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Curvature- and temperature-dependent interfacial tension in classical nucleation theory

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Curvature- and temperature-dependent interfacial tension is introduced in classical nucleation theory (CT-CNT). In this case, the nucleation rate depends on temperature, T, viscosity, η, the reduced surface tension, α, the difference between the chemical functions of the liquid and solid phase, $\Delta\mu$, and, unlike with the common classical nucleation theory (CNT), also on the derivative of this function, $\partial\Delta\mu/\partial T$. Because of this latter dependency, the nucleation rate is highly sensitive to $\Delta\mu$ and no approximation formula can be used for this function Kauzmann's catastrophe can be introduced artificially by approximation formulas that are commonly used in CNT. The latter theory is not sensitive to this problem.

1. Introduction

Classical (isothermal) nucleation theory (CNT), as developed by Volmer–Weber, Becker–Doering and Turnbull–Fisher, considers a 'droplet' of the new, appearing phase (e.g. the solid phase) in the supersaturated (supercooled) parent phase (e.g. liquid phase). The generalized expression 'droplet' is used, even for the solid phase, because this word expresses best the idea of the action of the surface or interfacial tension (droplet model). The difference of the Gibbs free energy due to the existence of the solid 'droplet' in the liquid, at constant temperature, is then

$$\Delta G = n''(\mu''(p'') - \mu'(p')) + \sigma A, \qquad (1)$$

where n is the number of molecules (or formula units), μ is the molecular chemical function, p is the pressure, σ is the interfacial tension and A is the interfacial area, and where ('') refers to inside the droplet and (') to outside [1,2]. Evidently, p'', σ and A are functions of the radius, r, of the nucleus or of the number, n'', of molecules inside the nucleus.

When the solid 'droplet' is in equilibrium with the supercooled liquid, it follows that

$$\mu'(p') = \mu''(p''^*), \qquad (2)$$

where p''^* is the pressure inside the 'droplet' of radius r^*. One obtains then

$$\Delta G^* = \sigma^* A^* \qquad (3)$$

for the solid 'droplet' in equilibrium with the liquid phase, where the sign (*) indicates that the equation is restricted to equilibrium.

The isothermal work to create such a solid 'droplet' equals the isothermal variation of the Helmholtz free energy, F, which can be obtained from the relation

$$\Delta F = \Delta G - n''v''(p'' - p'), \qquad (4)$$

where v'' is the (incompressible) molecular volume of the solid. One obtains

$$\Delta F^* = -n''v''(p''^* - p') + \sigma^* A^*, \qquad (5)$$

where $(p''^* - p')$ is the capillary pressure which is given by Laplace's formula

$$p''^* - p' = 2\sigma^*/r^*. \qquad (6)$$

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IMPORTANT
1. Please correct the proofs carefully [illegible]

With the approximation

$$\mu''(p'') = \mu''(p') + [\partial\mu''(p')/\partial p](p'' - p')$$
$$= \mu''(p') + v''(p'' - p'), \qquad (7)$$

one obtains

$$\mu''(p''^*) - \mu'(p') = \mu''(p') - \mu'(p')$$
$$+ v''(p''^* - p') = 0, \qquad (8)$$

and it follows from eqs. (6) and (8) that

$$r^* = (2v''\sigma^*)/\Delta\mu, \qquad (9)$$

with

$$\Delta\mu = \mu'(p') - \mu''(p'). \qquad (10)$$

Eqs. (5), (6) and (9) lead then, considering that $n''v'' = 4\pi r^3/3$, to

$$\Delta F^* = \tfrac{1}{3}\sigma^* A^* = \frac{4\pi}{3} r^{*2}\sigma^* = \frac{16\pi(v'')^2(\sigma^*)^3}{3(\Delta\mu)^2}, \qquad (11)$$

which is a result obtained already by Gibbs [3].

The adaption of the Volmer–Weber–Becker–Doering nucleation theory to the liquid–solid phase transition by Turnbull and Fisher [4], together with further developments [5,6], leads then to

$$I = A \exp(-\Delta F^*/kT), \qquad (12)$$

with

$$A = \frac{2Nv''^{1/3}(kT\sigma^*)^{1/2}}{3\pi\lambda^3\eta}, \qquad (13)$$

where I is the number of appearing nuclei per second, N is the total number of molecules (or formula units) of the system, k is Boltzmann's constant, T is the absolute temperature, η is the viscosity and λ is the 'jump distance' in diffusion processes (of atomic dimension).

2. Introduction of curvature- and temperature-dependent interfacial tension

Considering Tolman's equation [7] which originally was deduced for the vapour–liquid surface tension, but has been shown to be approximately valid for the liquid–solid interfacial tension also [8] (see the appendix for further comments about the curvature dependence of the interfacial tension),

$$\sigma = \sigma_\infty\left(1 + \frac{2\delta}{r}\right)^{-1}, \qquad (14)$$

where σ_∞ is the surface tension of the flat interface ($r = \infty$) and 2δ is approximately the intermolecular distance, one obtains with eq. (9)

$$r^* = \frac{2v''\sigma_\infty}{\Delta\mu} - 2\delta. \qquad (15)$$

Estimates of σ_∞ give [8]

$$\sigma_\infty = \delta\,\Delta h/v'', \qquad (16)$$

where $\Delta h(T)$ is the molecular latent heat of melting at the melting point, or in general the enthalpy difference between the two phases. 2δ is approximately equivalent to the intermolecular distance, so that $v'' \cong (2\delta)^3$. This relation can be written as

$$v'' = (\delta/\alpha)^3, \qquad (17)$$

with approximately

$$\alpha \cong \tfrac{1}{2} \qquad (18)$$

and, since δ in eq. (16) can be substituted by α with the help of eq. (17), α can be called the reduced surface tension. From eqs. (11) and (14–17) and with

$$\Delta\mu = \Delta h - T\,\Delta s, \qquad (19)$$

where $\Delta h = h'(p') - h''(p')$ and $\Delta s = s'(p') - s''(p')$, one obtains

$$\Delta F^*_{\text{CT-CNT}} = \frac{2\pi(2\alpha)^3(\Delta h - \Delta\mu)^3}{3(\Delta\mu)^2}$$
$$= \frac{2\pi(2\alpha)^3 T^3(\Delta s)^3}{3(\Delta\mu)^2}$$
$$= \frac{-2\pi(2\alpha)^3 T^3[\partial(\Delta\mu)/\partial T]^3}{3(\Delta\mu)^2}. \qquad (20)$$

Analogously, eq. (13) leads then, together with eqs. (14–17), to

$$A_{\text{CT-CNT}} = \frac{2N(\alpha k)^{1/2}}{3\pi\lambda^3\eta} T(\Delta s)^{1/2}$$
$$= \frac{2N(\alpha k)^{1/2}}{3\pi\lambda^3\eta} T[-\partial(\Delta\mu)/\partial T]^{1/2}. \qquad (21)$$

Equations (20 and 21) are the result of the troduction of curvature- and temperature-de- endent interfacial tension in classical nucleation eory (CT-CNT) and these equations can be ompared with the analogous equations, in which e curvature and temperature dependence of the terfacial tension was not taken into account NT).

The equations corresponding to eqs. (20) and 1), but with $\sigma = \sigma_x = \delta\,\Delta h_l / v''$, can be ob- ined from eqs. (11), (13) and (17):

$$F^*_{\mathrm{CNT}} = \frac{16\pi\alpha^3(\Delta h_l)^3}{3(\Delta\mu)^2} \tag{22}$$

d

$$_{\mathrm{CNT}} = \frac{2N(\alpha kT)^{1/2}}{3\pi\lambda^3\eta}(\Delta h_l)^{1/2}, \tag{23}$$

here eq. (22) is an equation used by Turnbull 11].

Discussion of possible approximation

With the approximation

$$(T) \cong c_p^{\mathrm{s}}(T) \tag{24}$$

elow the melting point, where $c_p^{\mathrm{l}}(T)$ and $c_p^{\mathrm{s}}(T)$ re the molecular specific heats of the liquid and lid, respectively, one obtains

$$\mu \cong \Delta h_l\ \Delta T/T_{\mathrm{M}}, \tag{25}$$

here T_{M} is the absolute melting temperature and $T = T_{\mathrm{M}} - T$ [9,10]. However, since in general $\neq c_p^{\mathrm{s}}$ below the melting temperature, eq. (25) as to be considered as an upper limit for $\Delta\mu$. ecause of eq. (24), the latent heat and latent ntropy cease then to be functions of the tempera- ure and because of eq. (16) also the surface nsion becomes essentially temperature-indepen- ent (if one neglects a slight possible temperature ependence of δ and v''). With eqs. (20), (21) and 5), one obtains then

$$F^*_{\mathrm{C\text{-}CNT}} \cong \frac{2\pi(2\alpha)^3\Delta h_l T^3}{3(\Delta T)^2 T_{\mathrm{M}}} \tag{26}$$

and

$$A_{\mathrm{C\text{-}CNT}} \cong \frac{2N(\alpha k)^{1/2}}{3\pi\lambda^3\eta} T\left(\frac{\Delta h_l}{T_{\mathrm{M}}}\right)^{1/2}, \tag{27}$$

where C-CNT stands for curvature-dependent (but temperature-independent) interfacial tension in classical nucleation theory.

With eqs. (22), (23) and (25), one obtains

$$\Delta F^*_{\mathrm{CNT}} \cong \frac{2\pi(2\alpha)^3\Delta h_l T_{\mathrm{M}}^2}{3(\Delta T)^2}, \tag{28}$$

which is a formula used by Turnbull [9–11] and

$$A_{\mathrm{CNT}} \cong \frac{2N(\alpha k)^{1/2}}{3\pi\lambda^3\eta}(T\,\Delta h_l)^{1/2}. \tag{29}$$

It is interesting to note that the result of the introduction of curvature-dependent (but temperature-independent) interfacial tension in CNT, consisting in the substitution of the approximation formulas eqs. (28) and (29) by the approximation formulas of C-CNT, eqs. (26 and 27), could formally also be obtained, postulating a temperature-dependent (but curvature-independent) interfacial tension, as proposed by Spaepen [12] and Spaepen and Meyer [13],

$$\sigma^* = \sigma_x(T/T_{\mathrm{M}}), \tag{30}$$

where σ_x is the interfacial tension at T_{M}. Introducing this formula in eq. (28), eq. (26) was also obtained by Spaepen and Turnbull [14]. Accepting eq. (16) one obtains then, however, (if one considers δ and v'' as temperature-independent) also

$$\Delta h = \Delta h_l(T/T_{\mathrm{M}}), \tag{31}$$

an equation that is in contradiction with eqs. (24) and (25).

Comparing the general result of CNT for the liquid–solid phase transition, eqs. (12), (22), (23), with the general result of CT-CNT, eqs. (12), (20), (21), one sees that, by contrast with CNT, in CT-CNT the nucleation frequency 'I' goes to zero, apparently independently of the viscosity, if

$$\Delta s = -\frac{\partial(\Delta\mu)}{\partial T} = 0. \tag{32}$$

The temperature, where $\Delta s = 0$, is the temperature, where $\Delta s = s'(p') - s''(p')$ goes from positive values to negative ones and is known as the temperature of Kauzmann's catastrophe [15]. This catastrophe would normally occur, if the trend of the specific heats, between T_{M} and $T \geq T_g$, where T_g is the glass transition temperature, was extrapolated to lower temperatures. (Near T_g, the viscosity is evidently high, so that eq. (32) is in fact not really independent of the viscosity.) The spontaneous drop of the specific heat of the amorphous phase at the glass transition temperature prevents the occurrence of Kauzmann's catastrophe.

This shows that the approximation proposed by Hoffman [16]

$$\Delta\mu = \frac{\Delta h_l\ \Delta T}{T_{\mathrm{M}}}\left(\frac{T}{T_{\mathrm{M}}}\right) \tag{33}$$

and by Thompson and Spaepen [17]

$$\Delta\mu = \frac{\Delta h_l\ \Delta T}{T_{\mathrm{M}}}\left(\frac{2T}{T_{\mathrm{M}} + T}\right) \tag{34}$$

cannot be used at lower temperatures in CT-CNT, because they would introduce Kauzmann's catastrophe at $T = 0.5T_{\mathrm{M}}$ and $T = 0.41T_{\mathrm{M}}$, respectively. On the other hand eq. (25) is clearly an overestimate.

4. Conclusions

There is no general approximation formula for $\Delta\mu$ which could be used for a serious test of CT-CNT. To test CT-CNT, there is only one possible procedure. (1) Measure $\Delta\mu$ (by the specific and latent heats) as a function of the temperature, e.g. for inorganic glasses which can also be obtained in the crystalline form and which crystallize slowly at temperatures where homogeneous nucleation experimentally occurs. (2) Measure also the nucleation rate as a function of the temperature. (3) Determine the viscosity of the amorphous phase as a function of the temperature. Then it would be possible to test CT-CNT by eqs. (12), (20) and (21) and CNT by eqs. (12), (22), (23) and both results could then additionally be compared with the adiabatic nucleation theory (ANT) [8,18–25] which, in spite of the fact that it does not predict the nucleation frequency quantitatively, predicts quite accurately if and at what temperatures homogeneous nucleation effectively occurs.

The results of tests of CT-CNT and CNT, with the help of experimental data from the literature of Na_2O-$2CaO$-$3SiO_2$, Li_2O-$2SiO_2$ and CaO-SiO_2 glasses, by Zanotto are given in table 1 [26,27]. The reported α-values, which cannot be predicted theoretically, were adjusted in such a way that the temperatures of the theoretical maximum nucleation frequencies, $I_{\mathrm{theor}}^{\max}$, were coincident with those of the experimental maximum nucleation frequencies, $I_{\mathrm{exp}}^{\max}$. The (decimal) logarithm of the fraction $I_{\mathrm{exp}}^{\max}/I_{\mathrm{theor}}^{\max}$ for CT-CNT can then be compared with the corresponding value of CNT. The table gives also the number of molecules of the nucleus at the temperature of maximum nucleation frequency, n^*.

Interestingly, there seem to exist typical mean α-values for both theories, $\langle\alpha\rangle = 0.74 \pm 0.02$ for CT-CNT and $\langle\alpha\rangle = 0.49 \pm 0.08$ for CNT. However the relative deviation, $\Delta\alpha/\langle\alpha\rangle$, for CT-CNT

Table 1

Comparison of experimental and theoretical maximum nucleation frequencies, as predicted by CT-CNT and CNT

Material	CT-CNT			CNT			Ref.
	α	$\log x$ [a]	n^*	α	$\log x$ [a]	n^*	
$Li_2O \cdot 2SiO_2$	0.75	−2	16	0.47	39	71	[26]
$Li_2O \cdot 2SiO_2$ [b]	0.72	≈0	15	0.48	35	60	[26]
$CaO \cdot SiO_2$	0.73	−6	24	0.57	21	75	[27]
Na_2O-$2CaO \cdot 3SiO_2$	0.76	−6	23	0.42	59	85	[26]
Mean values	0.74	−4	20	0.49	38	73	
Deviations	±0.02			±0.08			

[a] $x = I_{\mathrm{exp}}^{\max}/I_{\mathrm{theor}}^{\max}$.

[b] Different literature data for the specific heats.

is smaller (≈ 3%), compared with the corresponding value (≈ 16%) for CNT. Also the absolute mean value of $\log(I_{\mathrm{exp}}^{\max}/I_{\mathrm{theor}}^{\max})$ is much smaller (≈4) for CT-CNT), compared with the impressive corresponding value (≈ 38) of CNT. If these data were confirmed for other materials, one could conclude that the new modification of the classical nucleation theory, CT-CNT, agrees much better with experimental data than CNT.

If CT-CNT was confirmed for other systems, this would apparently be in contradiction with the fact that the adiabatic nucleation theory also indicates quite well, if and at what temperatures nucleation occurs. A possible explanation for this apparent paradox could be that nucleation is neither a strictly adiabatic nor a strictly isothermal phenomenon and that both theories are only approximations to a more complicated phenomenon. This point of view seems to be supported by the fact that the (critical) nucleus at the temperature of maximum nucleation frequency, obtained by CT-CNT, contains about 20 molecules, a number which is quite similar to 14, as postulated in ANT. More experimental and theoretical studies are necessary in order to obtain definitive conclusions.

The author is indebted to Professor E.D. Zanotto for the communication, prior to publication, of the results of the test of CT-CNT and CNT in Na_2O–2CaO·3SiO_2, Li_2O–2SiO_2 and CaO–SiO_2 glasses and for very useful discussions; and to be institutions CNP_q, FINEP and CEPG for financial support.

Appendix. Comments about the curvature dependence of the solid–liquid interfacial tension

There is a strong controversy about the question whether the solid–liquid interfacial tension increases or decreases with increasing curvature, when a solid sphere is inside an extended liquid phase.

A.1. The sharp interface or 'broken bonds' model

"It is assumed that the crystal is undistorted right up to its surface (solid–liquid interface), and that all the bonds have the same energy within the crystal" [28]. This model considers (almost) absolutely homogeneous phases up to a sharp dividing surface which still can be 'smooth' (flat) or 'rough' (irregular). All atoms belong either to the homogeneous liquid phase or to the homogeneous solid phase and only the bonds which cross the sharp dividing surface are special. The surface tension depends then on how many solid–solid bonds are substituted (broken) by solid–liquid bonds which have a higher enthalpy by $\Delta h_{L}/12$ in a close packed structure. If the solid 'sphere' is small, each atom at the surface has more liquid neighbours, there are more solid–liquid (or 'broken' solid–solid) bonds and the interfacial tension increases [28,29].

A.2. The 'diffuse' interface model

"In any multiphase assembly, there must be transition regions in which the atomic configuration changes from that characteristic of one phase to that characteristic of another. These regions are frequently only a very few interatomic distances thick, and the concept of an interphase boundary which may be regarded as a geometric surface is then still quite appropriate … . In terms of the discussion above, the distinction between liquid and solid phases depend mainly on the existence or not existence of long-range order of position, and this is only defined adequately in a finite volume. Thus there may be intrinsic difficulties in the concept of a 'sharp' liquid–solid interface, since we may only be able to state definitively that the structure is that of the liquid or solid for atoms well removed from the transition region … . Indirect evidence that the solid–liquid interface is 'diffuse' is provided by a thermodynamic argument due to Hilliard and Cahn [30]." [5]. The 'diffuse' interface model definitely considers an inhomogeneous interfacial layer of atoms (or molecules) of a thickness of one or several interatomic (or intermolecular) distances. The origin of the interfacial tension is then due to the fact that the atoms of the interfacial layer are forced into nonequilibrium intermediate (between the solid and liquid) enthalpic positions. The contribution of one atom to the interfacial tension of a non-

curved surface is then proportional to $\Delta h_{L}/2$. However in the case of a curved surface, the surface tension exerts a capillary pressure on the enclosed phase (solid phase in our case). The enthalpy of the enclosed solid phase increases because of this effect and the corresponding latent heat, $\Delta h_{L'}$ (which is the difference between the enthalpy of the liquid and the enclosed solid per atom), decreases. Because of this feedback the interfacial tension, which is now proportional to $\Delta h_{L'}/2$ per atom, is now smaller for a curved interface. The success of CT-CNT gives additional support to the 'diffuse' interface model and reforces the arguments of Hilliard and Cahn [30]. (These authors also commented that the solid–liquid interfacial tension obtained from nucleation experiments is smaller than the interfacial tension of the non-curved surface). This point of view is much more satisfactory also because (as can be verified, substituting σ from eq. (14) in eq. (6)) the capillary pressure does not diverge to very high values for very small radii (an infinitely high value for $r = 0$), as would be predicted by the 'sharp' interface model.

The parameter $\alpha = 0.75$ (see table 1) means physically that the effective thickness of the interfacial layer is equal to about 1.5 intermolecular distances. This means that there is one monomolecular layer in an intermediate enthalpic position and on each side another slightly disturbed monomolecular layer.

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