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Surface defreezing of glasses

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Abstract. – A glass surface may still flow below the bulk glass transition temperature, where the underlying bulk is frozen. Assuming the existence at $T = T_0$ of a bulk thermodynamical glass transition, we show that the glass-vapor interface is generally wetted by a liquid layer of thickness $l \sim -\ln(T_0 - T)$ when $T \rightarrow T_0^-$. Contrary to standard surface melting of crystals however, the integrated value of the diffusivity across the interface remains finite for $T \rightarrow T_0^-$. Difference in shape induced by bulk and by surface flow is discussed as a possible means of experimental detection of surface defreezing.

Glasses embody the paradigm of broken ergodicity in condensed classical systems. While most approaches to glasses address an infinite, homogeneous system, there is a clear scope for extension to inhomogeneous situations, as they may be variously realized in real life. The most common—and conceptually the simplest—kind of inhomogeneity is represented by the surface. The problem we wish to address here is the state of a free glass surface, in the neighborhood of the bulk glass transition temperature T_0 .

In crystals near the bulk melting temperature T_M , surface melting is well documented both experimentally and theoretically. As $T \rightarrow T_M$ along the solid-vapor bulk coexistence line, most crystalline faces of a majority of substances develop a microscopic liquid film which spontaneously wets, in full thermal equilibrium, the solid-vapor interface [1, 2]. The thickness of the film diverges as $T \rightarrow T_M$, explaining among other things why crystals with free surfaces cannot sustain overheating. The surface acts as a “defect” where the liquid phase microscopically nucleates.

Due in part to the lack of a comparable understanding of the properties of even bulk glasses, the possibility that similar phenomena might take place at the surface of glassy materials has been given very little attention so far, in spite of its potential importance, both conceptual and practical. Conceptually, the purely dynamical arrest typical of glasses provides a neater example of broken ergodicity than that of the solid, where the crystalline order parameter represents an additional complication. Practically, the possible flow of surfaces can be expected to play a role in measurable properties of glasses, such as friction, surface flow

under intense acceleration, interfacial contact, and other phenomena. In this letter, we base on a thermodynamic glass transition theory, of the type recently considered within the glass community [3], our first attack to the glass surface problem.

Given a thermodynamic formulation with a well-defined free energy *versus* some order parameter, such as the atomic density $n(r)$, or the energy density $e(r)$, the natural approach to try first is a Landau theory [2]. For crystals, it provides what certainly is the simplest microscopic theory of surface melting, summarized as follows. Call $f(n)$ the bulk free energy density, a function of the (uniform) atomic density n . The global free energy cost of a solid-vapor interface from the solid at $x = -\infty$, to the vapor at $x = +\infty$ is

$$F[n(x)] = \int_{-\infty}^{+\infty} [f(n(x)) + (J/2)(dn(x)/dx)^2] dx. \quad (1)$$

Strictly short-range forces are assumed, and the gradient term ($J > 0$) accounts as usual for reluctance of the order parameter n against spatial change, assumed to be sufficiently slow. Along the solid-vapor coexistence line, and just below the triple point T_M , $f(n)$ will exhibit, besides the two identically deep (solid and vapor) minima $f(n^s) = f(n^v)$ at $n = n^s$ and n^v respectively, a third, shallower minimum $f(n^l) = f(n^s) + \Delta$ at the intermediate liquid density n^l , in which $\Delta = \varepsilon_0(T_M - T)$, where $\varepsilon_0 > 0$ is a constant.

Minimization of the free energy (1) is formally identical, via the equivalence $n \rightarrow z$, $x \rightarrow t$, to minimization of the action of a classical point particle of coordinate z and mass J , moving in a potential $V(z) = -f(z)$, with energy exactly equal to $-f(n^s) = -f(n^v)$. The resulting equilibrium interface profile $n(x)$ exhibits, between the solid and the vapor, an intermediate liquid film. Calling γ the curvature of $f(n)$ at the liquid minimum, the thickness of the liquid film is given by $l \simeq -\sqrt{J/\gamma} \ln(\Delta)$, which diverges as T approaches T_M from below, demonstrating surface melting (in real crystals, the logarithmic divergence usually turns to a power law, due to long-range forces, not included in (1) [1, 2]).

To apply arguments similar to these to a glass-vapor interface we must have, as a starting point, a thermodynamical description for the properties of bulk glasses. For that, a first necessary assumption is that crystalline states of the system, even if lower in free energy than any of the glass configurations, can be ignored. Experimentally, crystallization of glasses can be kinetically avoided by a sufficiently rapid cooling in the absence of crystalline germs. With this assumption we can consistently speak of the glass transition as an equilibrium phenomenon, even though it actually occurs on a metastable branch of the phase diagram.

We will thus suppose that there is a thermodynamic glass transition for the bulk system. The configurational entropy of the system s_c as a function of the enthalpy h (to be used instead of the internal energy e , since we work at constant pressure) should vanish for h lower than some h_0 , and increase linearly for h greater than h_0 . The glass transition is in this scheme a second-order, mean field transition [4]. The critical temperature T_0 is given by $T_0^{-1} = \partial s_c / \partial h|_{h_0}$. For $T < T_0$ the system freezes in the configurational ground state, and thermodynamical variables such as specific heat give information only about the vibrational structure of the valley around the ground state. For $T > T_0$ a configurational contribution arises, that counts the number of different valleys that the system is able to sample. The specific heat has a finite jump at $T = T_0$, sometimes referred to as the Kauzmann temperature [5, 6].

A further connection of this thermodynamic picture with dynamical properties *at equilibrium* is given by the phenomenological Adam-Gibbs formula [7], that relates the configurational entropy to dynamical variables such as the viscosity, or the diffusivity D , in the form $D = D_0 \exp[-\frac{A}{Ts_c}]$, where $D_0 > 0$ and $A > 0$ are constants. This formula can be made

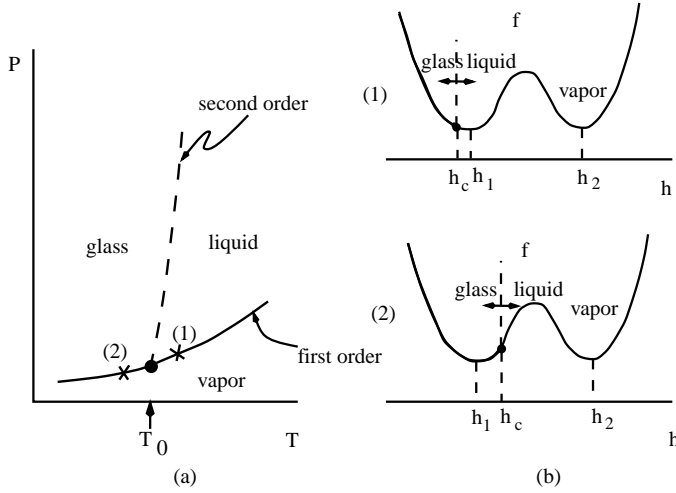


Fig. 1 – (a) Generic pressure-temperature phase diagram for a system with glass, liquid, and vapor phases (a possible crystalline phase is not indicated). (b) Free energy density as a function of the enthalpy at two coexistence points on the first-order line of (a). The coexistence is between liquid and vapor in (1), and between glass and vapor in (2).

heuristically plausible [7] but is not rigorous, and should be considered just a useful working hypothesis. As $T \rightarrow T_0$, s_c and thus D vanish, reflecting the impossibility for the system to jump between valleys, for only one is thermodynamically favored. When applied to the previous description of a bulk glassy phase, the Adam-Gibbs formula is consistent with a Vogel-Fulcher-Tammann-type temperature dependence of the diffusivity, which is experimentally well verified for many different glass formers [5].

Next, we will assume our system to possess in addition to the glass-liquid transition, a liquid-vapor transition. At each temperature below the liquid-vapor critical temperature the free energy $f(h)$ will have two minima, one corresponding to the vapor and the other to the condensed phase, the same minimum comprising both liquid and glass because, as fig. 1 indicates, the glass-liquid transition is second order. At the very minimum the system will be liquid or glassy depending on whether T is lower or larger than T_0 . The second-order nature of the glass-liquid transition reflects in a jump in the second derivative of $f(h)$ at some critical value of the enthalpy h_c (h_c may be different from h_0 due to vibrational contributions). On the phase boundary between the vapor and the dense phase the two minima of the free energy are degenerate, $f(h_1) = f(h_2)$.

We can now model the glass-vapor interface at bulk coexistence, where the bulk enthalpies of the two coexisting phases are h_1 and h_2 . We will suppose, as in the crystal-vapor interface, that the system can be assigned a well defined, slowly varying enthalpy density $h(x)$ at each position x across the interface. Moreover, for $x \rightarrow -\infty (+\infty)$, $h \rightarrow h_1 (h_2)$, forcing the existence of the interface through the boundary conditions. In the end, we will derive the interface profile $h(x)$ by minimizing a free energy functional qualitatively similar to that in (1), but using enthalpy as the order parameter instead of density, and with only two minima instead of three.

A schematic representation of the interface enthalpy profile $h(x)$ in the case $T < T_0$ is given in fig. 2. This function interpolates between the two minima h_1 and h_2 of fig. 1(b). We expect a weak singularity of $h(x)$ where $h = h_c$, the point in which $f(h)$ has a jump in

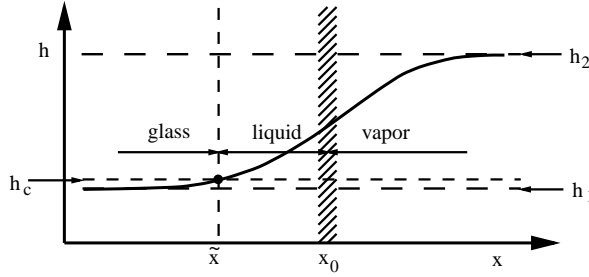


Fig. 2 – Evolution of the interface enthalpy density from the glass at the left to the vapor at the right ($T < T_0$). The glass-vapor interface is coated by a liquid film of thickness $l \sim x_0 - \tilde{x}$.

the second derivative. The corresponding point \tilde{x} marks the border between the glass at the left, and the liquid at the right. The liquid transforms into the vapor phase roughly at some $x = x_0$, where the maximum of $f(h)$ is overcome, and the rate of change of $h(x)$ should be maximum. The difference $l = x_0 - \tilde{x}$ can be identified with the thickness of the liquid layer that wets the glass-vapor interface. We are interested in the behavior of the system around $T = T_0$. Exactly at this point h_c coincides with the minimum of f , and for slightly different values it may be supposed to have a linear dependence on $T_0 - T$, namely $h_c - h_1 = \varepsilon(T_0 - T)$.

To calculate $h(x)$ and from that l , we proceed in the following way. As already mentioned, the free energy $f(h)$ is smooth except in the point h_c , where it has a jump in the second derivative. We will approximate $f(h)$ with its quadratic expansion close to h_c :

$$\begin{aligned} f(h) &= \gamma' h^2/2, & h < h_c, \\ f(h) &= \gamma(h - h_c(1 - \gamma'/\gamma))^2/2 + f_0, & h > h_c, \end{aligned} \quad (2)$$

where we have taken $h_1 = 0$ for simplicity. γ and γ' ($\gamma' > \gamma$) are constants related to the bulk properties of the material, and f_0 is a constant ensuring continuity of f at h_c . The Euler equation satisfied by the equilibrium profile $h(x)$ is, from (1),

$$df(h)/dh = Jd^2h/dx^2. \quad (3)$$

For $f(h)$ given by (2), the solution can be written in terms of exponentials, and a direct calculation shows that

$$\begin{aligned} h(x) &= Ae^{\sqrt{\gamma'/J}x}, & h < h_c, \\ h(x) &= (h_m + u)e^{\sqrt{\gamma/J}x} - u, & h > h_c, \end{aligned} \quad (4)$$

where $u = h_c(\gamma'/\gamma - 1)$ and $A = h_c[(h_m + u)/(h_c + u)]^{\sqrt{\gamma'/\gamma}}$ are values that depend on temperature through h_c . Here we have set $x_0 = 0$, assuming that the barrier of $f(h)$ is parabolic up to the maximum, that occurs precisely at h_m . Then the solution (4) describes the interface in the condensed region. Deviations are expected to occur around the liquid-vapor transition. The position \tilde{x} of the liquid-glass interface, namely the point at which $h(\tilde{x}) = h_c$ can be written as

$$\tilde{x} = -\sqrt{J/\gamma} \ln[(h_m + h_c(\gamma'/\gamma - 1))/(h_c\gamma'/\gamma)]. \quad (5)$$

This value diverges when $T \rightarrow T_0^-$, indicating the presence of a diverging liquid layer of thickness

$$l \simeq -\sqrt{J/\gamma} \ln \left[\frac{\varepsilon(T_0 - T)\gamma'}{h_m\gamma} \right]. \quad (6)$$

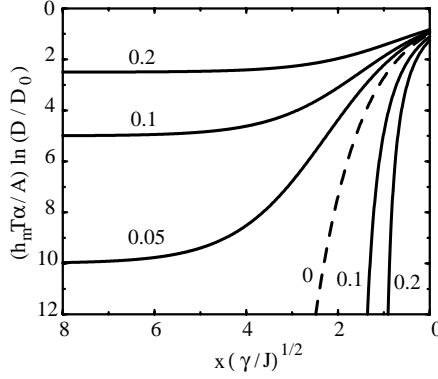


Fig. 3 – Diffusivity across the glass-vapor interface for different values of $\varepsilon(T_0 - T)/h_m$, indicated on the curves (the particular value $\gamma'/\gamma = 2$ was used). The dense phase (glass for $T < T_0$, liquid for $T > T_0$) is at the left, while for $x \gtrsim 0$ the system is in the vapor phase. The curve for the bulk glass transition temperature $T = T_0$ is shown as a dashed line. Note the finite diffusivity in a “melted” surface film for $T < T_0$, and also the residually higher surface diffusivity just above $T = T_0$.

The spatial scale for the thickness of the liquid layer is thus given by $\sqrt{J/\gamma}$, exactly as for a liquid layer at the crystal-vapor interface. This underlines a common physical origin, namely a lower surface free energy of the liquid relative to the solid.

The logarithmic increase of the liquid layer thickness close to T_0 is at first sight also the same as that of the liquid layer in short-range crystal-vapor surface melting. However the conceptual origin of the logarithmic behavior is different here, as it relates to a second-order liquid-solid transition, as opposed to a first-order one in the crystal case. In practice too, glass surface melting should be quite different. In crystals, the density jump associated with melting gives inevitably rise to different optical conductivities of solid and liquid, leading to a nonzero Hamaker constant H and to long-range dispersion forces $\sim H/l^2$ [8]. A positive Hamaker constant will thus enhance surface melting, and generally transform the logarithmic into a power law growth, $l \sim (T_M - T)^{-1/3}$ [1, 2]. A negative Hamaker constant will instead suppress, or block, surface melting [9]. So will, for a different reason, commensuration of surface layering with the spacing of crystal planes [10]. In the glass there are no crystal planes to block surface melting. Moreover, the bulk density and optical conductivity of glass and liquid are not expected to differ discontinuously and the Hamaker constant should basically vanish. In conclusion, in glass surface melting the logarithmic film growth behavior should be more robust.

We can also calculate the diffusivity profile $D(x)$. The configurational entropy vanishes linearly with h close to the liquid-glass transition, namely

$$\begin{aligned} s_c(x) &= \alpha(h(x) - h_c) = \\ &= \alpha \left[e^{\sqrt{\gamma/J}x} \left[h_m + h_c \left(\frac{\gamma'}{\gamma} - 1 \right) \right] - h_c \frac{\gamma'}{\gamma} \right], \end{aligned} \quad (7)$$

where α is some constant. Using the Adam-Gibbs formula, we obtain

$$\begin{aligned} \ln(D(x)/D_0) &= \frac{A}{T\alpha} \times \\ &\times \left[\varepsilon(T_0 - T) \left[\frac{\gamma'}{\gamma} - \left(\frac{\gamma'}{\gamma} - 1 \right) e^{\sqrt{\gamma/J}x} \right] - h_m e^{\sqrt{\gamma/J}x} \right]^{-1}, \end{aligned} \quad (8)$$

valid for T close to T_0 , and x close to the liquid-glass transition value \tilde{x} . For larger values of $x - \tilde{x}$, the non-quadratic nature of the free energy functional (particularly the maximum between the vapor and condensed phases) should be taken into account properly. If $T < T_0$, the previous expression is valid for $x > \tilde{x}$, and D is 0 for $x < \tilde{x}$. If $T > T_0$, *i.e.*, if the bulk system is in the liquid phase, then (8) is valid for all x . In this case $D(-\infty)$ is different from zero, and (8) predicts an enhancement of the diffusivity at the surface compared to that of the bulk. We have plotted the behavior of $D(x)$ in fig. 3 for different temperatures. It should be noted that the integrated diffusivity $\mathbf{D} \equiv \int D(x)dx$ tends to a finite value $\mathbf{D} \sim D_0 \sqrt{J/\gamma} \exp \left[\frac{-A}{T_0 \alpha h_m} \right]$, when $T \rightarrow T_0^-$. This is at variance with what happens for melting of crystal surfaces, where $\mathbf{D} \sim l$. Hence surface melting is in a sense much weaker on the glass surface than on the crystal surface.

Experimental detection of the liquid layer predicted by theory to exist at the glass-vapor interface should be possible. One method might be to look for “slumping” (thinning of one end and thickening of the other end) of initially shape-controlled glass samples in a centrifuge. The shapes expected for bulk-flow-induced and for surface-flow-induced slumping are different. Generally speaking, bulk flow under acceleration should preserve sharp edges and flat profiles, transforming, *e.g.*, a rectangular shape to a trapezium [11]. Surface flow under parallel acceleration will modify a given profile $y(x)$ in time according to an equation of the type [12]

$$\frac{\partial y}{\partial t} = C \frac{y''}{(1 + y'^2)^{3/2}}, \quad (9)$$

where $y' = \partial y / \partial x$, and C is roughly proportional to D and to acceleration g . This sort of nonlinear heat conduction evolution will not generally preserve sharp edges and flat profiles. Given, for example, an initial step function $y(x, t = 0) = y_0 \theta(x)$, it will evolve in the following manner. First, both edges, the upper one $y_0 < y < y_1(t)$, and the lower one $y_2(t) < y < 0$ will become smeared, while a central window $y_2(t) < y < y_1(t)$ of the face will remain flat. As the spatial extension of the smeared corners increases with time, the window will gradually shrink, and after a critical time t_c it will close, eliminating all traces of a flat face in the slumped profile. The time t_0 required for the surface smearing front to advance a distance \tilde{y} is roughly given by $t_0 \sim \tilde{y}^2 \eta_0 / (l_0^3 \rho g)$, where η_0 is the viscosity of the superficial defrozen film, *i.e.*, a value typical of the liquid, ρ is the density, and $l_0 \sim \sqrt{J/\gamma}$ is the film thickness. The possibility of observing this effect (macroscopically, by reflectivity, and even better microscopically, by some surface topographic technique) seems quite plausible.

In surface-sensitive calorimetry, alternatively, a progressive defreezing of the surface film could yield a detectable mark. Surface melting of crystals yields a singularity in the specific heat of the form $\sim (T_M - T)^{-1-1/(\nu-3)}$ when T approaches T_M from below (if long-range forces decay as $1/r^\nu$). In the glass, integrating the enthalpy profile (4) across the interface we obtain a singularity in the specific heat of the form $\sim -\varepsilon(\gamma'/\gamma - 1)\sqrt{J/\gamma} \ln(T_0 - T)$, when $T \rightarrow T_0^-$. This is again a divergence, as in crystal surface melting, but now a much weaker one. In compound or polar glasses, the surface static dielectric permittivity could also be a useful tool. Microscopically, finally, liquid-like surface flow could be detectable by surface-specific techniques, for example thermal atom scattering.

Glass surfaces can also be very effectively simulated. A simulation study of $\text{Pd}_{80}\text{Si}_{20}$ published some time ago does provide a first qualitative suggestion for surface defreezing in a realistic glass forming system [13]. The glass surface roughness drop demonstrated in that work upon cooling could now be further elaborated upon in terms of suppression of capillary fluctuations due to confinement of the liquid film. Our present mean-field theory does not include capillary fluctuations. Their effect on the liquid film thickness is known to be at

most marginal in three dimensions in crystal surface melting [14], but will require a specific treatment in the glass case. Experimental evidence of surprisingly flat glass surfaces [15] do exist and might be related, although the effect of gravity is not discounted. This is a line of research that will deserve further theoretical and experimental effort.

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