On thermodynamic and kinetic spinodals in supercooled liquids

Azat O. Tipeev [a,*], Jürn W.P. Schmelzer [b,c], Edgar D. Zanotto [a]

[a] *Department of Materials Engineering, Federal University of São Carlos, 13565-905 São Carlos, SP, Brazil*
[b] *Institut für Physik, Universität Rostock, Albert-Einstein-Strasse 23-25, 18059 Rostock, Germany*
[c] *Competence Centre CALOR, Faculty of Interdisciplinary Research, University of Rostock, Albert-Einstein-Str. 25, 18051 Rostock, Germany*

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ABSTRACT

In this Letter, we delve into theoretical considerations that address the absence of a thermodynamic spinodal in supercooled liquids, which has been incorrectly identified in some simulation studies. Additionally, we discuss the localization of the kinetic pseudo-spinodal, which has also been estimated in computational simulations.

1. Thermodynamic spinodal

Upon surpassing the equilibrium coexistence curve, condensed matter enters a range of metastable states in which it can exist for a certain time before eventually transitioning to a stable phase. As the deviation from the equilibrium coexistence increases metastable states can become unstable. The boundary curve distinguishing the metastable region from the unstable states is known as the thermodynamic spinodal. The spinodal is determined based on the principles of thermodynamic stability [1,2], and represents states in which these conditions are no longer met. For one-component systems, this spinodal represents the locus of critical points where the second derivative of Gibbs' free energy with respect to volume becomes zero. At the spinodal, a metastable system becomes thermodynamically unstable, undergoing phase separation triggered by infinitesimal perturbations in the state parameters.

A supercooled liquid (SCL) represents a unique metastable phase. One pressing question is whether further cooling of a liquid below its melting temperature could approach a spinodal. The scenario in this context differs considerably from other processes, such as liquid–gas phase transitions or segregation processes in solid and liquid solutions. Two primary distinctions can be noted [3]: (i) upon cooling, a liquid can turn into a non-equilibrium glassy state instead of a crystal; (ii) the liquid–solid transition is a disorder–order process and is accompanied by symmetry breaking. Based on this symmetry concept, Landau deduced the absence of an equilibrium critical point on the liquid–solid coexistence curve. This deduction implies the absence of a thermodynamic spinodal in a SCL [4,5]. Later on, the absence of a spinodal in one-

component melts was established by Skripov and coauthors through a thorough analysis of experimental data in Ref. [6] and further confirmed in Refs. [7,8]. To date, within the extensive amount of experimental data available, the crystallization of liquids has not exhibited features that suggest a potential equivalence between these two states. This contrasts with common observations at critical points and the spinodal in liquid–gas transitions or in segregation processes in solutions.

When applying the Classical Nucleation Theory (CNT) in conjunction with Gibbs' thermodynamic theory of heterogeneous systems [1,2], the assertion of the absence of a spinodal has been expanded to multi-component liquids, as detailed in Ref. [9]. According to the CNT [10], the steady-state nucleation rate, J, i.e., the average number of viable nuclei formed per unit time and volume, can be expressed via the work of critical cluster formation, W_c, as

$$J = J_0 \exp\left(-\frac{W_c}{k_B T}\right); \quad W_c = \frac{1}{3}\sigma A_c \qquad (1)$$

Here J_0 is the kinetic pre-factor determined by the kinetics of aggregation [11], k_B is the Boltzmann constant, T is the absolute temperature, σ is the solid–liquid surface tension, and A_c is the surface area of the critical cluster. Assuming a spherical shape of the critical nucleus, the latter is given as $A_c = 4\pi R_c^2$, where R_c is the critical radius, which is determined by the ratio between σ and the thermodynamic driving force for crystallization, Δg, as $R_c = 2\sigma/\Delta g$.

The temperature dependence of driving force is given by [12,13]

$$\Delta g(T, p_m) = -\int_{T_m}^{T} \Delta s(T, p_m) dT$$

$$= \frac{\Delta h_m (T_m - T)}{T_m} - \int_{T}^{T_m} \Delta c_p dT' + T \int_{T}^{T_m} \frac{\Delta c_p}{T'} dT' \tag{2}$$

where T_m is the melting or liquidus temperature, p_m is the melting pressure corresponding to T_m, Δs is the difference of the entropy per unit volume between the SCL and the crystal phases, Δh_m is the heat of melting, Δc_p is the difference between the liquid and crystal heat capacities at constant pressure.

It has been theoretically demonstrated [14] that the $\Delta g(T, p_m)$ dependence, Eq. (2), exhibits a maximum at a temperature where Δs *becomes zero*. This temperature is commonly denoted as the Kauzmann temperature, T_K. Below T_K, the driving force may even reach zero at a finite temperature, provided $\gamma_m \equiv \Delta c_p(T_m, p_m)/\Delta s(T_m, p_m) > 2$. However, in practice, such thermodynamic states at deep supercoolings, $T < T_K$, are unattainable for SCLs [15,16,17]. This is because they tend to either vitrify or crystallize at higher temperatures. The experimental values of Δg are normally constrained within two approximations, which assume $\Delta c_p = 0$ ($\gamma_m = 0$) and $\Delta c_p = \text{constant}(\gamma_m = 2)$ in Eq. (2) [12,14,18]. Employing these limiting cases, Eq. (2) can be written as [14,19]

$$\Delta g(T, p_m) = \Delta h_m \left(1 - \frac{T}{T_m}\right) \tag{3}$$

and

$$\Delta g(T, p_m) = \Delta h_m \left(1 - \frac{T}{T_m}\right)\left(\frac{T}{T_m}\right) \tag{4}$$

respectively. The potential range of values for Δg, as defined by Eqs. (3) and (4), is illustrated in Fig. 1. Summarizing the previous discussion, the driving force remains finite across the entire supercooling range, $0 < T/T_m < 1$, reaching its maximum at the Kauzmann temperature.

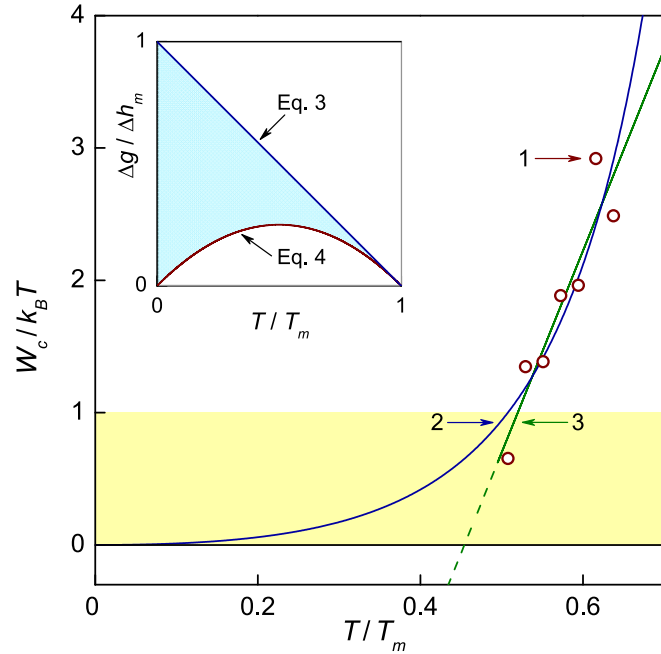The general Stefan-Skapski-Turnbull equation for the surface tension was derived in Ref. [20] and is formulated for a one-component system as:

$$\sigma = \chi v^{1/3} \left\{ T_\beta \left(s_\beta - s_\alpha\right) + \frac{3}{R_c} \left[s_\alpha \left(\frac{\partial \sigma}{\partial s_\alpha}\right)_{\rho_\beta, s_\beta} + \rho_\alpha \left(\frac{\partial \sigma}{\partial \rho_\alpha}\right)_{\rho_\beta, s_\beta} \right] \right\} \tag{5}$$

where χ is the numeric parameter, v is the molar volume divided by Avogadro's number, ρ is the number density, and the subscripts α and β refer to the crystal and liquid phases, respectively. Based on the theoretical analysis presented in Ref. [20], as supercooling increases at a constant pressure, the surface tension decreases but remains finite down to zero temperature.

At the spinodal points, the metastable and stable phases become indistinguishable. Thus, both the thermodynamic driving force and surface tension must reach zero simultaneously. A review of Eqs. (2)–(5) reveals that the conditions $\Delta g(T, p_m) = 0$ and $\sigma(T, p_m) = 0$ cannot be satisfied at $T > 0$ [14,20]. Therefore, from a theoretical standpoint, there is *no thermodynamic spinodal* for a SCL.

The thermodynamic spinodal can also be described as states in which no barriers exist for a phase transition, i.e., $W_c = 0$ [2,21]. A procedure for estimating the SCL spinodal through the $W_c(T) = 0$ condition was employed, for example, in Refs. [22,23]. However, the inadequacy of this approach has been already highlighted by Kelton and Greer ([10], page 107) in their discussion of the behavior model computations for W_c, where it converges to zero. They observed, "*The decrease of W_c to zero is a failing of this particular model, since there is no point at which the liquid becomes unstable relative to the solid.*" They further noted, "*Nonetheless, it does indicate that a properly constructed density-functional model could describe the transition from a nucleation-and-growth mechanism to a spinodal transformation, which the CNT cannot do.*" Some potentially feasible scenarios in this direction, such as examining the influence of supersaturation on the critical cluster's bulk state parameters or crystallization through the selective segregation of the liquid are explored in Ref. [24]. However, the works [22,23] did not consider these aspects, consequently leading to the absence of the thermodynamic spinodal in their findings. It is also worth noting that processes featuring zero thermodynamic barriers may occur in supercooled melts, for example, phase separation [25,26].

In a recent study conducted by Li et al. [23], the thermodynamic spinodal was estimated to be located at $T = 0.45 \cdot T_m$ in SCL Al by (artificially) linearly extrapolating the $W_c(T)$ dependence to zero (Fig. 1), where values of W_c were indirectly derived from the $J(T)$ slope, Eq. (1). In Fig. 1 we also show the possible approximation of the values of W_c within the CNT framework, using the equation, $W_c = 16\pi\sigma^3/3(\Delta g)^2$, with $\Delta g = \Delta h_m(1 - T/T_m)$ and $\sigma = \sigma(T_m, p_m) \cdot T/T_m$ derived from Eqs. (2) and (5), and assuming $\Delta c_p = 0$ the same premise as in the work [23]. It should be also noted that the obtained values of the nucleation barrier are consistently smaller than $3 \cdot k_B T$, making them comparable to thermal fluctuation energy, $1 \cdot k_B T$, and thus questioning the applicability of the CNT formalism in this scenario [12,27].

2. Kinetic spinodal

In addition to the fundamental thermodynamic spinodal, there is also the concept of a kinetic pseudo-spinodal introduced for SCLs. In his seminal paper [15], Kauzmann noted that the entropy of certain metastable liquids decreases rapidly upon supercooling and could even match the entropy of the corresponding crystal at temperature T_K. To resolve this paradoxical situation, Kauzmann proposed the concept of a pseudo-spinodal localized at the temperature T_{ps} above T_K, at which crystallization should inevitably occur, thereby preventing further persistence of the SCL. This crystallization arises from the reduction of the free energy barrier for crystal nucleation down to the barrier level associated with atomic motions controlling structural relaxation. Importantly, Kauzmann made a clear distinction between this pseudo-

Fig. 1. Reduced work of formation of the critical crystal nucleus, $W_c/k_B T$, derived from the $J(T)$ data (1) and linearly approximated (3) in Ref. [23]. The smooth line (2) is the CNT approximation, $W_c/k_B T = 16\pi\sigma^3/3kT(\Delta g)^2 = const(T/T_m)^2(1 - T/T_m)^{-2}$, assuming $\Delta c_p = 0$. The region of thermal fluctuations, $E \leq 1 \cdot k_B T$, is highlighted in yellow. Inset: Potential range of values for the thermodynamic driving force, $\Delta g(T, p_m)$, as defined by Eqs. (3) and (4).

spinodal state and a true thermodynamic spinodal. The kinetic spinodal in several SCLs has been recently discussed in Ref. [17].

In that same study conducted by Li et al. [23], the pseudo-spinodal point, $T_{ps} = 0.51 \cdot T_m$, was defined as the temperature at which the crystal nucleation and structural relaxation times match, i.e., $\tau_N(T_{ps}) = \tau_R(T_{ps})$. The nucleation time, τ_N, was determined as the birth time of the first critical nucleus, whereas the relaxation time, τ_R, was derived from the self-intermediate scattering function. However, this approach lacks a unique definition of the pseudo-spinodal because τ_N is notably influenced by the volume of the metastable liquid, $\tau_N = 1/JV$. Consequently, the derived value for $T_{ps} = 0.51 \cdot T_m$ is valid exclusively for the specific volume corresponding to $N = 108{,}000$ atoms in the system explored within the research. Here, we estimate it for the smallest possible volume, considering $V = 1$ nm^3 for this purpose [28]. Accordingly, we deduce that $T_{ps} = 0.49 \cdot T_m$.

In general, nucleation times include both τ_N and the time-lag, τ_{lag}, associated with the establishment of steady-state nucleation regime at a given temperature [29]. This time-lag can be expressed as [30]

$$\tau_{\text{lag}} = \frac{\omega}{2} \left(\frac{k_B T}{\sigma d_0^2} \right) \left(\frac{R_c^2}{D\tau_R} \right) \tau_R \tag{6}$$

where d_0 is the characteristic size of the crystallizing liquid. The numerical factor ω varies within the range $1 \leq \omega \leq 4$, contingent upon the methodology applied to derive Eq. (6). Above the decoupling temperature, T_d, $(T_d \approx 1.2 \cdot T_g)$ the product $D\tau_R$ becomes temperature-independent since the Stokes-Einstein-Eyring relation is valid. Conversely, this relation does not hold below T_d. Numerical evaluations accounting for the decoupling of diffusion and relaxation [31] show that the condition proposed by Kauzmann for the pseudo-spinodal curve is generally satisfied near or below the glass transition temperature, T_g, i. e., $T_{ps} \approx T_g$. In simulations, this relationship was recently identified for germanium in Ref. [28]. Note that within this same temperature region, the homogeneous steady-state crystal nucleation rates in inorganic glass formers reach their maximum [32], $T_{J\text{max}} \approx T_g$, thus resulting in $T_{ps} \approx T_{J\text{max}}$. The peak in $J(T, p_m)$ was observed in Ref. [23], coinciding with the one previously obtained for the 2NN-MEAM model of Al at $T_{J\text{max}} = 475$ K $\approx 0.51 \cdot T_m$ [33]. This finding supports the $T_{ps} \approx T_{J\text{max}}$ relation for Al and indirectly validates the correctness of $T_{ps} = 0.51 \cdot T_m$ as determined by Li et al. [23].

The $T_{ps} \approx T_g$ relationship can generally be confirmed. When crystals nucleate in viscous liquids, the effective stress parameter, ε, representing the elastic energy per particle in the crystal phase, is determined by the intricate interplay between stress evolution arising from crystallite formation and concurrent stress relaxation during this process. When considering relaxation as proceeding per Maxwell's law, the effective value of ε for a critical-sized crystallite as shown in Ref. [12] and the papers cited therein can be expressed by

$$\frac{\varepsilon(n_c)}{\varepsilon_0} \cong \frac{\tau_R}{\tau_{\text{lag}}} \left[1 - \exp\left(-\frac{\tau_{\text{lag}}}{\tau_R} \right) \right] \tag{7}$$

where ε_0 refers to a Hookean solid. Thus, according to Eq. (7), the influence of elastic stresses on crystal nucleation in glass-forming liquids is assessed by the ratio τ_R/τ_{lag}. For temperatures considerably above T_g, elastic stresses are expected to have minor significance, while for glasses they must have a similar order of magnitude as observed in Hookean solids. Consequently, as the temperature decreases, the τ_R/τ_{lag} ratio should shift from near-zero values around T_m to very large values below T_g to satisfy Eq. (7). As a result, the condition for the occurrence of the pseudo-spinodal, as formulated by Kauzmann, is met close to the T_g: $0.5 < T_g < 0.8$ for inorganic glass-forming melts [34] and $0.3 < T_g < 0.6$ for metallic glass-forming alloys [35,36]. Upon further cooling, the nucleation rate is reduced also because of the interplay between relaxation and crystal nucleation processes [3,24,31,37]. Thus, knowledge of

the τ_R/τ_{lag} is pivotal for understanding crystal nucleation, albeit in a context distinct from Kauzmann's supposition.

3. Conclusion

This work has outlined theoretical considerations that address the absence of a thermodynamic spinodal in SCLs and has discussed the localization of the kinetic spinodal. In summary, this Letter serves to draw the attention of interested readers to future research endeavors regarding the intricate characteristics of SCLs, which include the complex dynamics of liquid relaxation and crystal nucleation at deep supercoolings.

CRediT authorship contribution statement

Azat O. Tipeev: Funding acquisition, Visualization, Writing – original draft, Writing – review & editing, Formal analysis. **Jürn W.P. Schmelzer:** Conceptualization, Writing – original draft, Writing – review & editing. **Edgar D. Zanotto:** Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

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Data availability

Data will be made available on request.

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