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A UNIFIED THEORY OF MELTING
CRYSTALLIZATION AND GLASS FORMATION

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1. Introduction. — The purpose of this paper is to describe a model which provides a unified view of the phenomena of melting and glass formation, and to document supporting evidence culled from a variety of other phenomena some of which are not normally linked with either of these processes. The model is described in the next section, and the section following that is devoted to a review of pertinent data from several phenomena which, when suitably extrapolated, is found to have a bearing on the value of the glassy and liquid states. There then follows a discussion of those aspects of nucleation theory that are germane to...
the problem, and finally a description is given of a two-dimensional computer simulation of the rapid quenching of a liquid which illustrates some of the main points of the model.

The central and unifying idea of the model is that dislocations are implicated in melting and that the dislocation concept, in a generalized form, is valid in both the liquid and glassy states. Theories linking dislocations to the melting transition have appeared at various times in the literature during the last forty years. Mott and Gurney [1] suggested that liquids are essentially polycrystalline solids in which the grain diameter is no larger than a few interatomic spacings. Because grain boundaries can be regarded as arrays of dislocations, the Mott-Gurney picture of a liquid is equivalent to one of a crystal saturated with dislocations, Mizushima [2], Siol [3] and Ookawa [4] have subsequently enlarged on the idea that melting occurs by the spontaneous generation of dislocations. Kuhlmann-Wilsdorf [5] has developed that theory to the point that quantitative agreement is obtained with experiment, and has proposed a specific dislocation configuration consisting of dipoles. Kotze and Kuhlmann-Wilsdorf [6] have explored the possibility that the dislocation concept is applicable to the liquid state by showing that the pair distribution function changes from that of a crystal to that of a liquid if a sufficiently large number of dislocations are present. Although there has as yet been no experimental confirmation of the implication of dislocations in melting, computer simulations of the transition in both two-dimensional [7] and three-dimensional [8], [9], [10], [11] close-packed crystals have shown the predicted spontaneous dislocation generation. These computer models also give the correct change in volume, energy and entropy and they correctly predict the melting point.

Gilman [12] has discussed the possibility of describing the viscous flow of glasses in terms of dislocation motion. He finds that dislocations in a glass would be unlike those encountered in crystals in that the Burgers vector would not be constant along the individual dislocation lines. Apart from this generalization, however, the theory of the strain rate follows the same principles as in crystals and good agreement with experiment is obtained.

Dislocations have thus been linked, theoretically at least, to melting, to the liquid state, and to the glassy state. This is consistent with the fact that a glass is produced by supercooling a liquid. Moreover, the generalization to a variable Burgers vector might be expected to occur at a saturation density of dislocations, when the strain fields of the individual dislocations overlap considerably.

2. The model. — The central idea of this communication is that the concept of the dislocation, with suitable generalizations, provides a valid and viable method of describing the disorder present in both liquids and glasses. Evidence for the implication of dislocations in melting has already been cited. It is found that this phase transition is accompanied by the spontaneous generation of dislocation dipoles and that the concentration of these, when the transition is complete, is such that adjacent dislocation cores are mutually contiguous. It is debatable whether the liquid should therefore be described as a crystal saturated with dislocation cores. This is because the term core refers to the central part (with a diameter of three or four Burgers vectors) of a dislocation which is considerably larger in total extent, the region outside the core being crystalline material in which the strain does not exceed the elastic limit. In the above-outlined view there is no such crystalline material beyond the core because of the extremely high dislocation density. It might therefore be more appropriate to refer to the liquid state as corresponding to a saturation density of pseudodislocations, the defining characteristic of the latter being the familiar more open central region just as with the ordinary dislocation. The volume change on melting is quantitatively accounted for by the introduction of the dislocations, as has already been cited, while the sharp drop in viscosity (typically by a factor of $10^{17}$ or so) is explained by the high mobility of the pseudodislocations. (One can regard the relatively open regions at the centers of the pseudodislocations as being instantaneous concentrations of the free volume.) In the liquid the pseudodislocations are in a constant state of motion and they are constantly impinging upon one another and interacting to form new pseudodislocations. It is important to note here that it is possible to retain something of the idea of positive and negative dislocations in the liquid state in that a knowledge of the instantaneous positions of all the atoms would allow one to determine on which side of the pseudodislocation (relative to a fixed coordinate system) there is compression and on which side there is dilation. Because of the interactions between the pseudodislocations there will of course be a finite probability that dislocation-free regions (i.e. embryonic crystallites) could exist momentarily, but because the temperature is above the melting point these crystallites would quickly melt due to the spontaneous generation of further dislocations in them. (This process arises because the free energy of the dislocation becomes zero at the melting point.) As the temperature of the liquid is cooled below the freezing point, crystallization will occur if the pseudodislocations can be eliminated. This will be achieved by their interaction as mentioned earlier, but now without the spontaneous generation of new dislocations in the embryonic crystallites because the temperature is below the melting point. The driving force for the elimination of the dislocations arises because the dislocation free energy rises with increasing degree of supercooling.

The rate of crystallization will depend upon the pseudodislocation mobility, so that the rate will be lower for highly viscous liquids. The crystallization process can also be bypassed by very rapid cooling.
because the dislocations would then not have sufficient
time to move even if they were mobile. If the elimina-
tion process is not completed then dislocations will
remain in the resultant crystal. If the elimination
process either does not take place at all, or if it occurs
to only a limited extent, then the resultant solid will be
either as dislocated as was the liquid or nearly so. Such
a solid, saturated with dislocations, would be called a
glass according to the model advocated in this com-
munication. The dislocations would of course not be as
mobile as in the liquid, and their mobility would
decrease with decreasing temperature, becoming
finally zero at the glass transition temperature.

This model suggests a simple explanation of several
of the basic experimental observations on glasses. To
begin with the connection between volume change and
dislocation content taken together with the present
model shows immediately why the volume-temperature
curve has the observed form shown in figure 1 (which is

taken from the book of Jones [13]). The sudden increase
in volume is due to the sudden generation and
proliferation of dislocations as discussed earlier. The
more gradual rise below $T_M$, in the crystalline state, is
of course due to simple thermal expansion. When the
liquid is cooled under conditions that favour glass
formation the volume does not return to the crystalline
value and this is due to retention of dislocations. The
rate of decrease of volume with temperature is, how-
ever, still greater than in the crystalline state and this is
attributed to the fact that the dislocations are still
sufficiently mobile that some elimination can occur.
When the glass temperature is reached, however, the
dislocation mobility has fallen to zero, and the slope of
the volume-temperature curve is essentially identical to
that of the crystalline form. This indicates that disloca-
tions have a negligible influence on the thermal expan-
sivity.

The model also helps one to understand the slope of
the corresponding curve for the temperature depen-
dence of the specific heat. In contrast to what is observ-
ed to occur with the volume, the specific heats at
constant pressure of a crystal and a glass of the same
material differ only slightly below the glass tempera-
ture. This is illustrated by the curve for glycerol shown
in figure 2a [13]. The specific heat is of course deter-
mimed by the vibrational density of states, and this is
shown schematically in figure 2b for the three states
crystal, liquid and glass ($^1$). The important difference

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Fig. 1. — Schematic illustration of the temperature dependence
of the volume of the glassy, liquid, and crystalline states [13].

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Fig. 2a. — Molecular heat of glycerol in the liquid, glassy, and
crystalline states [13]. a, b, c, d and e represent liquid, supercooled
liquid, glass, crystal, and expected form of equilibrium curve for
supercooled liquid respectively.

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Fig. 2b. — Schematic illustration of the frequency spectra of the
liquid, glassy, and crystalline states [14, 15, 16].

($^1$) This schematic plot is a composite of individual plots for
the various states given by Bell [14], Egelstaff [15] and Ziman [16].
between the curves for the liquid and the glass is that the latter $Z(\omega)$ becomes zero at $\omega = 0$ just as for a crystal, because in both cases there is no marked diffusion. In the present model the diffusion in the liquid state is due to the movement of the pseudodislocations while the lack of diffusion in the glassy state is due to the fact that the pseudodislocations are immobile below the glass temperature. The less pronounced differences between the crystal and glass $Z(\omega)$ at finite $\omega$ apparently have a relatively negligible effect, and so difference between the specific heats of crystal and glass is fairly small (although the value for a glass is slightly higher).

3. Grain-boundary-dependent phenomena in the limit of very small grain size. — Having now outlined the basic concepts of the unified theory, and before going into the testing of the ideas contained in it, we will consider some consequences of the view that liquids and glasses can be looked upon as polycrystals in which the grain size is of near-atomic dimensions. In each case we will describe briefly the value of a phenomenon that is observed in a polycrystalline solid, and whose characteristic parameters are a function of grain size, and then we will go on to discuss the implications for these phenomena of an atomic-scale grain size.

3.1 Creep in polycrystals and the viscosity of liquids and glasses. — There are several different types of creep, depending on the stress level and temperature, but all have it in common that they involve time-dependent dimensional changes of a specimen under constant stress. High temperature creep, which is observed in the vicinity of the melting point, has been analysed by Nabarro and Herring [17] and has been found to be due to selectively directional self diffusion. The underlying idea is that stress causes local deformation of the lattice and thereby alters the vacancy formation energy. If there are stress inhomogeneities in a specimen, this will give rise to directional diffusion as the vacancies seek to migrate to positions of lower energy. In a specimen under unidirectional tensile stress, for instance, the diffusion is such as to promote elongation of the specimen. The Nabarro-Herring equation relates the viscosity, $\eta_0$, in the solid state, to the net distance, $R_n$, through which the vacancies move in travelling from a high-stress source to a low-stress sink. It is

$$\eta_0 = R_n^2 k T / (4Q_0 D_s)$$  \hspace{1cm} (1)

where $Q_0$ and $D_s$ are the atomic volume and solid-state self diffusion coefficient respectively. $x$ is a constant whose value can be shown to be about 4. The form of (1) is of course reminiscent of the Stokes-Einstein expression [17] for liquid viscosity, $\eta_L$, which is

$$\eta_L = kT / (3\pi\eta_d D_L)$$  \hspace{1cm} (2)

where $D_L$ is the liquid-state self diffusion coefficient and where $\eta_d$ is the diameter of an atom in the liquid.

We must now ask what becomes of (1) if we accept the model described in this paper. The grain size is determined by the dislocation density and the latter is so high that the mean nearest-approach distance between dislocations is just twice the core radius, $r_c$. Thus for our model liquid we have

$$R_n \approx 2r_c$$  \hspace{1cm} (3)

and the core radius can be written in the form

$$r_c = \beta d_0$$  \hspace{1cm} (4)

where $d_0$ is the nearest-neighbour distance and $\beta$ is a constant which lies between 1 and about 3.

We may also write

$$\Omega_0 = \gamma d_0^3$$  \hspace{1cm} (5)

where $\gamma$ will depend upon the crystal structure ($\gamma = 1 / \sqrt{2}$ for the FCC and HCP structures; $\gamma = 4 / 3 \sqrt{3}$ for the BCC structure). Using (3), (4) and (5) in (1) we obtain the viscosity of our model liquid

$$\eta_L = 4 \beta^2 kT / (\pi\eta_d D_L)$$  \hspace{1cm} (6)

where it is now assumed that $D_L$ will be the diffusion coefficient for diffusion along dislocations (i.e. the so-called pipe diffusion). The similarity between eq. (6) and eq. (2) is striking. Indeed they differ only by a small numerical factor. Furthermore, the use of eq. (1) for the crystalline state and, with the appropriate changes, for the liquid state also allows one to derive an expression for the ratio of the liquid and crystal viscosities. This is simply

$$\eta_L / \eta_0 = (R_s / R_n)^3 (D_s / D_L)$$  \hspace{1cm} (7)

Typical effective grain sizes in polycrystals follow from the fact that the dislocation density in well annealed crystals is usually of the order of $10^4$ cm$^{-2}$. Thus $R_s / R_n = 10^4$, using eq. (3). Moreover, the ratio of the diffusion coefficient in the two states has been measured for a wide range of substances and one finds that $D_s / D_L \approx 10^4$ (see also the next section). Hence one finds that

$$\eta_L / \eta_0 \approx 10^{16}$$  \hspace{1cm} (8)

which is in excellent agreement with experiments on an equally wide range of materials. We see, therefore, that the present model is capable of explaining in a quantitative manner the most striking difference between the crystalline and liquid states.

There remains the question of the difference between the viscosities of the liquid and glassy states of any given substance. This arises, according to the present model mainly from the fact that the glassy state exists at a lower temperature than the liquid and that this implies a lower diffusion coefficient. Following eq. (7) we can write, where the subscript $G$ stands for glass,

$$\eta_L / \eta_0 = (R_s / R_n)^3 (D_s / D_L)$$  \hspace{1cm} (9)

from which we see that any change in the effective grain size, in going from the liquid to the glass, will also have an effect on the viscosity. If there is a certain amount of dislocation-dislocation-interaction which leads to loss
of dislocations during the cooling down to the glassy state (which indeed has already been suggested earlier in this communication) then $R_G/R_a$ will be greater than unity and the glass will be more viscous. The main reason for the higher viscosity of the glass, however, will be due to its lower diffusion coefficient. This will have the form
\[ D = D_0 \exp(-E_D/kT) \]  
where both $D_0$ and $E_D$, the diffusion constant and diffusion activation energy respectively, now refer to the pipe diffusion mode of mass transport. The temperature dependence of $D$ is solely responsible for the temperature dependence of $\eta_G$ so long as the temperature is low enough to prevent appreciable dislocation motion, lowering of the dislocation density, and increase in $R_G$.

3.2 Superplasticity of certain alloy polycrystals, diffusion-accommodated deformation, and the flow of glass. — In recent years a steadily-increasing number of alloys have been discovered which have the remarkable property that they can tolerate large tensile strains, frequently up to several thousand percent, without necking. Numerous independent studies of these alloys, both in theory and experiment, have elucidated the underlying physical principles of this unusual behaviour. It is found that a necessary condition for the manifestation of superplasticity is a sufficiently small grain size (typically a few microns, or less than this), and that during superplastic deformation the individual grains behave as if they had a central undeformable core and an outer mantle in which both plastic deformation and diffusion occur simultaneously.

One of the most technologically important properties of glass is that it too deforms plastically without necking. According to the model described in this paper glass also can be looked upon as a polycrystalline aggregate with a grain size that is sufficiently low that it would be expected to exhibit superplasticity. Indeed the grain size is so small in a glass that there could hardly be any core in the average grain. Glass would therefore represent a limiting case of superplastic solid in which the mantle regions filled all the available space.

A recent analysis by Ashby and Verrall [18] has shown that the superplastic strain rate is given by
\[ \dot{\varepsilon} = (98\Omega_0/kT^2) (a\varepsilon - 0.72\Gamma/l) D_b(l + \pi\delta D_b/lD_s) \]  
in which $l$ is the grain diameter, $\Gamma$ the grain boundary free energy, $\varepsilon$ the tensile stress, $\delta$ the thickness of the mantle, $D_b$ is the grain boundary diffusion coefficient, and where the other symbols have already been defined. In the case of the glass model advocated here, $l$ would be simply 2 $\delta$ since there is no core. Since $D_b$ is considerably larger than $D_s$ (e.g. $D_b/D_s = 6.6 \times 10^3$ for lead at its melting point [10, [20]) this permits simplification to the form
\[ \eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{kT^2}{49\pi\Omega_0 D_s} \left( 1 - \frac{0.72\Gamma}{\sigma l} \right)^{-1} \]  
which is of course again reminiscent of the Stokes-Einstein and Nabarro-Herring equations, except for the final stress-dependent term. Regarding the latter, one notes that in metals $\Gamma$ is usually of the order of 100 ergs cm$^{-2}$ while $l$ in the present model is of the order of $2 \times 10^{-7}$ cm. Superplastic flow stresses are typically $10^{-3}$-$10^{-2}$ times the shear modulus, and the latter is typically $10^{11}$ dynes cm$^{-2}$. The two terms inside the remaining bracket in eq. (12) are therefore of comparable magnitude so that the viscosity will depend upon the exact magnitude of $\sigma$. This is also observed in the original Ashby-Verrall analysis.

3.3 The grain-size dependent strength of poly-crystals and the strength of glass. — Polycrystalline specimens are invariably stronger than single crystals, when tested at temperatures below the range at which creep effects begin to dominate. Not surprisingly this fact has been attributed to the power of grain boundaries to impede the free movement of dislocations and thus to inhibit plastic deformation. This being the case, one would expect that the greater the concentration of grain boundaries the greater would be the strength enhancement effect. Experiments on a wide variety of metals and alloys have endorsed this view and Hall and Petch have shown that the enhancement follows the relationship
\[ \sigma = \sigma_0 + K l^{-1/2} \]  
where $\sigma$ is the flow stress corresponding to a grain diameter $l$ and $\sigma_0$ is the flow stress for infinite grain diameter. The value of the constant, $K$, is for aluminium, for instance, $7.4 \times 10^8$ dynes cm$^{-2}$ $\mu$m$^{1/2}$ [21].

The form of the equation has also been derived analytically on the basis of a model in which the grain boundary acts as a barrier against which the dislocations in a deforming grain must pile up. When the number of dislocations in the pile up is sufficiently large, the stress level just ahead of the leading dislocation in the pile is sufficiently great to transmit stress across the boundary and into an adjacent grain. The adjacent grain can then begin to deform.

In the model described in this paper, the effective grain size is very small. This would imply a very high strength, and it is noteworthy that glasses are in general stronger than polycrystalline metals. For instance, the flow stress of aluminium for a grain size of 100 $\mu$m is about $2 \times 10^8$ dynes cm$^{-2}$ whereas the tensile strength of drawn silica is about $7.3 \times 10^{11}$ dynes cm$^{-2}$ [22].

In fact glasses exhibit a strength that approaches the ideal theoretical value; a property which is exploited in the industrial use of fibre-glass. It is interesting, in this connection, to use eq. (13) to derive a value of the grain size, $l^*$, that would be required to produce a flow stress equal to the ideal value of $G/2\pi$, where $G$ is the shear modulus. Using again the case of aluminium we have $G = 2.55 \times 10^{11}$ dynes cm$^{-2}$, and since $\sigma_0$ is negligible,
\[ l^* = 4\pi^2 K^2 G^2 = 3.3 \times 10^{-8} \text{ cm} \]
Thus we would expect ideal theoretical strength to be exhibited by a polycrystal with a grain diameter of about two nearest-neighbour distances. This is just about the grain diameter that is predicted by the model presented in this paper, since the model invokes a grain diameter of about twice the dislocation core radius, and the latter is about three nearest-neighbour distances in typical metals.

3.4 Grain growth and the possibility of bypassing crystallization to produce a glass. — When a polycrystalline material is heated to sufficiently high temperature it is found that the average grain size starts to increase. This is because grain boundary migration causes some grains to grow at the expense of others. The driving force for the migration is the local difference in stored energy between the two sides of the boundary and this in turn is due to local differences in the dislocation concentration. Electron micrographs have been published in which an advancing grain boundary points in the direction of maximum dislocation density while leaving behind in its wake a region almost devoid of dislocations.

In the present model the crystallization process has been characterized as one of the removal of the pseudodislocations as the liquid is cooled below the melting point. This removal is equivalent to grain growth, and it follows from the model, that if the grain growth process can be bypassed, a high dislocation density will be frozen into the material and a glass will result. The validity of such a view would depend upon a calculation of the rate of grain growth for grains having the very small diameter envisaged in the present model. The principles governing the rate of grain growth have been discussed in a number of publications [23, 24, 25], some of which have expressed the view that the process is peculiar in that it does not obey the normal laws of nucleation and growth. The latter laws arise in a physically quite transparent manner. The driving force for growth is proportional to the volume swept out by the moving boundary while the opposing force derives from the increasing area of the growing grain. At small radii the surface effect predominates, but beyond a certain grain radius the volume term wins and the grain grows spontaneously. It would be disconcerting if the otherwise ubiquitous nucleation and growth law did not apply to the obvious candidate under discussion here. Fortunately, it transpires that an apparent mistake in the algebra of the earlier publications has led to the erroneous conclusion that nucleation and growth theory is not relevant to the present problem. In appendix A of this paper the error is corrected, and it is shown that grain growth is not the exception that it was thought to be. In the next section the theory of nucleation is applied to the question of crystallization and glass formation in both three and two dimensions. The latter is included both because it differs in certain significant respects from the three dimensional case, and also because it can readily be checked pictorially in a molecular calculation. Such a calculation is presented in the penultimate section of the paper.

4. Application of nucleation theory to glass formation. — According to the model promoted in this paper there is nothing special about the instantaneous structure if a glass apart from its lack of crystallinity and the fact that its disorder can be described in terms of pseudodislocations. When a liquid is cooled below its freezing point the onus is on the crystalline form to establish itself, and if it fails to do this a glass will ultimately result by default. The driving force for the phase change is the difference in free energy between the stable (crystalline) phase and the metastable (supercooled liquid) phase. The amount of material that is transformed in a given period of time will depend upon both the rate of formation of crystalline nuclei and their rate of growth.

In the supercooled liquid the equilibrium concentration of crystalline embryos of a given size is determined by the difference in free energy between the embryos as units and the corresponding number of atoms in the liquid phase. This is given by

$$\Delta G^* = 4 \pi r^2 \gamma_{SL} + \frac{4}{3} \pi r^3 \Delta G$$

(15)

where \(r\) is the radius of the embryo, \(\gamma_{SL}\) the crystal/liquid interfacial energy, and \(\Delta G\) is the difference in free energy between the crystal and liquid phases for the number of atoms in unit volume of the embryo. It is clear that the \(\Delta G\) versus \(r\) characteristic has a maximum which defines the critical radius \(r_c\) (and hence critical number of atoms) together with the corresponding formation energy for the critical cluster size \(\Delta G^*\). For given values of \(P\) and \(T\) the system will adapt an equilibrium distribution of embryos, the number present with size \(n\) being given by

$$N_n = N' \left( \frac{N_1}{N'} \right)^n \exp \left( -\frac{\Delta G^*(n)}{kT} \right)$$

(16)

\(N_1\) is the number of liquid atoms that remain outside the cluster (i.e. remain as clusters each having a single atom). \(N'\) is given by

$$N' = \sum_{n=1}^{\infty} N_n$$

(17)

and is the total number of clusters (including those with a single atom).

For

$$\sum_{n=2}^{\infty} N_n \ll N_1,$$

we obtain the classical expression

$$N_n = N_1 \exp \left( -\frac{\Delta G^*(n)}{kT} \right).$$

(18)

The number of critical nuclei (clusters containing \(n_c\) atoms) is therefore given by

$$N_c = N_1 \exp \left( -\frac{\Delta G^*_{n_c}}{kT} \right).$$

(19)
From this the nucleation rate $I$ can be found by multiplying $N_e$ by the net flux of atoms across the critical nuclei's interface. Thus

$$ I = A \exp\left(-\frac{\Delta G_e^*}{kT}\right) \exp\left(-\frac{\Delta G_D}{kT}\right) $$

where $A$ is a constant which is normally written as $kT\eta_1/\hbar$ ($\hbar$ being Planck's constant), and $\Delta G_D$ is the activation energy for diffusion of atoms from the liquid phase to the nucleus interface.

It is customary to use a linear approximation for $\Delta G (= \Delta H - T \Delta S)$ and insert $\Delta S = \Delta H/T_M$ where $T_M$ is the melting point. This gives

$$ \Delta G = \frac{\Delta H}{T_M} \left(T_M - T\right) = \Delta H \left(1 - \frac{T}{T_M}\right). $$

Inserting this in the expression for the formation energy of the critical nucleus (found by setting $\partial \Delta G^*/\partial r = 0$) we have

$$ \Delta G_e^* = \frac{16 \pi}{3} \eta_3 \Delta G^{-2} $$

and hence

$$ \Delta G_e^* = \frac{16 \eta_3^2 T_M^2}{3 \Delta H^2 (T_M - T)^2}. $$

The nucleation rate is thus

$$ I = N_1 \frac{kT}{\hbar} \exp\left(-\frac{16 \eta_3^2 T_M^2}{3 \Delta H^2 (T_M - T)^2 kT} - \frac{\Delta G_D}{kT}\right) $$

this being valid only if the transient period that prevails as the system changes to a new equilibrium distribution is short compared with the period of observation.

If one desires information on the distribution of embryos, and its time dependence, it is necessary to study the temporal evolution of the system. Assume that a system which is initially in equilibrium at a temperature $T_1 > T_M$ is suddenly cooled to a temperature $T_2 < T_M$ and then held there. The problem is one of determining how the distribution of embryos $N_e(T, 0)$ changes with time ($N_e(T, t)$). This problem has been analyzed by Kantrowitz and Zeldovich (see ref. [25], p. 403). It is found that the transient change in the distribution of embryo sizes can be expressed as

$$ N_e(T, t) = N_e^0 \exp(-\tau/t) $$

$$ \tau = \frac{h n_e^2}{4 Z k T S_c} \exp\left(-\frac{\Delta G_D}{kT}\right) $$

where $Z$ is the Zeldovich factor [37] and $S_c$ is the surface area of the critical nucleus.

The relative simplicity with which defects can be detected in two-dimensional systems makes them a suitable subject for study in their own right. Two-dimensional studies of melting were referred to earlier in this paper, and the next section describes attempts to produce a two-dimensional glass by computer simulation. It is therefore appropriate to repeat the development given above for the two-dimensional case. Eq. (15) and (23) become

$$ \Delta G_e^* = 2 \pi \gamma + \pi r^2 \Delta G $$

while for the nucleation rate we find

$$ I = N_1 \frac{kT}{\hbar} \exp\left(-\frac{\pi r^2 T_M}{\Delta H(T_M - T)/kT} - \frac{\Delta G_D}{kT}\right) $$

The equations for $N_e$ and $N_e$ are the same as for three dimensions but with the appropriate substitutions for two dimensions of the quantities given above.

From the foregoing analysis it will be apparent that there are two quantities that are of interest when considering whether or not crystallization can be bypassed under a given set of experimental or simulational conditions. These are the distribution of embryo sizes as a function of temperature and the nucleation rate for embryos of critical size as a function of temperature. Figure 3 shows $N_e(T)$ for three dimensions and

![Equilibrium distributions of embryos for a three-dimensional Lennard-Jones system.](image)

The atomic concentration of 13-atom crystalline clusters at $T_M$ is about $10^{-5}$. One also sees that 13 is obviously less than the critical cluster number for temperatures near $T^*$. At $T_M$ the critical cluster size is of course infinite. As the specimen
is cooled, the absolute concentrations of the clusters grow, but the relative increase is higher for the larger clusters. This is the case for all clusters above the size of three which we will term the cross over size. The cross-over size can readily be found by finding that value of \( r \) for which \( \Delta N/\Delta T \) is zero, and substituting the various quantities derived earlier. The results are

\[
\begin{align*}
\rho_{\text{cross}} &= -3 \gamma/\Delta H \quad (\text{three dimensions}) \quad (29) \\
\rho_{\text{cross}} &= -2 \gamma/\Delta H \quad (\text{two dimensions}) \quad (30)
\end{align*}
\]

in which \( \Delta H \) is negative as defined. Comparing figure 3 with the corresponding curve for two dimensions (Fig. 4) one sees both that the critical nucleus size falls more rapidly as a function of temperature and that the concentration of a given cluster size at a given temperature is now much higher. In two dimensions there is a higher concentration of critical nuclei at a given temperature relative to the melting point. When this is added to the fact that fewer atoms are required in two dimensions to establish an embryo of a given diameter, it can be seen that nucleation is considerably easier in two dimensions. This is shown even more dramatically in comparing the plots of \( f(T) \).

For three dimensions (Fig. 5) this curve peaks at around 0.5 \( T_M \) while for two dimensions (Fig. 6) the peak is much closer to \( T_M \), and it is also much higher. The numerical values used in constructing these curves were obtained in the simulations of melting referred to earlier, and in the simulation of the two-dimensional case reported in the next section. The values are given in Appendix B.

5. Failure to bypass crystallization in two dimensions. Molecular dynamics simulation. — In the preceding section it was shown that crystallization is easier in two dimensions than in three. The existence in nature of numerous different types of glass attests to the fact that the crystallization process can be readily bypassed in three dimensions. It would be interesting to check whether or not one can produce a two-dimensional glass. This is possible by the type of molecular dyna-
mics simulation referred to earlier in this article, and the two-dimensionality would offer the advantage of visual monitoring of the results. From what has been discussed in the earlier sections, it will be clear that the obvious goal of such a simulation would be a check on the grain size of rapidly cooled liquids. If the grain size were so small that the implied dislocation density were at the saturation level, one would conclude that a glass had been formed. A considerably larger grain size would indicate failure to bypass crystallization.

We report here the results of such a molecular dynamics simulation of the rapid cooling of a two-dimensional Lennard-Jones liquid containing 918 atoms in the irreducible cell. We will not give the details of the actual method since this has been described elsewhere [7], [8], [9], [10], [11]. The results are shown in figures 7-10, and the various numerical values which are given in them are all in terms of the reduced units as dealt with in Appendix B.

Figures 7 and 8 show respectively the total energy and equivalent lattice parameter as a function of temperature. It is seen that the melting point is located at \( T = 0.528 \pm 0.012 \) and that the change in area on melting is \( 5.53 \% \pm 0.13 \% \). By measuring the assembly-averaged mean square displacement, the diffusion coefficient was determined as a function of temperature in the liquid state (see Fig. 9). This permitted one to find the diffusion activation energy and diffusion constant, and the result was \( \Delta G_0 = 2.76 \pm 0.18 \) and \( D_0 = 0.347 \pm 0.095 \). The liquid was then quenched at the fastest rate possible. The maximum rate at which an assembly of atoms can be cooled is determined by the strength of their interactions with each other. Kinetic energy is removed by simply setting all the velocities to zero. After this has been done the kinetic energy again increases as the atomic rearrangements remove potential energy from the system. Every time the kinetic energy reached a maximum, the velocities were again set to zero, and the inter-quench time was about 50 computational cycles (i.e., about \( 10^{-12} \) seconds of real time).

The number of dislocations found in the quenched structures for different quenching temperatures from the liquid state. The dislocation numbers are estimated from the excess area excluding the contribution from vacancies.

For a hexagonal lattice of dislocations with contiguous cores of radius 1.5 \( r_0 \) the number of dislocations would be close to 100.

<table>
<thead>
<tr>
<th>Quench temperature</th>
<th>No. of dislocations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>17.0</td>
</tr>
<tr>
<td>0.73</td>
<td>28.2</td>
</tr>
<tr>
<td>0.61</td>
<td>33.7</td>
</tr>
<tr>
<td>0.57</td>
<td>23.2</td>
</tr>
</tbody>
</table>

The number of dislocations found in the quenched structures for different quenching temperatures from the liquid state. The dislocation numbers are estimated from the excess area excluding the contribution from vacancies.
Figures 10a and 10b show a typical result of such a quench. The situation in the liquid immediately prior to the quench is shown in figure 10a, while 10b shows the situation immediately after the quench (things do not change thereafter because the final temperature is zero). In the liquid it is possible to get the impression of small (but not well defined) crystalline regions by looking at the figure at a low angle from various directions. In the quenched model it is quite clear that the grain diameter is now much larger, and the individual grains are quite well defined. The mean grain diameter is between ten and fifteen nearest-neighbor distances, which is well above what would fit our criterion for the glassy state. The simulation has therefore produced a relatively coarse polycrystal rather than a glass. Table I shows how the quenched-in dislocation density varies as a function of the temperature from which the liquid is quenched.

The production of a polycrystalline array rather than a glass, under the conditions of the simulation, should be considered in the light of the information contained in figure 4. The quenches start from various temperatures above the melting point. One notes that the higher the temperature the more rapidly does the distribution fall away for the larger cluster sizes. This difference in the initial cluster size distribution will affect the result of the quench experiments. This follows from eq. (25b) which, with the appropriate parameters inserted, results in relaxation times in two and three dimensions of the order of $10^3$ to $10^6$ timesteps, which should be compared to the quench time of roughly $10^3$ timesteps. The dependence of the dislocation density on the quench temperature, as reflected in table I, can thus be understood by assuming the growth of nuclei to proceed very rapidly. Since, at a given supercooling, systems quenched from higher temperatures will contain fewer nuclei, the rapid growth of these nuclei will ultimately produce a solid configuration with larger grains and thus with a lower dislocation density. This argument can be valid only if the growth in two dimensions is of the same order of magnitude as that found for three dimensional systems [38], and this indeed seems to be a reasonable assumption.

When considering the results of a simulation of this type, it is important to bear in mind the particular conditions that arise from the use of a system of limited size. There is always a finite probability of the existence of an embryo of any given size as long as the specimen is essentially infinite, but in a system with only 918 particles, as used here, an embryo containing more than 918 particles is of course excluded. Indeed, if the equilibrium distribution prevails, the maximum embryo size is even much lower than this since the sum of this distribution cannot exceed 918. Furthermore, the periodicity of the model precludes concentrations of embryos below $\approx 10^{-3}$. Another way of considering these aspects of the problem is to note that the limitation on the size of the model restricts one to the upper left region of figure 4, and this tends to lower the variation in dislocation density that can be observed in the simulation.

Finally it might be noted that all the qualitative arguments against the formation of a two-dimensional Lennard-Jones glass are less severe when applied to a three-dimensional system.

6. Discussion. — The key concept in the model presented in this paper is the pseudodislocation. Its existence in the liquid and glassy states provides a way of understanding the physical processes that deter-
mine the viscous behavior of those states. It must be
stressed that the pseudodislocation is different from the
crystal dislocation in several important respects. Since
there is no good crystal left in either a liquid or a glass
(i.e., no region of crystal in which the stress is not near or
above the elastic limit) the pseudodislocation cannot
have a long-range stress field. It also has no strictly
defined slip plane only a local direction in which motion
is easiest. The concepts of glide, climb and pipe diffu-
sion are distinct and different in a crystal dislocation,
whereas they converge towards becoming one and the
same thing in liquids and glasses.

One might then wonder what characteristic is left for
a pseudodislocation to enable one to define it. How is it
to be identified as existing above the general level of
randomness that otherwise prevails in these states?
It is important to bear in mind that a liquid is not truly
random as is a perfect gas. The pair distribution func-
tion (which describes the probability of atom-atom
separations) has a structure which departs from the
random situation. One reason for this is the impossi-
bility of separations less than about an atomic dia-
meter. The shortcoming of this distribution function is
that it is non-directional, and that it is space averaged.
(When obtained from experiment, it is also time
averaged.) The question then arises: if a close-packed
assembly of atoms is not truly random, what identi-
fiable departures from randomness will it display? In
particular, what will be the spatial form of the non-
random features? The two obvious possibilities are a
network of lines along which the assembly is more open
than elsewhere or a random array of what might be
called pseudovacancies and pseudointerstitials. In the
model favored here one has a constantly changing
network of curved lines, the pseudodislocations, the
individual segments being only a few nearest-neighbor
distances in length. Atomic motion is envisaged as
taking place by a type of pipe diffusion, which not only
moves the position of the diffusing atom but also the
local position of the pseudodislocation itself.

The unified theory described in this paper is not so
much an original suggestion as a development and
more precise statement of what has been discussed by
previous authors. Twenty years ago, for instance,
Shockley suggested that a liquid could be regarded as
*a solid densely packed with dislocations* [31]. Another
pioneering paper, by Mott and Gurney [1], was cited in
the introduction as were several pertinent papers that
have appeared in the last two decades. One can also
find an implicit reference to the possible connection
during dislocations and the liquid state in Bragg’s
estimate of the core energy of a dislocation [32]. Exper-
imental support for the views expressed here has
appeared in the literature during the last decade. Fessler,
Kaplow and Averbach [33] have for instance found that
their X-ray diffraction data on liquid and
solid aluminum is best explained in terms of a quasi-
 crystalline model for the liquid state. There is also the
recent electron microscopy data on the amorphous
state of germanium collected by Rudee and Howie [34,
35]. They find that their specimens were best described
as polycrystalline arrays with a grain diameter of
about 14 Å. This is about the same grain diameter as
would be required in the model described in this paper.
A particularly interesting feature of the Rudee-Howie
observations is that the small crystallites had a wurtzite
structure rather than a diamond structure. Howie
[private communication] has observed that disloca-
tions in crystalline germanium dissociate into partials
with a separation of 70 Å and that the resultant stacking
fault causes the local structure to transform to the
wurtzite structure. The 70 Å separation has no signifi-
cance in the present context, but the result shows that
the energetically favorable partial dislocation in ger-
manium is connected with the wurtzite structure.
The implication is that the amorphous form is essen-
tially the crystalline form saturated with the most
favorable partial dislocations. This corresponds to what
has been observed in the computer simulations of the
melting of FCC crystals [8, 11], namely the generation
and rapid proliferation of the most favorable partial
dislocation in that structure: the Shockley partial.

It is worth reiterating the fact of the valuable role
played by computer simulation in that it enables one to
check at a microscopic level the ideas put forward here.
The insertion of dislocations until saturation is reached
has already been shown to produce a liquid-like pair
distribution function [6, 9] in three dimensions and
dislocations have also been linked to two-dimensional
melting [7]. Finally, the two-dimensional quenching
described in the foregoing section is instructive because
it explores the borderline region in which the glassy
phase is apparently not quite reached.

7. Conclusion. — A model has been proposed which
provides a unified view of the melting, crystallization,
and glass formation processes, and of the nature of the
liquid and glassy states. The unifying concept is the
dislocation, which is already well known in the crystal-
line phase. It is proposed that this concept can be
retained in a more generalized form, the pseudo-
dislocation, in the liquid and glassy states. These states
are to be regarded as polycrystalline arrays in which the
grain diameter is about twice the dislocation core
radius. The difference in the viscosities of the liquid
and glassy states is attributed to the difference in the
mobility of the pseudodislocations. The sudden decrease
in the mobility of the pseudodislocations at the glass tran-
sition temperature is presumably due to the cessation
of the formation of point dislocations by thermal activa-
tion. This, taken together with the tendency of disloca-
tions to arrange themselves in low-energy grain bound-
ary structures, will effectively increase the grain size.

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APPENDIX A

On the applicability of nucleation theory to the problem of grain growth. — If there is a difference in the dislocation densities on the two sides of a grain boundary, there will be a driving force which will tend to make the boundary bulge out in the direction of the higher dislocation density. This situation was first considered by Bailey [23]. In what follows we call the low density side A and the high density side B.

We will follow the general approach of Burke and Turnbull [36]. Let $\Delta F$ be the difference in free energy per atom between the regions close to the boundary and on either side of it, and let $\Delta F_A$ be the activation free energy for atomic movement. The frequency at which atoms jump from B to A is

$$f_{BA} = v \exp\left(-\Delta F_A/kT\right) \quad (A.1)$$

while from A to B it is

$$f_{AB} = v \exp\left(-\Delta F_A + \Delta F/kT\right) \quad (A.2)$$

where $v$ is the atomic vibration frequency. The net frequency for movements B to A is

$$f = f_{BA} - f_{AB} = v \exp\left(-\Delta F_A/kT\right) \left(1 - \exp\left(-\Delta F/kT\right)\right) \quad (A.3)$$

Using the approximation that $\exp(-x) = 1 - x$ for small $x$, this reduces to

$$f = v(\Delta F/kT) \exp\left(-\Delta F_A/kT\right). \quad (A.4)$$

Following Cahn [24] and Christian [25] we also write

$$\Delta F = \Delta F_S - \gamma b^3(dA/dV) \quad (A.5)$$

where

$$\Delta F_S = F^B_S - F^A_S \quad (A.6)$$

and where $F^A_S$ and $F^B_S$ are the free energies per atom in grains A and B respectively. $\gamma$ is the grain boundary energy and $b^3$ is the atomic volume. $b^3(dA/dV)$ expresses the growth of grain boundary area where one atom moves from grain B to grain A, $dA$ being the increase in area and $dV$ the increase in volume. Eq. (A.4) can now be written

$$f = (v/kT)(\Delta F_S - \gamma b^3 dA/dV) \exp(-\Delta F_A/kT). \quad (A.7)$$

The number of atoms in the bulged-out boundary (see Fig. A.1) that have a chance to migrate from B to A is $Ab/b^3 = A/b^2$ where $A$ is the area of the bulge.

$$\text{Hence the net rate of volume change per unit time is given by multiplying } fA/b^2 \text{ by the atomic volume } b^3. \text{ Thus}$$

$$\frac{dV}{dt} = fA/b^2 = f_{AB} = (v/kT) A(\Delta F_S - \gamma b^3 dA/dV) \times \exp(-\Delta F_A/kT). \quad (A.8)$$

This expression agrees with corresponding expressions given by Cahn and Christian. We will clearly require the quantities $dA/dt$ and $dA/dV$. These are given

$$\frac{dA}{dt} = \frac{dA}{dV} \frac{dV}{dt} \quad (A.9)$$

The geometry of the bulge is such that (see Fig. A.1)

$$A = 2\pi R h \quad (A.10)$$

$$V = \pi h^2(R - h/3) \quad (A.11)$$

$$L = R \sin \alpha \quad (A.12)$$

$$h = R(1 - \cos \alpha) \quad (A.13)$$

which leads to

$$\frac{dV}{dz} = \pi R^3 \sin^3 \alpha \quad (A.14)$$

$$\frac{dA}{dz} = 2\pi R^2 \sin \alpha \quad (A.15)$$

$$\frac{dA}{dV} = 2/(R \sin^2 \alpha) \quad (A.16)$$

Thus we have finally

$$\frac{dA}{dt} = \frac{2\pi R^2 \sin \alpha}{kTR} \left(\Delta F_S - \gamma b^3 \frac{2}{R \sin^2 \alpha}\right) \times$$

$$\times \exp\left(-\Delta F_A/kT\right) \frac{1}{\sin \alpha(1 + \cos \alpha)} \quad (A.17)$$

which is to be compared with Cahn's expression [24]

$$\frac{dA}{dt} = \frac{2\pi R^2 \sin \alpha}{kTR} \left(\Delta F_S - \gamma b^3 \frac{2}{R}\right) \frac{1 + \cos \alpha}{\sin \alpha} \quad (A.18)$$

and the expression given by Christian [25]

$$\frac{dA}{dt} = \frac{2\pi R^2 \sin \alpha}{kTR} \left(\Delta F_S - \gamma b^3 \frac{2 \sin \alpha}{R}\right) \times$$

$$\times \exp\left(-\Delta F_A/kT\right) \frac{1 + \cos \alpha}{\sin \alpha}. \quad (A.19)$$

Growth will proceed if $dA/dt$ is greater than zero, and the three different expressions given above lead to the following conditions for growth

$$\sin^2 \alpha > \frac{2\gamma b^3}{R \Delta F_S} \quad (\text{Present analysis}) \quad (A.20)$$

Fig. A1. — Definition of the quantities appearing in the mathematical description of grain growth.
A UNIFIED THEORY OF MELTING, CRYSTALLIZATION AND GLASS FORMATION

\[ 1 > \frac{2 \gamma b^3}{R \Delta F_S} \quad \text{(Cahn's analysis)} \]  
\[ \frac{1}{\sin \alpha} > \frac{2 \gamma b^3}{R \Delta F_S} \quad \text{(Christian's analysis)}. \]

These three conditions are of course all equivalent for the special case of \( \alpha = \pi/2 \), and they all then give \( R > 2 \gamma b^3/\Delta F_S \) for growth.

In their general forms, however only (A.21) leads to the necessary condition that the bulge must be larger than a certain size in order that growth will continue spontaneously. Thus only (A.21) is consistent with the normal conditions of nucleation.

Let us now adopt an alternative course and assume at the outset that nucleation theory does hold. Then in the usual way \( \Delta F \) will have a surface component and a volume component that will oppose one another. We have for the free energy difference for the entire system with and without the bulge

\[ \Delta F = A\gamma - \frac{V}{b^3} \Delta F_S. \]

Regarding \( \Delta F \) as a function of \( \alpha \), for constant \( R \), the condition \( d \Delta F/d\alpha = 0 \) will give the critical value of \( \alpha \) and hence the critical nucleus size. Using (A.11)-(A.14) we have

\[ \Delta F = 2 \pi R^2 (1 - \cos \alpha) \gamma - \frac{\pi R^3}{3 b^3} \times \]
\[ \times (1 - \cos \alpha)^2 (2 + \cos \alpha) \Delta F_S \]  
\[ \text{(A.25)} \]

and

\[ d \Delta F/d\alpha = 2 \pi R^2 \gamma \sin \alpha - \frac{\pi R^3}{b^3} \sin^3 \alpha \Delta F_S. \]

(A.26)

From which the condition for spontaneous growth becomes

\[ \sin^2 \alpha = \frac{2 b^3 \gamma}{R \Delta F_S}. \]

(A.27)

The conditions (A.27) and (A.21) are of course equivalent. Thus we have found that the growth of a grain by the bulging out of a grain boundary is governed by the normal principles of nucleation.

APPENDIX B

Values of the constants used in section 4. — The various constants used in the calculations of embryo size distribution and nucleation rate were obtained from molecular dynamics simulations of both two- and three-dimensional systems, using a Lennard-Jones 6-12 interaction. The only difficulty in obtaining appropriate numerical values occurs in the case of the two-dimensional liquid-crystal interfacial energy \( \gamma_{SL} \). In three dimensions the experimental surface energy for krypton, \( \gamma_{SG} \) (for solid-gas), is 54.5 ergs cm\(^{-2} \), which is 3.72 in the reduced units employed here [26]. This is in agreement with recent calculations on microcrystals [27]. Using the well-established rule that \( \gamma_{SL} \approx \gamma_{SG}/10 \) [28], this gives \( \gamma_{SL} = 0.372 \) for the three-dimensional case. This is also consistent with the empirical result of Kotze and Kuhlmann-Wilsdorf [29] that \( \gamma_{SL} \approx \gamma_{GB}/2 \), where \( \gamma_{GB} \) is the average grain boundary energy, and the fact that for a number of metals \( \gamma_{GB} \approx \gamma_{SG}/5 \) [30]. In two dimensions the situation is more complicated. It has been found by computer simulation that \( \gamma_{GB} \approx \gamma_{SG} \approx 1.2 \) for such a system. It seems therefore that the rule \( \gamma_{SL} \approx \gamma_{GB}/2 \) does not apply in two dimensions, but the relationship \( \gamma_{SL} \approx \gamma_{SG}/10 \) has been asumed to hold nevertheless because this gives a value of \( r_{clos} \), which is similar to that obtained for three dimensions. Use of the rule \( \gamma_{SL} \approx \gamma_{GB}/2 \) in two dimensions would have produced a much larger value of \( r_{clos} \), which seems physically unreasonable. Hence we have, for two dimensions, \( \gamma_{SL} = 0.12 \).

The results of both simulations will be given in the following reduced units

\[ \varepsilon = r_0 = k = m = 1 \]

(B.1)

where \( k \) is Boltzmann’s constant, \( m \) is the atomic mass, and where \( \varepsilon \) and \( r_0 \) are the constants of the Lennard-Jones potential

\[ V(r) = \varepsilon ((r_0/r)^{12} - 2(r_0/r)^{6}). \]

(B.2)

The results were as follows.

Two dimensions

\[ \Delta G_D = 2.76 \pm 0.18 \]
\[ D_0 = 0.347 \pm 0.095 \]
\[ T_M = 0.528 \pm 0.012 \]
\[ L_M = 0.242 \pm 0.010 \]
\[ \left( \frac{\Delta A}{A} \right)_M = 5.53 \% \pm 0.13 \% \]
\[ P = 1.20 \pm 0.06 \]
\[ \gamma_{SL} = 0.12 . \]

The value of \( L_M \) must be multiplied by \( 2/\sqrt{3} \) if it is required in terms of unit area.

Three dimensions

\[ \Delta G_D = 2.10 \pm 0.11 \]
\[ D_0 = 0.93 \pm 0.20 \]
\[ T_M = 0.7 \]
\[ L_M = 0.973 \pm 0.148 \]
\[ \left( \frac{\Delta V}{V} \right)_M = 15.0 \% \]
\[ P = 0.0 \pm 0.12 \]
\[ \gamma_{SL} = 0.372 . \]

The value of \( L_M \) must be multiplied by \( \sqrt{2} \) if it is required in terms of unit volume.
References


[34] Rudee, M. L. and Howie, A., Phil. Mag. 25 (1972) 1001.