A Universal Criterion of Melting[†]

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Melting is analyzed dynamically as a problem of localization at a liquid−solid interface. A Lindemann-like criterion of melting is derived in terms of particular vibrational amplitudes, which turn out to equal a universal quotient (about one-tenth) of the molecular spacing, at the interface. The near universality of the Lindemann ratio apparently arises owing to strongly overdamped dynamics near melting, and despite the anharmonic interactions being system-specific. A similar criterion is derived for structural displacements in the bulk of the solid, in particular the premelted layer; the criterion is no longer strictly universal, but still depends only on the harmonic properties of the solid. We further compute the dependence of the magnitude of the elemental molecular translations, in deeply supercooled fluids, on the temperature and the high frequency elastic constants. We show explicitly that the surface tension between distinct liquid states, near the glass transition of a supercooled liquid, is nearly evenly split between entropic and energetic contributions.

1. Introduction: What Is "Melting"?

The word "melting" turns out to mean more than one thing. (For reviews, see refs 1−12.) At a high enough temperature, the shear modulus of a perfect crystal would vanish, which, according to Born,[7,13] would lead to melting. This type of melting is sometimes called *mechanical* melting. Experience shows nevertheless that, in real crystals, the lattice always begins to desintegrate at significantly lower temperatures, when the shear resistance of the bulk still exceeds at least a half of its zero temperature value.[1−3] This type of melting, called *thermodynamic* melting, appears to usually initiate at defects, most notably at the free surface, but also at grain boundaries, impurity sites, etc.[1,2] Another well known peculiarity of the melting/fusion transition is, while liquids are relatively easy to overcool, overheating a crystal seems very difficult, except under special circumstances, such as when the free surface is "clamped", or in the case of water, which contracts upon melting thus allowing for internal melting.[8] Surface melting phenomena are very complicated, as is just about anything about surfaces: The melt may or may not wet the crystal surface; the thickness of the "premelted" layer, separating the crystal from the vapor, often exhibits power law scaling with the proximity to the melting temperature; the surface itself is usually reconstructed and often experiences roughening transitions below melting.[10,11] One should add here the effects of lattice anisotropy[14,15] and possible polymorphic transitions near the melting temperature.[16] To summarize, conceptualizing melting as a dynamical process is not straightforward and depends on specific circumstances.

In view of the complications above, it comes as a surprise that there should be the following simple, nearly universal phenomenological criterion, due to Lindemann[17,6,18]: At melting the typical vibrational displacement, for a given crystalline class, should be some fixed fraction of the lattice spacing. Lindemann posited that the ratio should be about a half, implying direct collisions between the atoms constituting the lattice would become possible, leading to the lattice's demise. One may note

that the Lindemann argument accounts for anharmonicities in the problem but in a very generic fashion, through the existence of collisions. The value of the Lindemann ratio was later revised by Gilvarry[19] to be about one tenth and works rather well indeed. Data compilations[8,20] show only a variation of 10% or so within a given crystal structure type, and the overall range is between 0.068 and 0.114.

It is in the context of the Einstein's theory of vibrations in solids that Lindemann formulated his criterion; perhaps for this reason, the criterion has been a benchmark in density functional studies (DFT) of crystal melting (see, e.g., refs 21 and 22), which are accurate in the short-wavelength, Einstein limit. Nevertheless, it was not until a DFT study of aperiodic crystals when the Lindemann ratio turned up on a first principles basis as an order parameter. Wolynes and co-workers[23,24] demonstrated that a liquid, if failed to crystallize, should settle into (long-living) aperiodic structures. The transition, or rather a crossover, is characterized by a discontinuous change in the localization length from an effectively infinite to a finite value; the latter gives the vibrational displacement at the mechanical stability edge. This length therefore directly corresponds to the Lindemann length; its DFT-computed value matches well that observed in crystals, and, in the first place, the neutron scattering data in supercooled liquids and frozen glasses.[25,26] Lindemann-like criteria also naturally arise in treatments of energy landscape models of protein folding and collapse,[27,28] mean-field models of the structural glass transition,[29] and in vortex lattice melting in superconductors.[30] Even in the absence of a first principles justification, the Lindemann rule is often used on purely empirical grounds, evidently owing to its remarkable circumstantial consistency, and its simplicity. Applications range from vortex lattices in rotating Bose condensates[31] to estimating the native state entropy of a protein.[32] Generalized Lindemann criteria have been applied to defect-induced amorphization of a crystal,[33] or melting in one-component plasmas (see ref 34 and references therein). An inverse Lindemann criterion has been suggested for crystallization.[35] An increasingly useful application of the Lindemann criterion is in molecular dynamics simulations

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(see, e.g., ref 36), where definitive observation of melting is usually beyond current computational technology.

Perhaps, the most immediate objection to the Lindemann's criterion is that it involves characteristics of only *one* of the two phases coexisting at melting; a proper criterion, presumably, should compare some property of both phases. For example, in the absence of extensive defects, comparing the bulk free energies would be adequate. In addition, as we now understand, a proper analysis of dynamical melting should proceed with reference to processes at the liquid/solid interface. The present work implements these two notions in the following way.

First, in subsection 2.1, we consider the escape of a molecule from the solid/liquid interface into the liquid. Here, two length scales of molecular motions will arise, whose ratio to the molecular spacing is universal at melting. One length scale is the size of the metastable minimum harboring a molecule which is about to change its location (for example, to exit into the liquid); the other is the extent of the transition state during the exit. The relation of the two scales to the vibrational amplitudes proper will depend on the detailed morphology of the region in question; so for example, the surface roughness or the specific crystal face will affect surface melting. Under most circumstances, nevertheless, the derived criterion will amount to a simple Lindemann-like criterion.

Second, we ask in subsection 2.2, what would be the magnitude of the (weakly activated) molecular displacements in the bulk of the solid, in the presence of alternative structural states. For glass-forming substances, these displacements are actually present in the bulk of the material, if it is supercooled. Otherwise, alternative structural states are present only in a "premelted" layer, if any. A proper melting criterion will be formulated, which amounts to comparing the vibrational molecular amplitudes to the structural displacements: in a stable solid, the former should less than the latter. We will further deduce the dependence of the structural displacements on the material's stiffness and the temperature. The results apply directly to premelted layers and supercooled liquids.

2. Derivation of a Melting Criterion

2.1. Melting at the Interface. It will be most straightforward to see how a melting criterion arises for molecules that are directly at the solid−liquid interface, in the sense that here, simply an isolated activated event is required in order for a molecule to exit irreversibly into the liquid. A number of conventions as to what an "interface" is are possible and are subject to the same ambiguities as the definitions of the phases themselves. It is beyond reasonable doubt that the surface region of a melting solid is far from the simplified text-book pictures, even ignoring surface roughening effects: The interface is not sharp, and often extends for up to several tens of atoms, as could be deduced, somewhat indirectly, from studies of (pre)melted layers demarcating a solid from its vapor.[14,37] (See also a recent review[12] on surface ice melting.) That the interface is "diffuse" near melting has been also concluded theoretically, via density functional studies[38] employing specific ansatzes for the equilibrium distribution functions in the solid and liquid. Furthermore, the heterogeneity across the layer is not only structural but must also involve a heterogeneity in relaxation times, i.e., the lifetimes of long-living local structures. Similar to the density, the lifetimes in the premelt layer interpolate between those in the liquid and the solid. Several ways to deal with the ambiguity in defining a solid−liquid interface may be proposed. For example, Oxtoby and Haymet[38] employ an appropriate equilibrium order parameter changing continuously when going

from liquid to solid. Trayanov and Tosatti[39] analyze premelted layers, in a mean-filed fashion, based on two order parameters, "density" and "crystallinity". Here, to focus on the dynamical aspects of melting, we will use the lifetimes of local metastable structures to establish an operational criterion of whether a molecule is in the solid, or part of the liquid. While the equlibrium interfacial region may be discussed only in a broad sense, as a "diffuse" entity, the dynamic interface will turn out to be thin and well defined.

We will distinguish between the liquid and the solid in the usual way, via symmetry, and will specifically focus on the time scale on which the symmetry is broken/restored. Consider a substance consisting of a single, relatively compact molecular species, in the classical regime. The crystal breaks the translational symmetry in that here, one can *label* the molecules based solely on their each being located within a particular, well-defined cell (c.f., however, the incommensurate quantum crystals[40]). One may speak of a fluid, on the other hand, when such labeling is impossible. The corresponding translational symmetry is physically maintained by particle transport. Call τ_0 the time it takes a molecule to diffuse a distance defining the volumetric density of the liquid. Choose a compact, specific cell, in space, whose volume is equal to the volume per molecule in the liquid. Since the time τ_0 is significantly longer than the time scale of density fluctuations, it is guaranteed that another, identical molecule will have visited the chosen cell, within time τ_0, upon the exit of the previous cell's dweller, thus erasing the possibility that one be able to label a molecule by its spatial location. It is therefore at times exceeding τ_0 that one may speak of a liquid state. Recall also that we are considering compact molecules, and so rotational diffusion/equilibration is not an issue. It is useful, for future reference, to compute the particle exchange time τ_0 in terms of the collisional time. Let $1/a^3 \equiv n$ be the molecular concentration in the fluid, so that a is the average volumetric molecular spacing. The typical collisional, or auto-correlation time (also defining the density fluctuation time-scale) is $\tau_{auto} = m/\zeta$, where $\zeta \simeq 6\pi a\eta$ is the friction coefficient, η is the viscosity, and m is the molecule's mass. The time τ_0 it takes to diffuse a distance a is roughly $a^2/6D$, where D is the diffusion constant, related to the friction through the Einstein's relation $D = k_B T/\zeta$. As a result,

$$\frac{\tau_0}{\tau_{auto}} \simeq \frac{6\pi^2 \eta^2 a}{\rho k_B T} \tag{1}$$

where ρ is the liquid's mass density. One may directly check that, near melting, this ratio is generically about 10^3 but varies within an order of magnitude or so between different substances: For instance, cobalt and sodium yield 1.3×10^3 and 2.1×10^3, respectively. This indicates that it takes about a thousand molecular collisions or so, per molecular volume, to establish local thermal equilibrium in a liquid. Finally, note that the large value of the ratio in eq 1 is an internal test of the argument's consistency: To give a counter example, it would be incorrect to use analogous logic to estimate equilibration times in dilute gases. Here one would find, using the elementary kinetic theory, that $\tau_0/\tau_{auto} \simeq 9(\sigma/a^2)^2 < 1$, where σ is the molecular scattering cross section; clearly τ_0 does not correspond to an equilibration time scale. Of course, the rate-limiting step during equilibration in dilute gases is diffusion in the momentum space, which is responsible for establishing the Maxwell distribution of velocities; whereas in dense liquids near fusion, the rate-limiting step is configurational equilibration.

Consider now a region of space occupied by a solid and its melt, at some temperature T just above the lowest temperature,
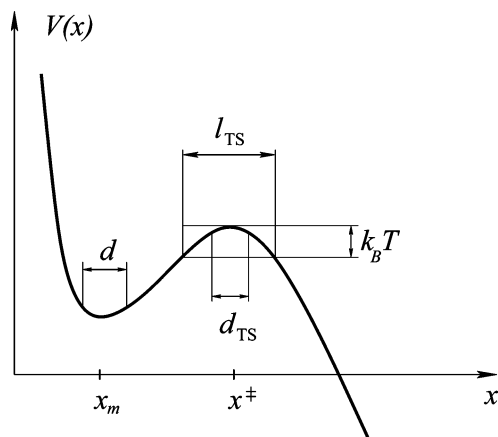
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Figure 1. Generic schematic of an escape free energy profile. l_{TS}, the transition state size, demarcates the vicinity of the saddle point within the thermal energy from the top. d and d_{max} are defined in text.

T_m, at which surface melting is possible. Suppose there is a molecule in the region that fails to move a distance a in the time τ_0. (To avoid confusion we note that if long wavelength sound is present in the system, one should stipulate that the local reference frame move with the sound.) All such molecules cannot be regarded as part of the liquid, as just discussed, and so we must regard them as part of the solid. The boundary of any (spatially) closed set of such molecules may therefore be defined as the solid−liquid interface. On the other hand, the inability of a molecule to move the distance a in time τ_0 is equivalent to saying the molecule is residing in a metastable free energy minimum. In other words, a molecule is part of the solid, if the escape time τ_{escape} from its current neighborhood exceeds the exchange time τ_0:

$$\tau_{escape} > \tau_0 \tag{2}$$

The escape time τ_{escape} will generally differ for distinct crystalline faces, or various distinct surface morphologies. The above stipulation that

$$T = T_m + 0^+ \tag{3}$$

implies that there is at least one specific face/morphology that is in near equilibrium with the liquid, and there are no face/morphologies that are melting in a spontaneous fashion. In the following we will specifically consider those faces that are melting in a quasi-equilibrium fashion. For these,

$$\tau_{escape} = \tau_0 \tag{4}$$

One may regard this expression as the dynamical definition of a solid/liquid interface. A melting temperature T_m, as defined above, will generally differ from the usual calorimetric melting temperature if the solid melts anisotropically. (The latter is usually the case.)

To estimate τ_{escape}, we shall adopt the approach of Frauenfelder and Wolynes (FW)[41] (see also refs 42 and 43), who have delineated the various activated transport regimes and computed the corresponding rates, in terms of several characteristic length scales. First note that, owing to the frequent collisions (see also below), the motion of the reaction coordinate corresponding to the escape mode is strongly overdamped. An operational criterion of this is that the particle's mean free path be significantly shorter than the transition state size: $l_{mfp} \ll l_{TS}$. (A schematic of the free energy profile along the progress coordinate is shown in Figure 1.) As a result, the particle stays

in the transition state region for a long time, relative to the molecular collisional time τ_{auto}, leading to a large number of barrier crossings, while at the top of the barrier $N_c = l_{TS}/l_{mfp}$. The corresponding rate may therefore be estimated using the standard transition state result, multiplied by a (small) transmission factor $\kappa \simeq 2l_{mfp}/l_{TS} = 2\tau_{auto}v_{th}/l_{TS}$, as appropriate in the overdamped Kramers limit. Here, $v_{th} = \sqrt{3k_bT/m}$ is the thermal velocity of the particle. As a result, the Kramers rate reads

$$\tau_{escape}^{-1} = \frac{1}{2} \frac{\langle|v|\rangle}{(\sqrt{2\pi}d)} \frac{2\tau_{auto}v_{th}}{l_{TS}} e^{-V^{\ddagger}/k_BT} \tag{5}$$

where

$$d \equiv \frac{1}{\sqrt{2\pi}} \int_{x_m} dx \exp^{-[V(x)-V(x_m)]/k_BT} \tag{6}$$

is the "size" of the metastable basin. (The label x_m in the integration limits indicates that the integral is understood in its asymptotic sense in terms of the basin's width.) The coefficient $1/\sqrt{2\pi}$ was incorporated in the definition so that $d = \langle(\Delta x)^2\rangle^{1/2}$, if the potential is strictly harmonic at the minimum x_m. $\langle|v|\rangle = v_{th}\sqrt{2/3\pi}$ is the thermally averaged particle speed that enters the expression for the molecular flux at the barrier top. Last, $V^{\ddagger} \equiv V(x^{\ddagger}) - V(x_m)$ is the barrier height. The latter is actually quite easy to evaluate after one realizes that an escape event will have occurred if a particle's displacement just exceeds the typical thermal vibrational amplitude of the interface. This is because the particle will have crossed the thermally definable boundary of the solid and must be regarded as part of the liquid. For this simple argument to be valid, it is essential, again, that the specific face of the solid be wetted by the liquid, i.e., the face be actually melting. Since the typical energy of the surface vibrations is exactly k_BT, the particle's typical displacement free energy cost will not exceed k_BT, hence $V^{\ddagger} = k_BT$. Further, we define

$$d_{TS} \equiv \frac{1}{2\sqrt{2}} l_{TS} \tag{7}$$

where the numerical factor is chosen so that if the barrier is parabolic at the top, then $d_{TS} = \langle(\Delta x)^2\rangle^{1/2}$ in the inverted potential at the saddle point. By definition, $m(\omega^*)^2(l_{TS}/2)^2/2 = k_BT$, where ω^* is the under-barrier frequency, see Figure 1. After putting all this together and recalling that $\tau_0 = a^2/6D = a^2m/6k_BT\tau_{auto} = a^2/2v_{th}^2\tau_{auto}$, one has by eq 4

$$\frac{dd_{TS}}{a^2} = \frac{1}{4\sqrt{6\pi e}} \simeq 0.01 \tag{8}$$

universally. We therefore observe that it is possible to formulate a purely *kinematic* criterion of melting, in terms of the ratio of length scales characterizing molecular motions in the interface region. The numerical constants on the rhs of eq 8 should not, perhaps, be taken too seriously; nevertheless the estimate is expected to be accurate within a factor of 2 or so.

A number of comments are due here. First of all, can one even apply a transition state argument when the barrier is so low? The answer is yes, because of the high friction. Indeed, suppose for a moment there were no barrier. Even so, the exit would be far from instantaneous, being subject to (frequent) collisions with the nearby molecules, just as are the molecular motions in the neighboring liquid. Using the Smoluchowski diffusion-limited reaction rate expression (in 1D), one still gets

the same basic scaling for the escape rate: $k_{escape} \sim D/l_{TS}^2 \sim v_{th}^2 \tau_{auto}/l_{TS}^2$ (see also ref 32). The overdamped character of the molecular motion is essential in the present context, and so one should like to estimate the actual value of the l_{mfp}/l_{TS} ratio, which is effectively the small parameter of theory. The estimate in eq 1 suggests that this ratio is indeed quite small. Numerically it is on the order of 10^{-2}, considering that $d_{TS}/a \sim 0.1$. At any rate, molecular motions in liquids are overdamped near T_m, and so must be the motions in the corresponding crystals near T_m because they are of comparable (usually greater) density.

Despite simplifications due to the high friction, the shallowness of the metastable potential complicates the interpretation of the simple result in eq 8. Since the transition state size is virtually equal to the reaction path length, it probably makes little sense to differentiate between d_{TS} and d. For those same reasons, the integral in eq 6 is only meaningful in the lowest order in the reactant basin width, the expansion being asymptotic of course. This leads to a simpler yet relation

$$\tilde{d}_L \equiv \frac{d_L}{a} \simeq 0.1 \qquad (9)$$

where $d_L \simeq d \simeq d_{TS}$ stands for the amplitude of the reversible motion in the molecular metastable minimum at the liquid–solid interface. The subscript "L" alludes to "Lindemann"; the parameter d_L will be sometimes referred to as the "Lindemann length". Importantly, d_L is a measure of the displacement in the direction of the fastest escape, which is perpendicular to the surface. Further, a signifies the molecular spacing right at the interface. Strictly speaking, this implies our (volumetric) molecular spacing is a variable changing continuously across the interface. This appears reasonable as the crystal and liquid density differ actually relatively little, not by much more than the typical thermal density fluctuations in the crystal, near the melting temperature. (See also the earlier mention of the Oxtoby and Haymet's order parameter.[38]) Finally, the parameters d and d_{TS} should be dererminable in a simulation, with a modest computational effort.

Are the simple relations (8) and (9) consistent with the general notions of surface melting? Yes, in a rather plain way. To give an example, suppose the surface is rough, so that it has a corner or an edge. Clearly the vibrational amplitudes at corners and edges are larger than those at extended flat faces, because there are fewer neighbors. This is consistent with the expectation that corners (and edges) melt first, i.e., at lower temperatures than say flat faces. The relation in eq 9 is quantitatively consistent with Valenta's calculations of the vibrational displacements at the three distinct crystall faces of lead, i.e., (110), (100), and (111).[44] These faces are known to premelt at increasingly higher temperatures. According to ref 44, the vibrational displacements at all three faces turn out to be of nearly the same magnitude of 0.22 Å or so, at the respective premelting temperatures. In any event, one should expect that more densely packed, stiffer faces will exhibit lesser vibrational displacements normal to the interface and therefore will melt at increasingly higher temperatures. This qualitative notion is consistent with the results of MD simulations on an FCC crystal by Kojima and Susa,[45] and on a BCC crystal by Sorkin at el.[4]

2.2. A Thermodynamic Melting Criterion in the Bulk. Let us now discuss the implications of the relations (8) and (9) for the molecular motion amplitudes in the bulk of the solid. The typical *vibrational* displacements, $d_{vib}(0)$, at the surface and in the bulk, $d_{vib}(z)$, will be certainly comparable. The variable z measures the distance from the interface, see Figure 2. In the bulk, the greater lattice stiffness in the bulk will be partially
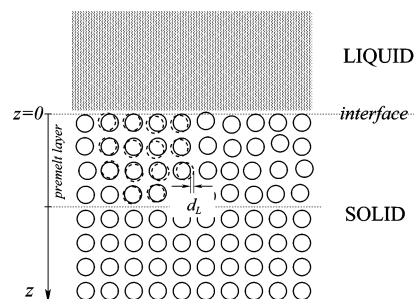

Figure 2. Cartoon of a solid–liquid interface, including the premelt layer; the latter is characterized by some disorder. (Here, we ignore possible roughness or reconstruction of the surface.) The area containing the doubled circles illustrates a region undergoing a cooperative structural reconfiguration. The cooperativity is necessary to minimize density variations during the transition. The solid and the dashed circles denote the atomic configurations before and after a structural transition. An individual, elemental displacement is of magnitude $d_L(z)$ mildly dependent on the distance to the interface. Each of these elemental displacements are nearly activationless; whereas the total cooperative event has a high barrier because the probability of a large number of concerted elemental events is low.

compensated by a smaller lattice constant, save the substances that expand upon freezing. As a result, the local $(d_{vib}(z)/a(z))$ ratio, while also generically of about 0.1 in value in the bulk, is no longer expected to be strictly universal, in contrast to that at the interface (see below). Now, one must bear in mind that motions resulting in a locally different structure, may also be present on the *solid* side of the interface. In the preceding subsection, we have computed the magnitude of the displacements d_L such that would lead to the exit of an atom from the solid into the liquid. In this section, we will compute the magnitude of analogous irreversible atomic displacements, but inside the solid. Here, the atom also exits its present lattice site but to find itself in a reconfigured lattice, not in the liquid. Given the lattice is reconfigured and is poised to accept a particle, the latter will transfer in a nearly activationless fashion, similarly to exiting into the liquid. The lattice reconfiguration itself is a cooperative event consisting of a large number of those elemental, nearly activationless transitions occurring on the time scale τ_{escape}. The latter must occur in a concerted fashion, implying the cooperative reconfigurations are rare and occur on much longer time scales:

$$\tau_{str} \gg \tau_{escape} \qquad (10)$$

where the index "str" indicates "structural".

First of all, do such rare structural reconfigurations take place in the bulk? We argue in the following that they do indeed, within premelted layers. According to the surface calorimetric studies of Santucci at el.,[46] the excess entropy of the "premelted" surface layer of the Li (110) face, relative to the bulk crystal, is about a half of the bulk liquid entropy excess, see Figure 3b of ref 46. (The author is aware of surface calorimetric estimates only on this particular substance; however, comparable values of the surface entropy are expected for other materials as well, see ref 46 and references therein.) This clearly implies that the excess entropy, s_c, within the premelt layer, is intermediate between that of the crystal and the liquid. Furthermore, this entropy must decrease into the bulk, so as to interpolate between the liquid and the solid values. The latter is zero. The relatively high density of states in the premelt, corresponding to $s_c \sim k_B/2$ per particle, would be impossible to account for by translations of vacancies: the vacancy concentration would be too small,

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considering that the density and the compressibility of the pre-melt are comparable to those in the solid bulk. (The vacancy formation energies are in the eV range, of course, see e.g., ref 47.) As a result, the room for molecular translations is provided not by diffusing vacancies, but by some other structural degrees of freedom that involve more than one particle. Another possibility is dislocations, whose significance seems less straight-forward to estimate than that of vacancies. At the present stage of theory, however, it appears that dislocations become important closer to the point of mechanical melting, which they most likely orchestrate in the first place. The mechanical melting temperature seems to be several tens of degrees above the bulk thermodynamic melting point (see refs 1−3 and references therein).

What is the detailed microscopic nature of the configurational degrees of freedom in the surface premelted layer? It is likely that they correspond to transitions between long-living structures analogous to the local metastable structures predicted by the random first-order transition (RFOT) theory of supercooled liquids and glasses of Wolynes and co-workers.[48−50] The transitions span regions 3 to 6 molecular units across and have been directly observed by a variety of nonlinear spectroscopies, see ref 51 for a recent review. The configurational entropy of a supercooled liquid, just above the glass transition, is about $0.8k_B$ per molecular unit. It is therefore comparable to that in the premelted layers. To complete the analogy, note the viscosity of supercooled melts, near T_g, is extremely high, consistent with the premelted layers exhibiting progressively slower relaxation away from the interface proper.

One may estimate, semiquantitatively, how the magnitude of the elemental displacements decreases away from the surface, as the stiffness increases. The magnitude of the displacements will generally depend on the distance from the interface, i.e., $d_L = d_L(z)$, see Figure 2. Because a particle exits not into the liquid but into a matrix poised to receive the particle, we no longer have the convenience of the barrier being equal to the thermal energy. We may say, nevertheless, that the barrier will increase into the bulk because the lattice stiffness increases away from the surface. Let us denote this z-dependent barrier as $V^{\ddagger}(z)$, so that

$$V^{\ddagger}(0) = k_B T_m \qquad (11)$$

Now, it turns out that both τ_{auto} and τ_{escape} are z-independent, because of the detailed balance: There is no net particle transport at these time scales. The actual net particle transport occurs at the much slower time scale, τ_{str}, of the extended structural transitions and is consistent with the existence of a density gradient in the premelt layer. (The detailed balance argument above is valid only when the elemental and the structural transitions are time scale separated, which is indeed true in view of eq 10.) The constancy of τ_{auto} and τ_{escape}, together with eqs 5 and 11, yield that the following quantity is invariant throughout the solid:

$$\left[\frac{d_L(z)}{d_L(0)}\right]^2 e^{(V^{\ddagger}(z)/V^{\ddagger}(0))} = e \qquad (12)$$

This statement can be used to self-consistently determine the value of the $d_L(z)/d_L(0)$ ratio, after one recalls that the activation barrier $V^{\ddagger}$ arises from the elastic strain of the lattice. Since the thermally relevant vibronic displacements are within about one-tenth of the molecular spacing or less, the elastic energy, as a
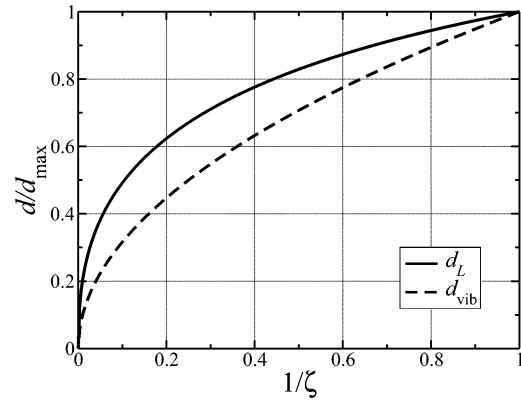

Figure 3. Dependences of the Lindemann and the vibronic displacements, relative to their maximal value $d_{\max}$, achieved at the surface, as functions of the dimensionless stiffness ζ. The latter is the product of the elastic constant and the lattice constant, in terms of the minimum value of this product achieved at the surface.

function of the lattice strain, is dominated by the quadratic component, i.e.:

$$V^{\ddagger}(z) \simeq K(z)\left[\frac{d_L(z)}{a(z)}\right]^2 a^3(z) = K(z)a(z)d_L^2(z) \qquad (13)$$

Here, $K(z)$ is a local effective elastic modulus that depends both on the isotropic compressibility and the shear modulus, and $a(z)$ is the *local* volumetric spacing; in other words $V^{\ddagger}(z)$ gives the elastic energy arising from the local strain $[d_L(z)/a(z)]^2$, per molecular volume. (The ratio $[d_L(z)/a(z)]^2$ is a measure of the thermally averaged square of the dimensionless elastic strain used here as in the standard elasticity theory.[52]) One obtains, as a result:

$$\left[\frac{d_L(z)}{d_L(0)}\right]^2 e^{\zeta(z)[d_L(z)/d_L(0)]^2} = e \qquad (14)$$

where, again, $[d_L(0)] \simeq 0.1a$ and the parameter $\zeta(z)$ gives the stiffness of the lattice, at distance z from the interface, relative to its value at the interface:

$$\zeta(z) = \frac{K(z)a(z)}{K(0)a(0)} \qquad (15)$$

Note that $K(0)a(0)d_L^2(0) = V^{\ddagger}(0) = k_B T_m$. We stress again that the (very low) barriers, implied in eqs 13 and 14, correspond to elemental translations that would occur given that another structural state exists and therefore apply to *all* of the bulk. Because the elemental events are subject to the existence of an underlying structural transition in the corresponding region, it is appropriate to term the displacements d_L as *fiduciary* displacements, or *presumable* displacements.

It is easy to solve, numerically, eq 14 for the $d_L(z)/d_L(0)$ ratio as a function of the dimensionless stiffness $\zeta(z)$, with the result shown in Figure 3. The fiduciary displacement $d_L(z)$ should be compared to the thermal vibrational amplitude $d_{\text{vib}}(z)$, which is fixed by the equipartition theorem:

$$K(z)a(z)d_{\text{vib}}^2(z) = k_B T \qquad (16)$$

The lhs of the equation gives the usual elastic energy density of the solid, times the volume of a unit cell. As follows from the discussion in the preceding subsection,

$$d_{\text{vib}}(0) = d_L(0) \equiv d_{\max} \qquad (17)$$

The vibronic displacement $d_{vib}(z)$ depends on the stiffness in a very simple way, and is shown in Figure 3, alongside the ζ-dependence of the fiduciary, Lindemann diplacement. Note that here we did not have to treat explicitly the anisotropy of elastic properties, as long as we were consistent in measuring the displacements $d_L(0)$ and $d_{vib}(0)$ normal to the free surface.

Since the z-variable is a dummy label, it is appropriate to simply think of the displacements d_L and d_{vib}, relative to their maximal values achieved at the surface, as functions of the dimensionless stiffness ζ. According to Figure 3, it is always true that

$$d_{vib}(z) < d_L(z), (z > 0) \qquad (18)$$

(cf. eq 2). We therefore observe that solids may be defined as collections of molecules in which the magnitude of purely vibrational excitations is always smaller than the extent of the fiduciary structural displacements. As a result, a solid is (typically) capable of sustaining vibrational excitations without irreversible structural changes. According to Figure 3, a more stable solid corresponds to greater values of the stiffness parameter ζ, corresponding to larger values of the difference $(d_L - d_{vib})$. One may therefore interpret eq 18 as saying that the stiffness of a lattice that allows for alternative structures is somewhat smaller than the stiffness of the corresponding lattice which is strictly elastic, i.e., mechanically stable. We thus observe that vanishing of the shear modulus is *not required* in order for the lattice to be locally mechanically unstable. Now, the limiting situation where $d_{vib}(z) = d_L(z)$, at $z = 0$, bears a dual meaning: (a) it signifies melting and (b) it defines the boundary between the solid and the liquid phase. In view of eq 12, the statements in this paragraph are valid regardless of the elastic free energy being strictly quadratic in the displacement. Finally, note that eqs 14 and 16 are laws of corresponding states for the structural and vibrational displacements in a solid.

We have thus found that formulating a criterion of melting and defining a solid, in the first place, requires introducing *fiduciary* structural modes, in the sense that these modes may or may not be readily observed in a real material. We have argued that such modes probably exist in a sufficiently extended premelt layer. Otherwise, there is still a way to force the solid to sample the spectrum of those structural excitations, even at temperatures below the melting point, namely by quenching the corresponding substance from its liquid state into a frozen glass. Many polymers simply do not form crystals and are difficult to characterize morphologically in a definite way, in the first place. In these, there is no shortage of structural transitions. A similar comment applies to folded proteins. Certain substances that are very difficult to supercool, such as ice, amorphize under pressure (see e.g., ref 53). Finally, energetic particle beams may be employed to locally force a crystal into a structurally excited state. The possibility of such externally induced structurally excited states is actually a physical realization of a Maxwell construction! To give an analogy, the Maxwell construction in a nonideal gas also uses presumable states such that $(\partial p/\partial V)_T > 0$, in deriving a criterion of a first-order transition, i.e., boiling/condensation.

Now, suppose there *is* a significant premelt layer on the surface. Direct spectroscopic observations of these are intrinsically difficult, since a beam (neutron or X-ray) sufficiently intense to produce useful signal, would also inevitably heat up and liquefy the surface. On the other hand, surface, near-atomic resolution techniques, such as those employed by Israeloff,[54] may be helpful in characterizing structural surface modes. Importantly, a conclusive surface study must be nonlinear, so as to sense *dynamic* heterogeneity, to distinguish irreversible structural relaxations from purely vibrational excitations.

Finally, for completeness, one should like to see whether the arguments above would also be robust in systems other than single-component liquids. Unfortunately, mixtures necessitate considering many additional factors, well beyond the scope of this article, primarily owing to the details of interaction between the constituents of the mixture, phase separation, etc. Here we will limit ourselves to a few remarks. Suppose the molecules are (chemically identical) rigid, relatively weakly interacting rods. Clearly the melting will occur from the face parallel to the orientation of the rods, otherwise the molecule would have to slide out of the matrix, which would be too costly energetically. (We assume the rods are closely packed, in a collinear fashion.) The "melting displacement" d is therefore perpendicular to the orientation of the rods, and, consequently, is also about one tenth of the *monomer* size, but probably not universally. Analogous logic applies to a crystal made of weakly interacting disk-shaped molecules, which will melt off the crystallographic plane parallel to the disk planes. (This is in the case when the disks are stacked in a coplanar manner.) The case of monovalent ionic melts is probably adequately viewed as that of a single-component substance with a slightly elongated molecule, since the melt will tend to be locally electrically neutral, on average. Again, we recover the basic estimate from eq 9 where a is the volumetric spacing between the distinct moieties, *not* the unit cell size; d is the displacement between the neighboring atoms.

3. Activated Motions in Supercooled Liquids as Local Melting

The analysis of subsection 2.2 was conducted on the assumption that solids exist, of course. In other words, the argument by itself could not be used to establish the existence of a solid state, but could only give the conditions of stability of a solid once it is formed. The details of solidification, below T_m, are known to depend on how fast one cools the substance and on the viscosity of the liquid. If either the cooling speed or the viscosity is high enough, the nucleation of the crystalline phase will be prevented, with the liquid finding itself in a supercooled state for a significant amount of time.

Here, we will estimate the temperature dependence of the elemental displacements in a liquid that was cooled below its fusion point but has failed to crystallize. Since the structural equilibration has never occurred, displacements must take place such that they imply a change of the local structural state. Since these displacements are at the mechanical stability edge of the material, we may also denote their magnitude with $d_L(T)$, where we explicitly indicate the temperature dependence of the magnitude of the elemental displacements. (Clearly, $d_L(T_m) = d_L(z=0)$.) Therefore in a supercooled liquid, the displacements d_L are no longer fiduciary, but strictly factual. On the other hand, the regular liquid state, which does not discriminate between molecular displacements of less than size a (recall our "labeling" discussion), now becomes a fiduciary state! (For reference, we point out such a regular liquid state explicitly arises, for instance, in the DFT study of aperiodic crystals in ref 23, or of the mean-field Potts glasses.[55]) We may use this new fiduciary state to write the law of corresponding states from eq 14 at a temperature T *below* T_m:

$$\left[\frac{d_L(z, T)}{d_L(0, T)}\right]^2 e^{\zeta(z,T)[d_L(z,T)/d_L(0,T)]^2} = e \qquad (19)$$

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Here, even though the z variable is dummy, it is strictly implied that $z = \infty$, i.e., the interface is infinitely remote from the bulk, by construction. Since the universal quantity $\tilde{d}_L \equiv d_L(0)/a(0)$ is, by its very meaning, temperature independent, it is convenient to rewrite the above relation in the following form:

$$\frac{(d_L/a)^2}{\tilde{d}_L^2} e^{\zeta(Ka^3/T)[(d_L/a)^2/\tilde{d}_L^2]} = e \tag{20}$$

where

$$\zeta(Ka^3/T) \equiv \frac{K(T)a^3(T)/k_B T}{K(T_0)a^3(T_0)/k_B T_0} \tag{21}$$

As a reminder, $K(T_0)a^3(T_0)\tilde{d}^2/k_B T_0 = 1$, for any T_0. While, in principle, the interface at any temperature $T_0 \leq T_m$ may be used as a reference state, in practice one can measure the stiffness only at the physical melting temperature T_m; therefore, most conveniently one would set $T_0 = T_m$ in eq 20. Again, we have arrived at a law of corresponding states, even though the variables are distinct from those entering eq 14. The displacements are in relation to the lattice spacing; the running coupling constant Ka^3/T, governing the displacements magnitude, is dimensionless too, and is of the order 1. The latter suggests that below the melting temperature (but above vitrification!) the system remains at a delicate balance between energetic and entropic contributions to its free energy (see also ref 49 and the discussion of the surface energy below).

As already mentioned, the RFOT theory has built a constructive, microscopic picture of structural relaxations in deeply supercooled liquids and frozen glasses. We learn from the RFOT theory that one may think of structural rearrangements in deeply supercooled liquids as activated growth of distinct aperiodic phases within each other. The corresponding activation profile is:[48,49]

$$F(N)|_{T>T_g} = \gamma\sqrt{N} - Ts_c N \tag{22}$$

where N is the number of particles in the nucleus of the new structural state within the previous structural state. The configurational entropy (the $-Ts_c N$ term) drives the transitions, while the barrier arises due to the mismatch energy penalty, $\gamma\sqrt{N}$, between distinct states. This mismatch may be thought of as the surface tension of a *domain wall* separating the two alternative structural states. As already mentioned, the elemental displacements occur on a conditional basis, if an alternative structural state is present locally. As a result, the full RFOT structural relaxation rate is:

$$\tau_{RFOT}^{-1} = \tau_{escape}^{-1}(T, z = \infty)e^{-F_{RFOT}^{\ddagger}/T} \tag{23}$$

(The time scale τ_{str}, introduced earlier, was an analogue of the time scale τ_{RFOT} but in the context of structural relaxations in premelted crystalline layers.)

The elemental translations, corresponding to the length d_L, play an important role in the RFOT theory, for a number of reasons. First of all, the corresponding length scale arises as an order parameter during a first-order crossover from the "regular" liquid state to the one where metastable structures persist for a discernible time. (For a deep enough quench, this time is given by τ_{RFOT}^{-1} from eq 23.) In the course of this crossover, the localization length of a molecule jumps from infinity to a finite value, i.e., d_L itself.[23] This localization length depends only

weakly on the temperature/density, as the DFT study in ref 23 suggested. The near constancy of the Lindemann ratio d_L/a turned out instrumental in establishing the near universality of the surface tension coefficient between locally competing liquid structures in deeply supercooled liquids. This surface tension was computed by Xia and Wolynes (XW)[49] without adjustable parameters: it depends only logarithmically on the Lindemann ratio leading to the following expression for the tension coefficient γ:

$$\gamma = \frac{2\sqrt{3}\pi}{2}k_B T \ln\left[\frac{(a/d_L)^2}{\pi e}\right] \tag{24}$$

(The notations are from refs 51 and 56.) This result, among other things, enabled XW to calculate the numerical value of the barrier for structural reconfiguration from eq 22, leading to specific estimates of the size of a cooperatively rearranging region. This size grows from a few molecular units ("beads"), near T_m, to roughly 200 beads near the glass transition, implying each region is about 5–6 beads across near T_g. (A bead typically consists of a few atoms; for a detailed discussion see ref 57, and also ref 58).

The present arguments enable one to compute explicitly the temperature dependence of the Lindemann ratio, based on the relation in eq 20. The result is shown, again, in Figure 3, where $\zeta^{-1} = k_B T/(K(T)a^3(T))$ now, see eq 21. The lattice spacing of the liquid will decrease and the elastic constants will increase with lowering the temperature, albeit weakly. Here, of course, we mean the high-frequency elastic constants, which are definable on time scales shorter than the lifetimes of the long-living metastable structures. For most substances, the ratio $T_g/T_m \sim 2/3$, empirically. As a result, the parameter ζ^{-1}, in Figure 3, will decrease at most to the value of 0.67, before the liquid freezes into a glass, leading to $d_L(T_g)/a(T_g) \simeq 0.9\tilde{d}_L$, according to the figure. We have thus established, on a first-principles basis, that the d_L/a ratio indeed varies little with temperature, at most by 10%. This corroborates the use of the Lindemann criterion, by the RFOT theory, to establish the near universality of the surface tension on the basis of a near universality of the molecular displacement at the mechanical stability edge, relative to the molecular spacing. Finally, the computed temperature dependence of the Lindemann length d_L should be measurable by neutron scattering, as in ref 26.

Further we can see explicitly what parameters in the problem drive the surface energy γ, by substituting the running value of the d_L/a ratio from eq 20 into the logarithm in eq 24:

$$k_B T \ln\left[\frac{(a/d_L)^2}{\pi e}\right] = k_B T[\ln(4\sqrt{6}) - 1] + V^{\ddagger}(T) \tag{25}$$

where $V^{\ddagger}(T) = K(T)a(T)d_L^2(T)$ is the actual energy barrier for a typical elemental translation, as stemming from the lattice strain; also, $[\ln(4\sqrt{6}) - 1] \simeq 1.28$. It follows from the equation above that the energetic and entropic contributions to the surface tension are actually comparable at all temperatures above vitrification: $T > T_g$. For the reference, we show in Figure 4 the $V^{\ddagger}(T)/k_B T$ ratio, which is easily computed from eq 20, as a function of ζ. At $\zeta^{-1} \simeq 0.67$, $V^{\ddagger} \simeq 1.21k_B T$. It is not entirely clear, at present, what significance should be attributed to the ζ^{-1} interval that corresponds to temperatures below vitrification.

Finally, it seems instructive to make an explicit estimate of the $\tau_{escape}^{-1}(T, z = \infty)$. As already mentioned, the number of collisions per unit time, for a harmonically confined particle, scales linearly with energy, leading to $\tau_{auto}(T)/\tau_{auto}(T_m) = T_m/T$. This and eqs 5–8 yield:

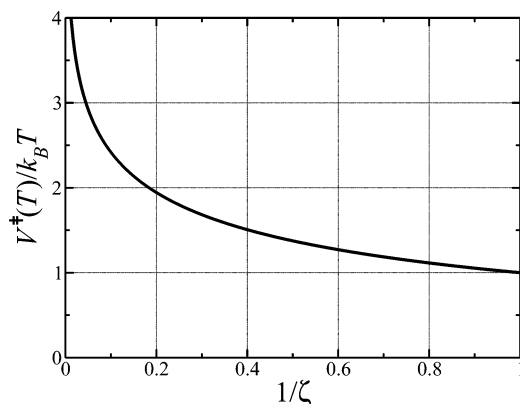**Figure 4.** Ratio of the energy barrier to the temperature, for an elemental translation, as a function of ζ.

$$\tau_{\text{escape}}^{-1} = \sqrt{3/8}\,\frac{D(T_\text{m})}{\pi dd_{\text{TS}}}e^{-V^{\ddagger}/k_\text{B}T} = \tau_0^{-1}(T_\text{m})e^{1-V^{\ddagger}/k_\text{B}T} \quad (26)$$

where $D(T_\text{m})$ and $\tau_0(T_\text{m})$ are the regular diffusion constant and the equilibration time scale τ_0 of the corresponding liquid at the melting temperature T_m. The term $\tau_0(T_\text{m})$ is about 10 picoseconds, and the exponential part actually does not lead to an activated temperature dependence, but a much weaker one, in view of Figure 4.

4. Summary

We have established the existence of a universal criterion of melting in terms of the ratio of length scales characterizing the escape of a particle from its current metastable configuration. The criterion is therefore purely kinematic. The obtained quantitative results are consistent with earlier studies of displacements at crystal surfaces for several specific substances.[4,44,45] The said length scales are closely related to the vibrational amplitudes in the crystal bulk, which was argued to underlie the otherwise puzzling consistency of the empirical Lindemann criterion.

A proper treatment of bulk mechanical stability has been performed, and has required considering "fiduciary" alternative structural states in the lattice. Such alternative states are known to exist in supercooled liquids and glasses and were argued here to exist in a premelted layer at the liquid−crystal interface. A proper criterion of mechanical stability was formulated; it stipulates that the vibrational molecular displacements be less than the elemental displacements that would occur during the multiparticle structural transitions. We have seen that vanishing of the shear modulus is not necessary for the lattice to be mechanically unstable, consistent with the apparent high configurational entropy of premelt layers. Direct observation of cooperative rearrangements in such layers is difficult, but may be possible with available surface techniques.

We have computed the dependence of the elemental displacements on the material's stiffness and on the temperature. When taking place in supercooled liquids, these can be measured, for instance, by neutron scattering.

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