\frac{1}{1 - (x_m + y_m)^2} - \frac{1}{1 - (x_m - y_m)^2}\right] + \beta\phi_{xy}$$

$$E_{22} = \frac{1}{4}\left[\frac{1}{1 - (x_m + y_m)^2} + \frac{1}{1 - (x_m - y_m)^2}\right] + \tfrac{1}{2}\beta\phi_{yy} \qquad (5.8)$$

These last expressions involve the second partial derivatives of ϕ with respect to the order parameters.

Time-dependent states not too far displaced from equilibrium should also possess Q's that vary slowly over many contiguous vertices. Consequently quadratic Taylor expansions are again applicable to the kinetic equation (5.6). A lengthy sequence of manipulations then produces the following partial differential equation for Q:

$$\partial Q/\partial t = -\nabla \cdot [(\mu \cdot \mathbf{F})Q] + \beta^{-1}\nabla \cdot (\mu \cdot \nabla Q) \qquad (5.9)$$

where ∇ acts in the x,y space, and where μ is a symmetric mobility tensor and $\mathbf{F}$ is a mean force vector in this space. These latter have the following specific forms:

$$\mu_{xx} = \mu_{yy} = \beta BD^{-2}\{[1 - (x + y)^2]^{1/2} + [1 - (x - y)^2]^{1/2}\}$$

$$\mu_{xy} = \beta BD^{-2}\{[1 - (x + y)^2]^{1/2} - [1 - (x - y)^2]^{1/2}\} \qquad (5.10)$$

$$F_x = -\beta^{-1}D(2E_{11}\Delta x + E_{12}\Delta y)$$

$$F_y = -\beta^{-1}D(E_{12}\Delta x + 2E_{22}\Delta y) \qquad (5.11)$$

Equation 5.9 is a Fokker–Planck equation[10] that describes probability flow in the x,y space under the combined influence

(9) DiMarzio, E. A. *Ann. N.Y. Acad. Sci.* **1981**, *371*, 1.

(10) Wang, M. C.; Uhlenbeck, G. E. *Rev. Mod. Phys.* **1945**, *17*, 323.

of a thermodynamic driving force (first term in the right member), and diffusion in that order-parameter space (second term in the right member). Notice that the force defined by eq 5.11 is β^{-1} times the gradient of the exponent appearing in Q_{eq}, eq 5.7; it clearly contains contributions both of combinatorial (entropic) origin as well as of interaction potential origin.

The relaxing solutions to Fokker–Planck equation 5.9 can be constructed in terms of appropriate combinations of harmonic oscillator wave functions (Hermite functions). On account of the anisotropy of the mobility tensor μ this involves technical details whose discussion is unnecessary for present purposes. Instead it suffices to notice that relaxation rates will essentially be controlled by mobility, which eq 5.10 reveals to have two important factors in all components: (1) symmetric transmission coefficient $B(x,y)$; (2) hypercube embedding dimension, as D^{-2} or equivalently θ^{-2} (see eq 4.2). Any realistic assignment of a form for B as a function of x,y, and E (or T) would account for the finite potential barrier heights that must be surmounted to effect transitions, and if these were to be especially large relative to $k_B T$ in the neighborhood of the "amorphous" square vertex at $x = 0$, $y = -1$ in Figure 1 a glass transition with diverging relaxation times would ensue. That an inverse power of θ is involved in mobility merely indicates that with fewer packing structures the transitions would tend to move the system farther in its configuration space; but of course this in turn would influence B as well.

VI. Discussion

The simple hypercube model utilizing just a pair x,y of order parameters exposes to view some of the basic aspects of equilibrium and of structural relaxation toward equilibrium. But it is clearly deficient in several ways. Most obvious perhaps is that phase coexistence is not properly described. Under constant-pressure conditions it should be possible to have (in the usual thermodynamic limit) arbitrary amounts of "crystal" and "liquid" simultaneously present. There should correspondingly be a pathway in Figure 1 connecting the two points labeled m with essentially constant free energy per particle. Conceivably some a posteriori modification of the interaction potential $\phi(x,y)$ exists which would effect such a change while leaving the pure-phase branches essentially as shown.

The phenomena associated with phase nucleation are closely related to this coexistence requirement. In particular classical nucleation theory[11] stresses the importance of localized heterophase fluctuations for the kinetics of macroscopic phase change, and these would have associated with them corresponding sets of natural packing structures. To incorporate such distinguished packings into the theory would probably necessitate a larger number of order parameters, perhaps even an infinite number. In any case it should still be possible to extract a Fokker–Planck equation for relaxation in the expanded order-parameter space, *including* relaxation into an alternate, more stable, phase via nucleation.

In the interests of realism it is also desirable to account for local variations in transmission rates B_{jl}. Specifically this can produce a strongly anisotropic mobility tensor μ. Accounting simultaneously for such anisotropy and for a large number of order parameters may hold the key to a successful comprehensive theory of the glass transition.

The simple model proposed in this paper is perhaps significant less for its own virtues than for the exciting extensions it suggests.

(11) Turnbull, D. *Solid State Phys.* **1956**, *3*, 225.