Rate equations for cluster formation in supercooled liquids.

V. Halpern

Department of Physics, Bar-Ilan University, 52900 Ramat-Gan, Israel
E-mail: halpern@mail.biu.ac.il

The formation of clusters in supercooled liquids close to the glass transition temperature is described by rate equations in which the coefficients are determined on physical grounds rather than in terms of thermodynamic quantities such as free energies and surface tensions. In particular, the density of free molecules in the liquid as a function of temperature is determined self-consistently. Calculations for a very simple model indicate that such rate equations are capable of producing physically reasonable results. Our results suggest that the difference between strong and fragile liquids may be associated with the strength of the binding of a surface molecule to a cluster, and they also provide indications about the nature of the glass transition and the structure of the resulting glass.

I. INTRODUCTION

The slowing down of molecular rearrangement processes in supercooled liquids as the temperature is reduced, until the system effectively freezes into a glass (i.e. a non-crystalline solid) at the glass transition temperature $T_g$, is a phenomenon common to a very wide range of materials, from the common silicate glasses used in windows to natural and artificial polymers. The variety of unusual features found experimentally in these materials have been the subject of several recent reviews [1] [2] [3], as have the variety of theories proposed to account for them [4]. Most of these theories are of a general nature, because they have to account for features observed in so many very different materials. One of the most successful of them, which only assumes the existence of non-linear interactions between density fluctuations, is mode coupling theory (MCT) [5]. However, the original version of MCT ignores the possibility of thermally excited processes, and predicts that the system undergoes a phase transition into a frozen state at a temperature $T_x$ that is much higher than $T_g$. While MCT has been extended to include thermally activated processes that enable this freezing to be avoided, and so to describe the behavior of the system at temperatures between $T_x$ and $T_g$, these extensions involve specific assumptions about the types of activated process and so are no longer so general. Numerous other types of general theory have been advanced to describe the behavior of supercooled liquids in this temperature range. Most of these involve the use of thermodynamics, which is quite natural since this is a general framework, and in particular because one of the main unusual features of the glass transition is the behavior of the system’s entropy as the liquid is cooled towards $T_g$ [2]. However, a major problem in many of these theories is to relate the assumptions that they use to the molecular structure of the different supercooled liquids and the microscopic properties associated with them.

In this paper we describe an alternative approach to the problem of the glass transition, in terms of the rate equations for the formation of solid-like clusters of molecules in the supercooled liquid. There is considerable experimental evidence for the existence of such clusters, which cause the system to be inhomogeneous on certain length and time scales [6], and they are also postulated in many theoretical approaches [4]. However, not much attention is usually paid to the dynamics of the formation and dissociation of such clusters, which in general can be described by rate equations. Rate equations are well known in the theory of the nucleation of liquid-like droplets in a vapor and of crystallites in a normal liquid, where it is usually described by classical nucleation theory [7] [8]. It is also widely used in the theory of the nucleation and growth of thin films on a substrate [9]. In both these cases, the calculation of the rate constants for the growth and decay of clusters involves well-defined thermodynamic concepts such an expression for the difference in the free energy between the two phases, their chemical potentials and the surface tension of the interfaces between them. A number of authors, including Xia and Zinke-Allmang [10] henceforth referred to as XZ, have used a similar approach involving free energies and surface tensions. However, in a supercooled liquid it may not be possible to define such properties, or even if one does define them to relate them to those of the crystalline solid and the normal liquid. One problem is that the temperature dependence of the density of free molecules (which presumably correspond to those of a normal liquid) is determined by the self-consistent solution of the rate equations, which makes the definition of the chemical potential of the liquid quite problematic. This point is totally ignored in classical nucleation theory, and is not relevant for film growth on a substrate where the free molecules (or atoms) are deposited at a constant rate. Another possible problem with the use of these thermodynamic quantities is the very irregular shapes of the clusters, as found in molecular dynamics simulations [11], which certainly do not correspond to minima of the free energy in a classical picture. Accordingly, we formulate here a very general approach to the rate equations for the growth and dissociation of such clusters, and consider some of their consequences. In principle, such
a theory can describe not only the structural properties of the system but also its dynamic properties, such as the frequently observed non-exponential relaxation with time of correlation functions, the dielectric response, and similar features. However, in the initial analysis presented in this paper, we consider mainly the structural properties.

The starting point of our approach is to postulate growth and decay rates for clusters of molecules, without relating them in advance to the thermodynamic potentials, and examine how their behavior influences the properties of the system. In this paper, for the sake of simplicity we restrict our analysis to the growth and decay of clusters one molecule at a time. The rate of attachment of molecules to clusters is assumed to be proportional to the density of single molecules, which it is convenient to refer to as monomers. This is essentially a mean field approximation, and ignores the possible existence of depletion zones around the clusters [9] and the effects of density fluctuations. The process of detachment of monomers from a cluster is thermally activated, involving the breaking of the bonds between a molecule on the surface of a cluster and the other molecules of the cluster. A key novel feature of our approach, as noted above, is that the monomer density (which is determined by or determines the chemical potential of the liquid), is calculated self-consistently rather than postulated. In section 2, we present the rate equations for the system for discrete cluster sizes, and their solution for the steady state of an extremely simple model. Such a steady state involves the dependence of the monomer concentration and that of clusters of different sizes on the attachment and detachment parameters, and so the temperature dependence of these provides valuable information about how the steady state properties of the system change with temperature. In the process of our analysis, a fundamental difficulty is discovered in the continuum approximation used by XZ [10] to treat large clusters, which is discussed in the Appendix. The results of our calculations are presented in section 3, and in section 4 we discuss their significance and implications. In particular, our analysis naturally leads to the model of glass structure recently proposed by Stachurski [12] of a “maximum random jamming” state, with small number of “rattler” particles between them, rather than random close packing to describe structures of ideal amorphous solids. A summary of our results and conclusions is presented in section 5.

II. THE RATE EQUATIONS AND THEIR STEADY STATE SOLUTION.

In a supercooled liquid, the total concentration of molecules is constant, in contrast to the situation for thin film growth. Hence the most useful form of the rate equations seems to be that of XZ [10], and we use their formulation, but with a somewhat different notation. Let \( n_0 \) be the total density of molecules, \( n_j \) the density of clusters of \( j \) molecules, and let \( A_j n_1 \) be the rate of single molecule attachment to and \( R_j \) the rate of detachment or release of single molecules from a cluster of \( j \) molecules. If such clusters can have a variety of shapes, the coefficients \( A_j \) and \( R_j \) are suitably weighted averages. Then the basic rate equations are

\[
dn_1/dt = -2A_1n_1^2 + R_2n_2 + \sum_{j=2}^{n_0} (R_j - A_j n_1) n_j, \tag{1}
\]

where the term \( R_2n_2 \) arises from fact that dissociation of a dimer produces 2 monomers, while the dissociation of a larger cluster produces only one monomer, and

\[
dn_j/dt = n_1 (A_{j-1}n_{j-1} - A_j n_j) + (R_{j+1}n_{j+1} - R_j n_j) \tag{2}
\]

In addition, in our mean field approximation the total density of molecules in the system is fixed, so that

\[
\sum_{j=1}^{n_0} j n_j = n_0 \tag{3}
\]

In view of this equation, equation (1) must follow from the sum for \( j > 1 \) of \( j (dn_j/dt) \) as given by equation (2), a point that is readily checked and makes it unnecessary to use equation (1).

While the continuum approximation discussed in the Appendix may be needed for analyzing the growth and decay of clusters, for the steady state solution it is simpler (and also more accurate) to use the exact equations (2)-(3). In order to obtain qualitative ideas of how the solution behaves, we consider the case where \( A_j \) and \( R_j \) both depend on \( j \) only through the surface area \( g_j \) of a cluster of \( j \) molecules (which could be a reasonable approximation for large clusters) and ignore the fact that clusters containing the same number of molecules may have different shapes and so different surface areas and binding energies of the surface molecules. Thus, we write

\[
A_j = A_0 g_j, \quad R_j = R_0 g_j, \quad j \geq j_0. \tag{4}
\]
It is convenient to write

\[ g_j n_j = f_j, \]

so that equation (2) for the steady state can be written in the form

\[ n_1 A_0 (f_{j-1} - f_j) + R_0 (f_{j+1} - f_j) = 0, \quad j \geq j_0 + 1 \]  

Equation (6) is a simple second order linear difference equation for \( f_j \), the general solution of which is

\[ f_j = c_1 z_1^j + c_2 z_2^j, \]

where \( z_1 \) and \( z_2 \) are the roots of

\[ R_0 z^2 - (R_0 + n_1 A_0) z + n_1 A_0 = (z-1)(R_0 z - n_1 A_0) = 0 \]

The root \( z = 1 \) leads to \( n_j = c/g_j \), which leads to the divergence of the sum in equation (3) unless \( \lim_{j \to \infty} (g_j/j^2) > 0 \), and this is obviously impossible. Hence the only solution of interest is

\[ f_j = cz_0^j, \quad z_0 = (A_0/R_0)n_1 \equiv bn_1 \]

For convenience, we assume that

\[ g_j = B_0 j^\alpha, \]

and extend the sum in equation (3) to \( \infty \), which is justified since this sum then converges for \( 0 < z_0 < 1 \) according to the ratio test. In view of the definition of \( g_j \) in equation (4), we can choose \( B_0 = 1 \).

In the simplest (but totally unrealistic) case that equation (4) holds for all \( j \geq 1 \), it follows from equation (3) that \( z_0 = bn_1 \) is the root of the equation

\[ \sum_{j=1}^\infty j^{1-\alpha} z_0^j = n_0, \]

subject to the condition that \( z_0 < 1 \), i.e. \( bn_1 < 1 \). Moreover, since by definition the number of isolated molecules is also the number of clusters of single molecules, \( n_1 = f_1 = cz_0 = c(bn_1) \), and so \( c = 1/b \). Hence, finally, in this case \( n_1 \) is the root of the transcendental equation

\[ \sum_{j=1}^\infty j^{1-\alpha} (bn_1)^j = bn_0 \]

Intuitively, one expects that the exact values of \( A_j \) and \( R_j \) for small values of \( j \) will not affect the qualitative behavior of the results. In order to test this hypothesis, we performed calculations for the above system, which we call system 1, and for system 2 in which equation (4) is not assumed to be valid for dimers, so that \( j_0 = 3 \). Since the thermally activated dissociation of a dimer only involves the breaking of one bond, while the release of a molecule from a trimer usually involves the breaking of two bonds, we chose the activation energy of \( R_2 \) to be half that of \( R_0 \), and wrote \( A_2/R_2 = \sqrt{(A_0/R_0)} \), while since a monomer has only one site for attachment and a dimer has two sites we chose \( A_1 = A_0 \) and \( A_2 = 2A_0 \). After simple calculations, we then find that \( n_j = c(bn_1)^j \) for \( j \geq 3 \), \( n_2 = (\frac{3}{2}b) n_1^2 \), and \( c = b^{-1.5} \), and also adjust accordingly the first two terms in the sum in equation (11).

III. RESULTS OF THE CALCULATIONS

In order to understand the physical significance of the results of our calculations, before presenting them we consider the temperature dependence of the parameters \( A_0 \) and \( R_0 \), and hence of the parameter \( b \), which determines the value of \( n_j/n_0 \). The release of a molecule from a cluster requires the breaking of bonds between it and the remaining molecules in the cluster, and so is expected to be a thermally activated process. Hence \( R_0 \) should depend exponentially on the temperature \( T \), and we write \( R_0 = R_{00} \exp[-E_a/(kT)] \). The addition of a molecule to a cluster, on the other hand, will often be controlled by diffusion [8], with a very weak intrinsic temperature dependence (although it may well be affected by the temperature-dependent cluster density), and even if it does require some thermal activation the energy required is far less than that required to detach a molecule from the cluster. Thus, to the order of approximation inherent in our very simple model systems, we can assume that
with a positive activation energy $E_0$, so that an increase in the parameter $b$ corresponds to a decrease in the temperature $T$.

The results that we report are all for $n_0 = 1$, and for $\alpha = 2/3$, which is the appropriate value for spheres in three dimensions; the exact value of $\alpha$ does not affect the qualitative behavior of the results. In figure 1, we show the value of $n_1$ as a function of $\log(b)$ for the two systems. The main point to notice is that for both systems $n_1$ decreases as $b$ increases, which corresponds to a decrease in the concentration of monomers as the temperature is lowered. For system 2, the value of $n_1$ is lower than in system 1 for $b < 1$ and higher than in system 1 for $b > 1$, because here $A_2/R_2 = \sqrt{(A_0/R_0)} = \sqrt{b}$, which is larger than $b$ for $b < 1$ and less than $b$ for $b > 1$, while as noted above an increase in $b$ leads to a decrease in $n_1$. The difference is greatest for the low values of $b$ because in this region dimers are of greater importance. As can be seen clearly in figure 2, in which the results of figure 1 are replotted on a double logarithmic scale, the decrease in $\log(n_1)$ with increasing $b$ for $b > 5$ is linear in $\log(b)$, so that in view of equation (12) in this region $n_1 = n_{10} \exp[-E_1/(kT)]$, and a least squares fit shows that $E_1$ is virtually the same as $E_0$. For both systems we find that this exact exponential decrease occurs when $n_1 < 0.2$, while the decrease is nearly exponential from $b = 1$, where $n_1 = 0.46$ and 0.47 for systems 1 and 2 respectively. For lower values of $b$, $n_1$ decreases much more slowly as $1/T$ increases.

A much more interesting difference between systems 1 and 2 is with regard to the cluster size $j_{\text{max}}$ containing the largest number of molecules. The value of $j_{\text{max}}$ is given by the maximum of $j n_1$, i.e. of $j^{1-\alpha} z_0^\alpha$, which occurs at $j = (1 - \alpha)/\ln(1/z_0)$, where $z_0 = b n_1$. We find that for system 1 $j_{\text{max}} = 3$ when $b = 14$ and $n_1 = 0.065$, and $j_{\text{max}} = 10$ when $b = 80$ and $n_1 = 0.012$, while for system 2 the corresponding values are $b = 6.3$, $n_1 = 0.14$ and $b = 20$, $n_1 = 0.05$ respectively. While in both cases the values of $n_1$ are much too small to be realistic, the appearance of clusters of a given size at appreciably larger values of $n_1$ for system 2 than for system 1 indicates that our general physical picture is reasonable, so that more realistic descriptions of the size dependence of the accretion and removal rates of particles should lead to physically meaningful results.

Finally, we consider the temperature dependence of the system’s configurational entropy. For monomers, this should correspond to that $S_l$ of molecules in the liquid, while for molecules within clusters it should as a first approximation be zero, as for molecules in the solid, but for molecules on the surface of a cluster it should have an intermediate value $S_{\text{surf}}$. Accordingly, we write for model 1

$$S = n_1 S_l + a \left( \sum_{j=2}^{\infty} j^{\alpha} n_j \right) S_{\text{surf}}$$

(13)

where $a$ is a geometrical factor. Since $j^{\alpha} n_j = f_j = z_0^\alpha/b$, it follows that

$$S = n_1 S_l + a S_{\text{surf}} z_0^2 / (b - b_0)$$

(14)

In figure 3 we show the contribution to the configurational entropy from the molecules on the surfaces of the clusters, and the total entropy for the arbitrary choice of $a S_{\text{surf}} = S_l/3$, as a function of $\log(b) = \log(b_0) + E_0 \log(e)/(kT)$. As can be seen, the decrease of the configurational entropy with decreasing temperature (increasing $b$) is qualitatively similar to that which is observed experimentally. Also, at low temperatures (large $b$) the main contribution to this entropy comes not from the small number of monomers but rather from the molecules on the surfaces of the clusters.

IV. DISCUSSION

While the model presented above is obviously far too simple to represent any real system, it does indicate various trends that are physically plausible and worthy of detailed investigation using suitable extensions of our models. The first of these regards the approach to the glass transition in supercooled liquids. Here, our results show the crucial role played by the parameter $b$, which is the ratio of the attachment rate to a cluster per monomer around it to the rate of detachment of the molecule from the cluster. We found that for small values of $b$ the monomer concentration is not very sensitive to its value, but for large values of $b$ it decreases rapidly as $b$ increases. Physically, the reason for this is that large values of $b$ correspond to the molecules on the surface of a cluster being strongly bound to it, so that the formation of clusters permanently depletes the monomer population, and the temperature dependence of the detachment rate dominates the value of $b$. For weakly attached surface molecules, on the other hand, the reduction of the diffusion rate of monomers as the temperature is lowered and the cluster density increases will have a much larger effect on the temperature dependence of the parameter $b$, which will become non-exponential as a result. Since a non-Arrhenius temperature dependence is typical of fragile glasses, this suggests that the distinction between strong
and fragile glasses may be related to whether the molecules on the surface of a cluster are strongly or weakly bound to the cluster.

While our model does not directly consider the viscosity of the system, which is a dynamic rather than a structural property, since it does determine the cluster density it could be used to determine the viscosity in conjunction with cluster models for this, such as that of Fan and Fecht [13], without making their assumptions about the free energies of the clusters as they do. Similarly, our model can account for the observed rapid transition of particles from fast states, corresponding to free molecules, to slow states corresponding to bound ones that is observed experimentally [6]. This transition also has a strong effect on the dielectric response of the system, since in a correct treatment of the dielectric response and relaxation functions [14] the greater response of free molecules to an applied field plays an important role.

Finally, our analysis strongly supports the models of Bakai [15] and Stachurski [12], without their assumptions about the thermodynamic potentials, that the transition from a supercooled liquid to a glass occurs when the solid clusters coalesce or combine with each other and jam, forming a system in which free molecules can no longer percolate. Such coalescence can also explain the strange shapes of clusters found in molecular dynamics simulations [11]. While the coalescence of clusters is of vital importance for properties of the system such as viscosity, correlation lengths and slow modes, such a coalescence as a result of the proximity of a pair clusters or the growth or a bridge between them will often only lead to only a small change in the attachment and detachment rates of monomers, so that it should be sufficient to use the rate equations for small clusters.

V. CONCLUSIONS

In this paper, we proposed that the densities of clusters of different sizes in a supercooled liquid be calculated from the steady state solution of rate equations rather than from postulated values of the thermodynamic potentials or free energies and the surface tensions. The advantage of such an approach is that the values of the attachment and detachment coefficients appearing in the rate equations can be given a simple physical significance, and it should be possible to relate them to the elementary properties of the molecules in the system. Our calculations for a very simple model shows that the rate equations are capable of giving qualitatively reasonable results, so that it is worthwhile to use them to study more sophisticated models and time-dependent properties. One consequence of our approach is that it is not necessary to assume that large cooperatively rearranging regions appear as an entirely new phenomenon near the glass transition temperature, since the temporary coalescence of small clusters can give rise to such domains. Moreover, according to this approach the glass transition occurs when the density of clusters is so large that they can no longer move independently, i.e. when their motion is jammed.

VI. APPENDIX - THE CONTINUUM APPROXIMATION

For treating clusters containing a large number of molecules in supercooled liquids, XZ [10] proposed replacing the discrete index \( j \) for \( j > 2 \) by the continuous variable \( x \), and replacing the second order difference equation (3) in \( j \) by a first order differential equation in \( x \),

\[
\frac{d}{dt}n(x,t) \approx -n_1(t)\frac{\partial}{\partial x}[A(x)n(x,t)] + \frac{\partial}{\partial x}[R(x)n(x,t)]
\]

(A1)

A basic problem with the above continuum approximation is that in the steady state equation (A1) becomes

\[
n_1(d/dx)[A(x)n(x)] = (d/dx)[D(x)n(x)], \quad x \geq 3
\]

(A2)

The solution of this equation is \( n_1A(x)n(x) = D(x)n(x) + c \), and since \( n(x) \to 0 \) as \( x \to \infty \) one expects that \( c = 0 \), in which case \( n_1A(x) = D(x) \). This solution corresponds to the root \( z = 1 \) in our exact analysis, which as we saw is physically untenable. Hence, a better continuum approximation is required, and this can be obtained by writing down the difference between equation (2) for \( j \) and \( j + 1 \)

\[
(d/dt)(n_{j+1} - n_j) = -n_1(A_{j+1}n_{j+1} + A_{j-1}n_{j-1} - 2A_jn_j) + (D_{j+2}n_{j+2} - D_jn_j - 2D_{j+1}n_{j+1})
\]

(A6)

and then applying the continuum approximation. For the time-dependent equation it gives a non-linear partial differential equation of second order in \( x \) and first order in \( t \), which has to be solved together with an equation for the conservation of particles which involves integrals of the solution. For the steady state, the continuum equation corresponding to this is
\[ n_1 \left( \frac{d^2}{dx^2} \right) [A(x)n(x)] = \left( \frac{d^2}{dx^2} \right) [D(x)n(x)], \quad x \geq 3 \tag{A7} \]

with a solution \( n_1 \left( \frac{d}{dx} \right) [A(x)n(x)] = \left( \frac{d}{dx} \right) [D(x)n(x)] + c \), which is more promising, even if \( c = 0 \) for the same reasons as previously, since its solution need not contradict the equation for particle conservation. In fact this solution corresponds to the root \( z_0 = (A_0/R_0)n_1 \equiv b_{n_1} \) in our exact analysis, which as we saw was the physically correct one. Hence the approximation of XZ of replacing the exact rate equations by continuum equations involving only first derivatives in the cluster size does not seem to be justified.

Captions for figures

Figure 1: The density \( n_1 \) of free molecules (monomers) as a function of log(\( b \)). The full curve is for system 1, and the broken curve for system 2.

Figure 2. The logarithm of the density of free molecules (monomers) log(\( n_1 \)) as a function of log(\( b \)). The full curve is for system 1, and the broken curve for system 2.

Figure 3. The entropy \( S \) of the system, for \( S_{surf} = S_1/3 \) (full curve) and \( S_{surf} \) (broken curve) as functions of log(\( b \)).
\[ \log(n) \]
