Viscoelasticity and Metastability Limit in Supercooled Liquids

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A supercooled liquid is said to have a kinetic spinodal if a temperature T_{sp} exists below which the liquid relaxation time exceeds the crystal nucleation time. We revisit classical nucleation theory taking into account the viscoelastic response of the liquid to the formation of crystal nuclei and find that the kinetic spinodal is strongly influenced by elastic effects. We introduce a dimensionless parameter λ, which is essentially the ratio between the infinite frequency shear modulus and the enthalpy of fusion of the crystal. In systems where λ is larger than a critical value λ_c the metastability limit is totally suppressed, independently of the surface tension. On the other hand, if $\lambda < \lambda_c$ a kinetic spinodal is present, and the time needed to experimentally observe it scales as $\exp[\omega/(\lambda_c - \lambda)^2]$, where ω is roughly the ratio between surface tension and enthalpy of fusion.

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When a liquid is cooled below its freezing point without forming a crystal, it enters a metastable equilibrium phase known as supercooled [1]. A supercooled liquid is squeezed in an uncomfortable time region: if we are too *fast* in measuring its properties, the system cannot thermalize and an off-equilibrium *glass* results; on the other hand, if we are too *slow,* the system has the time to nucleate the solid, and we obtain an off-equilibrium *polycrystal,* and, eventually, a thermodynamically stable crystal [2,3]. What is the maximum degree of supercooling a metastable equilibrium liquid can reach?

The tricky point about this question is that it mixes aspects of the experimental protocol with intrinsic properties of the system. If we stick to cooling the system linearly in time, there is a minimum cooling velocity below which the system is bound to crystallize [3]. This velocity is inversely proportional to the minimum nucleation time as a function of temperature [4]: we cannot cool slower than this minimum cooling rate; otherwise crystallization occurs. On the other hand, as we cool, the relaxation time increases steeply, and therefore the system necessarily leaves the supercooled phase, and becomes a glass, at the temperature where the relaxation time becomes too large for this minimum cooling rate.

To penetrate deeper in the supercooled region, one can use an *ad hoc* nonlinear cooling protocol: cool fast close to the temperature where crystallization is a concern [4], and where relaxation time is still small; and slow down at lower temperatures, to cope with the increasing relaxation time, once the nucleation time starts raising again. Therefore, we may think that the unique limitation to the extent of supercooling is given by our capability of cooling a sample slow and fast enough, and that in principle there is no bound to supercooling a metastable equilibrium liquid.

In fact, our experimental capability is *not* the only limitation to supercooling a system. If at a certain temperature the relaxation time of the liquid τ_R exceeds the nucleation time of the crystal τ_N, no equilibrium measurements can be performed on the liquid sample and the supercooled phase does not exist anymore. Such a temperature is called *kinetic spinodal* T_{sp}, and it marks the metastability limit of the supercooled phase [1,2]. Such a metastability limit does not depend on the cooling protocol and is rather an intrinsic property of the sample. Below T_{sp} the only equilibrium phase (either stable or metastable) is the crystal, whereas glassy and polycrystalline off-equilibrium configurations can be obtained if we cool fast or slow enough, respectively. The aim of this work is to answer the following question: What is the main mechanism determining whether or not a metastability limit is present in a given liquid?

Our answer to the question above is that this mechanism is *viscoelasticity.* The central idea is that on time scales shorter than the structural relaxation time, deeply supercooled liquids exhibit a solidlike response to strains [5]. In particular, the inclusion of a crystalline nucleus in the liquid matrix produces a strain [6,7], and thus a long-range elastic response [8–11]. Therefore, the thermodynamic drive for crystal nucleation gets depressed by an elastic contribution, which depends on the ratio between the relaxation time τ_R and the time scale τ_N over which nucleation occurs. In this way a self-consistent equation involving nucleation and relaxation times is obtained.

We show that liquids can be classified according to the magnitude of their elastic response relative to their bare thermodynamic drive to crystallization (that is the liquid-crystal Gibbs free energy density difference δG). We find that elastic effects can be large enough to suppress the metastability limit, opening the possibility to supercool a liquid down to the point where its entropy reaches the entropy of the solid, the so-called Kauzmann temperature T_k [2]. Moreover, even if a metastability limit is present, the viscoelastic response determines how large is the relaxation time at the kinetic spinodal, and it thus establishes

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whether the metastability limit is accessible within the maximum experimental time, or is hidden by the off-equilibrium glassy phase.

According to classical nucleation theory (CNT), the Gibbs free energy barrier to nucleation is given by [12]

$$\Delta G = \frac{a\sigma^d}{[\delta G(T)]^{d-1}}, \tag{1}$$

where d is the dimension, σ is the surface tension, δG is the (positive) Gibbs free energy difference per unit volume between the two phases, and a is a numerical constant (for a spherical nucleus in $d = 3$, $a = 16\pi/3$).

When the nucleus of the stable phase forms in an elastic background, there is an extra energetic price that has to be paid [8–11]. Because of the long-range nature of the elastic strains, the elastic price is proportional to the nucleus volume, and thus it corrects the bare thermodynamic drive δG,

$$\Delta G = \frac{a\sigma^d}{[\delta G(T) - E_{\text{elastic}}]^{d-1}}. \tag{2}$$

In a perfect isotropic solid, assuming that the elastic parameters are the same in the two phases, the elastic energy density is given by $E_{\text{elastic}} = \epsilon_0 G_\infty$ where G_∞ is the (constant) elastic shear modulus, and where [11]

$$\epsilon_0 = \frac{(d-1)K}{dK + 2(d-1)G_\infty}\left(\frac{\delta v}{v}\right)^2 \tag{3}$$

is a dimensionless constant: K is the bulk modulus and $\delta v/v$ is the stress-free volume misfit between the two phases. In a viscoelastic liquid we have a stress-relaxation function, or time-dependent shear modulus, $G(t)$ [13]. In this case, Schmelzer and co-workers have shown that the time-dependent elastic contribution can be written as

$$E_{\text{elastic}} = \epsilon_0 G_\infty f(t), \tag{4}$$

where the infinite frequency shear modulus is $G_\infty = G(t = 0)$, and the dimensionless function f is [6,7]

$$f(t) = \frac{1}{t}\int_0^t dt' G(t')/G_\infty. \tag{5}$$

For a Maxwell liquid [13] $G(t) = G_\infty e^{-t/\tau_R}$, and thus $f(t/\tau_R) = (1 - e^{-t/\tau_R})\tau_R/t$. We do not assume the Maxwell form, but we still make the hypothesis that the stress-relaxation function G depends on the ratio t/τ_R, where τ_R is the liquid's structural relaxation time. In this case also $f = f(t/\tau_R)$. In log scale the function f typically has a steplike shape, going from $1 = f(0)$ to $0 = f(\infty)$ with a sharp drop at $f(1)$. The physical meaning is clear: for times much larger than the relaxation time the liquid is able to relax the stress, and there is no elastic contribution, while for times much smaller than τ_R it responds as a solid, with finite shear modulus.

What is the time t we have to plug into $E_{\text{elastic}}(t/\tau_R)$? The viscoelastic contribution to the nucleation barrier is due to the formation of a crystal nucleus, and this happens on a time scale of the order of the nucleation time. Therefore we must set $t = \tau_N$, and write

$$\tau_N = \tau_N^0 \exp\left\{\frac{a\sigma^d}{k_B T[\delta G(T) - E_{\text{elastic}}(\tau_N/\tau_R)]^{d-1}}\right\}. \tag{6}$$

From this formula we clearly see that the main effect of the elastic contribution is to increase the nucleation time. This effect becomes dramatic in solid-solid phase transitions, where nucleation may be totally suppressed, even with a nonzero thermodynamic drive δG, whenever $\delta G(T) < E_{\text{elastic}} = \epsilon_0 G_\infty$ [8–11]. In liquids, however, the stress is always relaxed for long enough times, and Eq. (6) always admits a solution $\tau_N(T)$, as long as $\tau_R < \infty$.

In order to solve Eq. (6), we have to discuss the T dependence of the various quantities. For the relaxation time we assume a Vogel-Fulcher-Tamman (VFT) form, which is known to describe very well a wide variety of supercooled liquids on a large range of times [14],

$$\tau_R = \tau_R^0 \exp\left(\frac{\Delta}{T - T_k}\right). \tag{7}$$

This form of the relaxation time implies a singularity at T_k, which is normally identified with the Adam-Gibbs thermodynamic transition [15], and it is approximately equal to the temperature where the liquid-crystal entropy difference δS vanishes. The Gibbs free energy difference is often fitted to a linear form, $\delta G = (1 - T/T_m)\delta h/\nu$, where T_m is the melting temperature, δh is the molar enthalpy of fusion, and ν is the molar volume of the crystal [16,17]. However, recalling that $\delta G = -\partial(\delta S)/\partial T$, consistency with (7) requires that δG must reach its maximum at T_k. Therefore, we write

$$\delta G(T) = g(T/T_m)(1 - T_k/T_m)\delta h/\nu, \tag{8}$$

where the dimensionless function g satisfies the relations: $g(1) = 0$ and $g(T_k/T_m) = 1$. The surface tension σ is assumed to be a constant, which is a reasonable hypothesis within CNT [17].

The prefactor of nucleation τ_N^0 in (6) is significantly T dependent. According to CNT, τ_N^0 is proportional to the product of an elementary thermal time scale, $h_{\text{plank}}/k_B T$, and an Arrhenius term due to the barrier B a particle has to overcome to cross the nucleus interface, $\exp(B/k_B T)$ [12]. It is customary to approximate such a term by $1/D$ (D is the self-diffusion coefficient), and, by using the Stokes-Einstein (SE) relation, to write $\tau_N^0 \sim 1/D \sim \tau_R$ [3]. However, as the system becomes viscous, the SE relation breaks down [18–20], and typically $1/D \ll \tau_R$. Indeed, in the extreme case of solids, even though the shear viscosity (and thus τ_R) is infinite, D remains nonzero. Thus, the prefactor τ_N^0 remains much smaller than the relaxation time at low temperatures, and it cannot by itself grant the fact that $\tau_N \gg \tau_R$.

A second delicate point about τ_N^0 is its dependence on the sample's volume. The quantity studied by CNT is not directly the nucleation time, but the nucleation rate J, that

is, the number of nuclei per unit time, per unit volume. J is a constant for large enough samples, and therefore the nucleation time of a given sample of volume V scales as $1/V$ [3]. Taking very small samples is, indeed, a well known trick to increase nucleation time. However, there is a limit to this procedure, given by the volume v_0 below which the $1/V$ scaling breaks down: below v_0 the nucleation rate is not anymore constant, either because surface effects become dominant over bulk properties or because the sample size is smaller than the critical nucleus [21]. The theoretical metastability limit of a liquid can be defined as the point where the *largest* possible nucleation time is surpassed by the relaxation time, and therefore we set $\tau_N = 1/(v_0 J)$. Anyhow, we recall that the results are rather insensitive to the choice of the reference volume, since this enters only in the prefactor τ_N^0, and not in the most relevant exponential factor.

We measure all times in Eq. (6) in units of τ_N^0, and define $x = \log(\tau_N/\tau_N^0)$ and $y = \log(\tau_R/\tau_N^0)$. In this way Eq. (6) can be rewritten as

$$T'x = \omega[g(T') - \lambda f(e^x/e^y)]^{1-d}, \tag{9}$$

where $T' = T/T_m$ is the reduced temperature, and

$$\omega = \frac{a\sigma^d}{k_B T_m}\left[\frac{\nu}{(1 - T_k/T_m)\delta h}\right]^{d-1}, \tag{10}$$

$$\lambda = \frac{\epsilon_0 \nu G_\infty}{(1 - T_k/T_m)\delta h}. \tag{11}$$

Two more dimensionless parameters are present in the theory: they are the rescaled Kauzmann temperature $T_k' = T_k/T_m$ and the rescaled VFT barrier $\Delta' = \Delta/T_m$. They both enter in the relaxation time, and thus in $y = y(T'/T_k', \Delta')$. If we set $\lambda = 0$, $T_k = 0$, and $g = (1 - T/T_m)$, we recover the classic expression for the nucleation time, where $\exp(\omega)$ gives the scale of the minimum nucleation time (see, for example, [17]). On the other hand, for $\lambda \neq 0$ we have elastic corrections to the nucleation time.

Equation (9) can easily be studied numerically once the forms of g and f are specified. However, the key physical features can be worked out in full generality. First, we note that for $T \to T_m$, $g \to 0$, whereas y remains finite, and thus the solution x of (9) diverges. As expected, $\tau_N \to \infty$ at the melting point. In the opposite limit $T \to T_k$ a graphical study of Eq. (9) shows that for $\lambda < 1$ the nucleation time remains finite, while $y \to \infty$, and thus a metastability limit $T_{sp} > T_k$ exists. On the other hand, for $\lambda > 1$, $\tau_N \to \infty$ for $T \to T_k$: in this case both relaxation and nucleation times diverge at T_k, but they still may cross at a kinetic spinodal. To check this last possibility we set $x = y$ in Eq. (9), and see whether there is a solution $T_{sp} > T_k$ of this equation,

$$T'\left(\Omega + \frac{\Delta'}{T' - T_k'}\right) = \omega[g(T') - \lambda f(1)]^{1-d}. \tag{12}$$

In this formula the factor $\Omega = \log(\tau_R^0/\tau_N^0)$ is not relevant, since it is large in modulus only at low temperatures, where, however, the factor $(T' - T_k')^{-1}$ dominates. We recall that, by construction, $f(1)$ is a number close to $1/2$ [in Maxwell's case $f(1) = 1 - 1/e = 0.63$]. The left-hand side of Eq. (12) diverges at T_k', whereas the right-hand side is finite at T_k' and diverges at a temperature larger than T_k', defined by $g(T') - \lambda f(1) = 0$. Given that $g(T_k') = 1$, we conclude that for $\lambda < 1/f(1)$ there is a solution T_{sp}', and thus a metastability limit, while for $\lambda > 1/f(1)$ there is no solution in the physical interval $g(T') - \lambda f(1) \geq 0$.

We recall that λ is, up to factors of order one, the ratio between the characteristic scales, G_∞ and δh, of the two competing mechanisms at work: the elastic forces, depressing nucleation, and the thermodynamic drive to crystallization, enhancing nucleation. What we have found is a critical value,

$$\lambda_c = 1/f(1), \tag{13}$$

separating systems with a kinetic spinodal, from systems without a kinetic spinodal. In those liquids where $\lambda < \lambda_c$ the metastability limit may be shifted at lower T by elasticity, but it still exists, while for $\lambda > \lambda_c$ elastic effects are strong, and the nucleation time is amplified enough to completely suppress the kinetic spinodal. This distinction is, of course, valid only to logarithmic accuracy: whenever $\lambda \sim \lambda_c$, the nucleation time may be only *slightly* larger than the relaxation time, and it is wise to assume that the liquid is not really stable against crystallization.

In Fig. 1 we show solutions of Eq. (9) for $\lambda > \lambda_c$ (left panel) and $\lambda < \lambda_c$ (right panel). In the first case, there is no spinodal, and thus the three phases, glass, supercooled liquid, and polycrystal, are well defined. In particular, the off-equilibrium glassy and polycrystalline states are well separated from each other by the "buffer" liquid phase. When $\lambda < \lambda_c$, however, the situation is rather different. The equilibrium liquid phase is still well defined as long as it exists, that is, for $T > T_{sp}$; however, it is hard to say what is the physical difference between the two off-equilibrium phases, i.e., glass and polycrystal. Although it may be operationally meaningful to distinguish glass from polycrystal when $T \gg T_{sp}$, there seems to be no obvious *qualitative* difference when $T \sim T_{sp}$, or, even worse, when $T < T_{sp}$. Close to the spinodal point, whether the system falls out of equilibrium by crossing the dashed or the solid line, is irrelevant. Glass and polycrystal blend into a single off-equilibrium phase [22].

In systems with $\lambda > \lambda_c$ the supercooled phase is well defined down to T_k, where the relaxation time diverges. In this case, a solution of Kauzmann paradox (for example, in terms of a thermodynamic transition at T_k) must be found. On the other hand, when a spinodal is present the supercooled liquid ceases to exist at T_{sp}, which is Kauzmann's resolution of the paradox [2].

When a kinetic spinodal exists, is it within the boundaries of experimental observation? To answer this question,

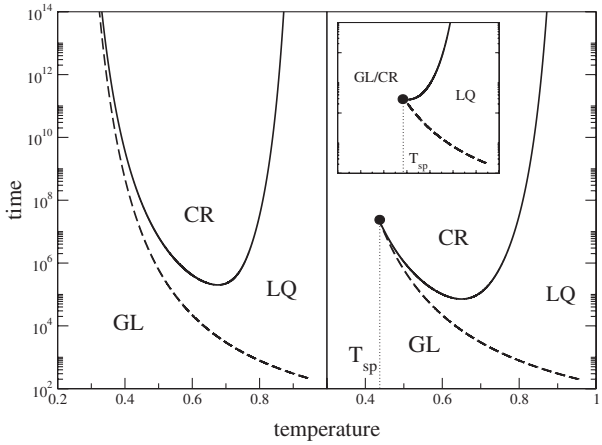

FIG. 1. Nucleation and relaxation vs reduced temperature $T' = T/T_m$, for different values of the parameter λ. Solid line, nucleation: $x(T') = \log(\tau_N/\tau_N^0)$. Dashed line, relaxation: $y(T) = \log(\tau_R/\tau_N^0)$. LQ stands for equilibrium liquid, GL for off-equilibrium glass, and CR for off-equilibrium polycrystal. Left: For $\lambda = 2$, larger than $\lambda_c = 1.58$, there is no kinetic spinodal. Right: For $\lambda = 0.3$, smaller than λ_c, a kinetic spinodal exists at T_{sp}. Inset: For $\lambda = 0.03$, the difference between glass and polycrystal is particularly ill-defined. The other parameters are $\omega = 4$, $\Delta/T_m = 4$, and $T_k/T_m = 0.2$. For $f(t/\tau_R)$ we have taken a Maxwell form, while $g(T')$ is a cubic.

we have to define a spinodal time, $\tau_{sp} = \tau_R(T_{sp})$, and compare it to the maximum time of the experiment, τ_{exp}. From Eq. (12) we obtain (for $d = 3$)

$$\tau_{sp} \sim \exp\left[\frac{\omega}{(1 - \lambda/\lambda_c)^2}\right]. \tag{14}$$

Therefore, as expected, the *position* of the kinetic spinodal depends also on the parameter ω: a large value of ω implies a large value of the surface tension σ compared to the drive to crystallization δh, and thus a larger nucleation time [3]. Therefore, when ω is significantly larger than $(1 - \lambda/\lambda_c)^2$, the spinodal time may be too large compared to the experimental time, and thus the metastability limit may be experimentally unaccessible [23].

Conventionally, a good glass former is a system that does not crystallize easily under a linear cooling, i.e., a system whose minimum cooling rate r_{min} is not too large. Given that $r_{min} \sim 1/\tau_{min}$, where τ_{min} is the minimum nucleation time as a function of T [4], the larger τ_{min}, the better the glass former. To what extent does τ_{min} depend on λ? When $\lambda \ll \lambda_c$ the kinetic spinodal typically takes place at a point where the nucleation time is still a decreasing function of T (Fig. 1, inset of right panel). In such a case τ_{min} is effectively given by the spinodal point. From (14) we therefore have $r_{min} \sim \exp[-\omega/(1 - \lambda/\lambda_c)^2]$, and the glass-forming capability of the system is strongly dependent on λ. On the other hand, when $\lambda \sim \lambda_c$ or $\lambda > \lambda_c$, τ_{min} is given as usual by the minimum of the nucleation curve. In this case $\tau_{min} \sim \exp(\omega)$, the glass-forming properties depend almost exclusively on ω, whereas their dependence on λ is weak.

In this work we studied the effects of viscoelastic response on the metastability limit of supercooled liquids. We defined a parameter λ whose value rules whether a kinetic spinodal exists or not. This parameter encodes the competition between elastic response and thermodynamic drive to crystallization: for values of λ below λ_c elasticity is relatively weak, the drive to crystallization always wins, and a metastability limit is present. For $\lambda > \lambda_c$ the elastic response is so large that nucleation is inhibited compared to relaxation, and a metastability limit is not present.

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