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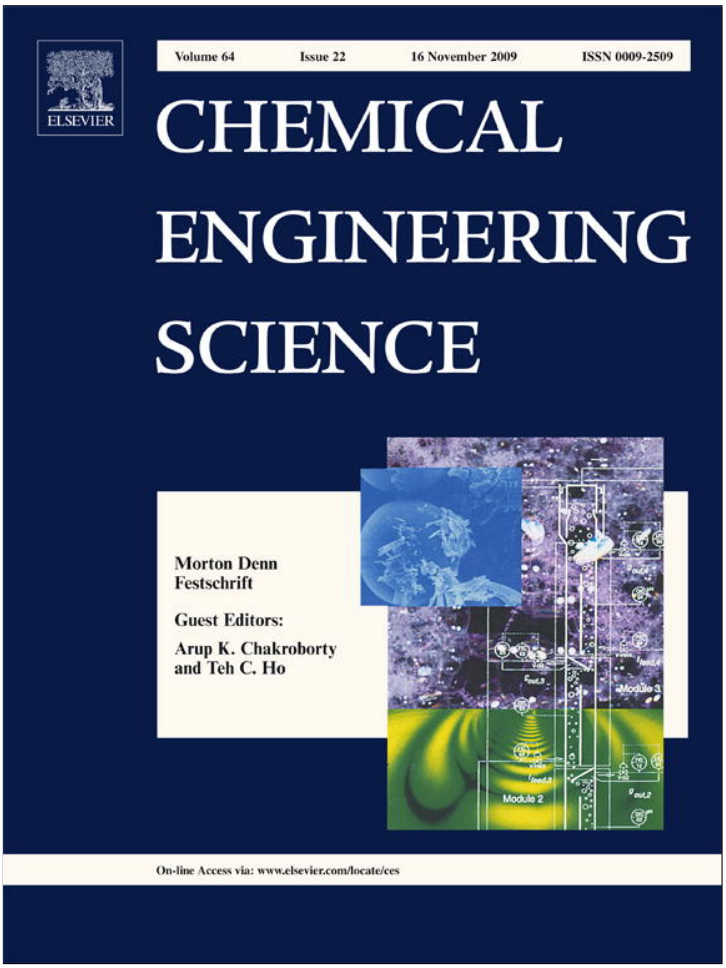

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Homogeneous crystal nucleation in droplets as a method for determining the line tension of a crystal–liquid–vapor contact

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ABSTRACT

The line tension of a three-phase contact is believed to play an important role in phase transition and phase equilibria in multiphase nanoscale systems hence the need in developing various methods for its experimental evaluation. In this paper we suggest an indirect experimental method for determining the line tension of a solid–liquid–vapor contact based on experiments on homogeneous crystallization of droplets. The underlying idea explores our recent finding that the line tension can give rise to an important contribution to the free energy of formation of a crystal nucleus in a surface-stimulated mode when one of its facets forms at the droplet surface and thus represents a "crystal–vapor" interface. The proposed method requires experimental data on the rate of homogeneous crystal nucleation as a function of droplet size. However, it can provide a rough estimate of line tension even if the rate is known only for one droplet size. Using the method to examine experimental data on homogeneous crystal nucleation in droplets of 19, 49, and 60 μm radii at $T = 237$ K, we evaluated the line tension of ice–(liquid)water–(water)vapor contact to be positive and of the order of 10^{-11} N consistent with the current expectations.

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1. Introduction

Wetting phenomena in many systems (e.g., adhesives, lubricants, melts in contact with solids, cell adhesion to biological membrane, etc., Adamson, 1990; Duncan-Hewitt et al., 1989) are often studied by means of contact angle based methods. The interpretation of the observed contact angle in real systems is complicated by many factors such as heterogeneity of the system, presence of surfactants, smoothness of the surface, and line tension, which all can affect the observed contact angle. All these factors need to be studied to better understand the contact angle and wetting phenomena in general. The line tension factor is becoming particularly important nowadays due to the fast development of nanotechnologies because line tension can play a major role in the behavior of nanosize systems. It is thus important to clearly establish the magnitude and sign of line tension to determine its relevance to (nano)technological applications.

Gibbs (1961) was the first to introduce the concept of line tension of a three-phase contact in the classical thermodynamics. However, "full scale" studies of this quantity have started only relatively recently (Boruvka and Neumann, 1977; Rowlinson and Widom, 1982; Amirfazli and Neumann, 2004). (Note that although the term "line tension" is mostly used in association with the contacts of three three-dimensional phases, it also often referred to the tension associated with the borderline of two two-dimensional phases; in what follows, only the former contact regions will be of interest, i.e., those of three three-dimensional phases.)

Thermodynamically, the line tension can be defined as follows. If three phases are in equilibrium, there may exist a three-phase contact region in addition to three two-phase interfaces. The distortion of the order parameter(s) spatial distribution(s) in the three-phase contact region gives rise to excess contributions to the extensive thermodynamic characteristics of the system. These are usually attributed to a three-phase contact line. Excess quantities per unit length of the contact line are called linear adsorptions. For three bulk phases in equilibrium, the interfaces between them can be treated as planar and the line of their intersection, that is, the contact line, as a straight line. The location of the contact line is arbitrary and among all linear adsorptions only one does not depend on its choice. This is the linear adsorption of the grand canonical potential also called "line tension" (Boruvka and Neumann, 1977; Rowlinson and Widom, 1982). All other adsorptions depend on the location of the contact line and hence are functions of its two coordinates. There are large discrepancies among theoretical, simulated, and experimental data concerning the magnitude and sign of line tension (Amirfazli and Neumann, 2004).

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The majority of theoretical (Rowlinson and Widom, 1982; Churaev et al., 1982; Toshev et al., 1988; Getta and Dietrich, 1998; Bauer and Dietrich, 1999; de Feijter and Vrij, 1972; Harkins, 1937; Widom, 1995; Bresme and Quirke, 1998, 1999) and simulated (Bresme and Quirke, 1998, 1999; Djikaev, 2005) predictions for line tension (except for conditions close to a wetting transition) range from 10^{-12} to 10^{-10} N, but values as high as 10^{-6} N are also reported. Unlike the surface tension (which is always positive), the sign of the line tension can theoretically be either positive or negative (de Feijter and Vrij, 1972; Indekeu, 1992; Varea and Robledo, 1992; Szleifer and Widom, 1992; Dobbs, 1999).

There are various experimental techniques for determining the line tension in both liquid–liquid–fluid and solid–liquid–vapor systems (see Amirfazli and Neumann, 2004, for a recent review). This diversity is partly due to the small magnitude of the line tension which requires considerable ingenuity in the design of experiments. Most experimental methodologies fall under one of the following categories: thin film arrangements, drop size dependence of contact angles, critical particle/liquid lens size, and heterogeneous nucleation. In all of the above techniques, the line tension is found indirectly by measuring such parameters as the contact angle or particle size, and inferring the line tension through appropriate thermodynamic or other theoretically developed correlations (e.g., the modified Young equation).

Most experiments in liquid–liquid–vapor and solid–liquid–vapor systems provided (Toshev et al., 1988; Getta and Dietrich, 1998; Bauer and Dietrich, 1999; Aveyard and Clint, 1996; Drelich, 1997) positive values for the line tension ranging from 10^{-9} to 10^{-6} N. However, studying the line tension dependence on the contact angle (Wang et al., 1999, 2001; Pompe and Herminghaus, 2000; Pompe, 2002), a change in sign was observed near the first-order wetting transition. For example, in Pompe (2002) the line tension of hexaethylene glycol on a silicon wafer changes from $+2.5\times10^{-11}$ N for a contact angle below 6° to -2×10^{-10} for a contact angle above 6°. In this paper we present a theoretical basis for determining the line tension of a "solid–liquid–vapor" contact region by means of experiments on homogeneous crystallization of droplets. The underlying idea is a natural result of recent advances in the thermodynamics (Djikaev and Ruckenstein, 2008) and kinetics (Djikaev, 2008) of surface-stimulated mode of homogeneous crystal nucleation in droplets.

Neglecting the effect of line tension associated with a crystal–liquid–vapor contact, it was previously (Djikaev et al., 2002, 2003) found that, if at least one of the facets of a crystal nucleus is only partially wettable by its own melt (Defay et al., 1966), then the droplet surface can stimulate *homogeneous* crystal nucleation so that the formation of a nucleus with that facet at the droplet surface (surface-stimulated mode) is thermodynamically favored over its formation with all the facets *within* the droplet (volume-based mode). However, as recently shown in Djikaev and Ruckenstein (2008), the line tension can give rise to an important contribution to the free energy of formation of a "surface-stimulated" crystal nucleus. Moreover, as will be shown in the present paper, this contribution (equal to the product of the tension and length of the three-phase contact line) can be evaluated with the help of experimental data on the rate of freezing of droplets.

2. Background: the thermodynamics and kinetics of homogeneous crystal nucleation in a droplet

For the sake of concreteness, we will hereafter discuss the formation of ice crystals in liquid water droplets surrounded by water vapor. Water constitutes an overwhelmingly dominant chemical species in atmospheric processes. Consequently, great importance is attributed to studying aqueous aerosols and cloud droplets as well as their phase transformations. The size, composition, and phases of aerosol and cloud particles affect the radiative and chemical properties (Pruppacher and Klett, 1997; Fletcher, 1962) of clouds and hence have a great impact on Earth's climate as a whole. On the other hand, the composition, size, and phases of atmospheric particles are determined by the rate at and mode in which these particles form and evolve (Pruppacher and Klett, 1997; Fletcher, 1962; Cox, 1971). Although, most phase transformations in aqueous cloud droplets occur as a result of heterogeneous nucleation on preexisting macroscopic particles, macromolecules, or even ions (Fletcher, 1962), in a number of important cases atmospheric particles appear to freeze homogeneously (Cox, 1971; Heymsfield and Miloshevich, 1993).

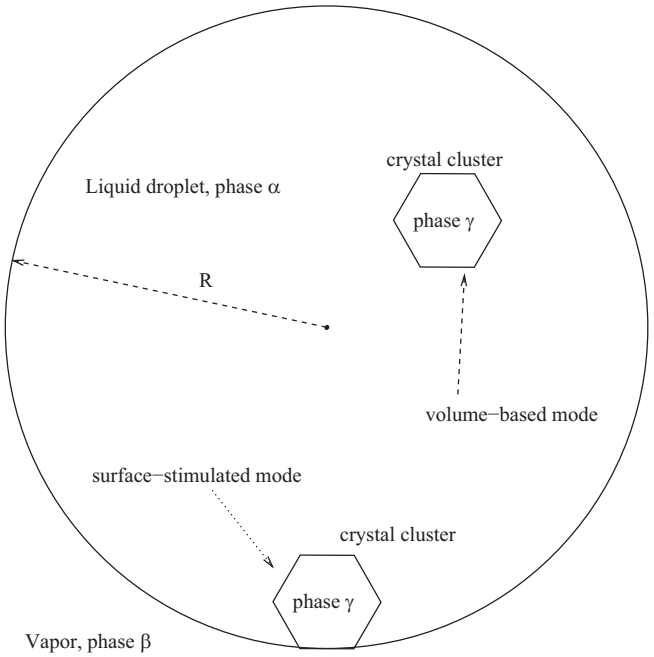

Fig. 1. Homogeneous crystal nucleation in a liquid droplet surrounded by vapor. In the volume-based mode the crystal cluster forms with all its facets completely immersed in a liquid droplet. In the surface-stimulated mode the cluster forms with one of its facets at the liquid–vapor interface, and all other facets representing the "crystal–liquid" interface.

2.1. Free energy of homogeneous formation of crystal nuclei in the surface-stimulated and volume-based modes

To determine if and how the surface of a liquid droplet of radius R can thermodynamically stimulate its homogeneous crystallization, it is necessary to compare the reversible works of formation of a crystal nucleus (critical crystal cluster) in two modes (Fig. 1). In the volume-based mode, the crystal cluster is formed with all the facets interfacing the liquid. In the surface-stimulated mode, the crystal cluster forms with one of its facets at the liquid–vapor interface, whereas all the others form the "crystal–liquid" interface. For simplicity, the droplet surface can be considered to be planar.

Consider a bulk liquid (in a container) whose upper surface is in contact with its vapor phase of constant pressure and temperature. Upon sufficient supercooling, a crystal nucleus may form homogeneously with one of its facets on the foreign particle. The crystal is considered to be of arbitrary shape with λ facets (Fig. 2).

Let us introduce the superscripts α, β, and γ to denote quantities in the liquid, vapor, and crystal nucleus, respectively. Double superscripts will denote quantities at the corresponding interfaces, and triple superscripts at the corresponding three-phase contact lines.

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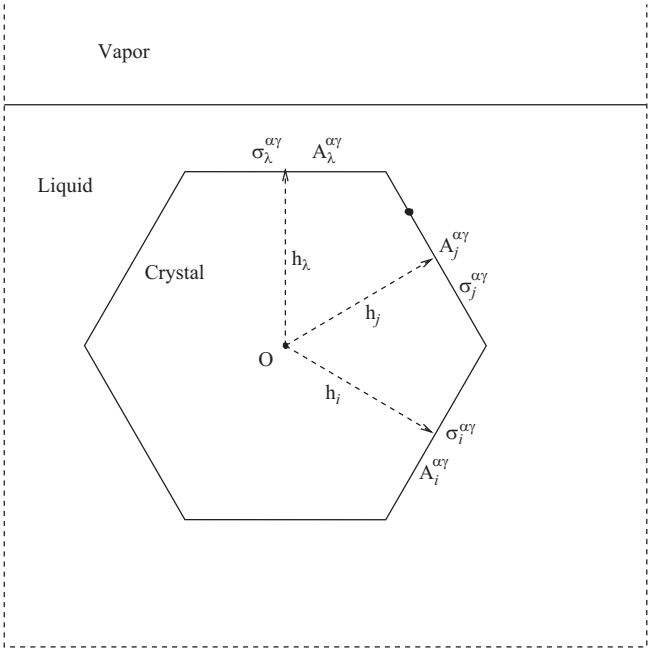

Fig. 2. Illustration to Wulff's relations. The surface area and surface tension of facet i are denoted by A_i and σ_i, respectively; h_i is the distance from facet i to reference point O.

The surface area and surface tension of facet i ($i = 1, \ldots, \lambda$) will be denoted by A_i and σ_i, respectively. (Anisotropic interfacial free energies are believed to be particularly important in determining the character of the nucleation process.)

The reversible work of homogeneous formation of a crystal in the volume-based mode (with all its facets within the liquid phase) is given by the expression (Djikaev and Ruckenstein, 2008; Djikaev et al., 2002)

$$W^{vb} = -v\Delta q \ln \Theta + \sum_{i=1}^{\lambda} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma}, \tag{1}$$

where v is the number of molecules in the crystal cluster, $\Delta q < 0$ is the enthalpy of melting per molecule (see, e.g., Defay et al., 1966), $\Theta = T/T_0$, T is the temperature of the system, T_0 is the melting temperature of the bulk ice ($T < T_0$). Eq. (1) implies that the supercooling $T - T_0$ is not too large or, alternatively, in the temperature range between T and T_0 the enthalpy of fusion does not change significantly.

The necessary and sufficient conditions for the equilibrium shape (known as the Wulff form) of the crystal are represented by a series of equalities, referred to as Wulff's relations (see, e.g., Defay et al., 1966), which can be regarded as a series of equilibrium conditions on the crystal "edges" formed by adjacent facets. For example, on the edge between homogeneously formed facets i and $i+1$ the equilibrium condition is

$$\frac{\sigma_i^{\alpha\gamma}}{h_i} = \frac{\sigma_{i+1}^{\alpha\gamma}}{h_{i+1}} \equiv \frac{m}{2} \quad (i = 1, \ldots, \lambda), \tag{2}$$

where h_i is the distance from facet i to a point O within the crystal (see Fig. 2) resulting from the Wulff construction.

In the above equations (as well as in those following), it is assumed that the mechanical effects within the crystal (e.g., stresses) reduce to an isotropic pressure P^γ, so that (Defay et al., 1966)

$$P^\gamma - P^\alpha = m. \tag{3}$$

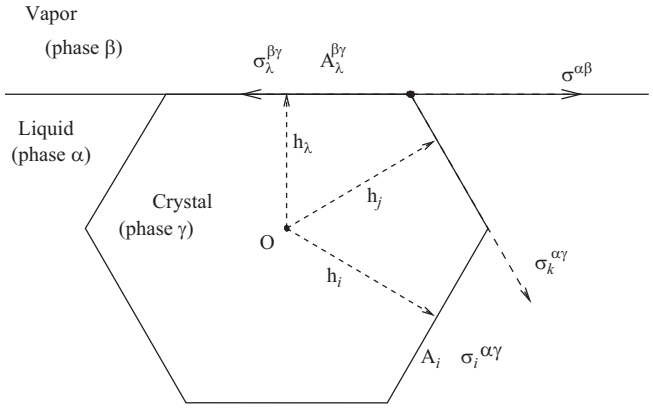

Fig. 3. Illustration to modified Wulff's relation when the crystal forms with one of its facets at the liquid–vapor surface.

The relations implied in Eq. (3) for a crystal are equivalent to Laplace's equation applied to a liquid. Thus, just as for a droplet, one can expect to find a high pressure within a small crystal. It is this pressure that increases the chemical potential within the crystal.

In the surface-stimulated mode, when one of the facets (say, facet λ) of the crystal cluster constitutes the crystal–vapor interface while all the others lie within the liquid phase (see Fig. 3), the reversible work of homogeneous formation of such a crystal can be written in the form (Djikaev and Ruckenstein, 2008)

$$W^{ss} = -v\Delta q \ln \Theta + \sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_\lambda^{\beta\gamma} A_\lambda^{\beta\gamma} - \sigma^{\alpha\beta} A_\lambda^{\beta\gamma} + \tau^{\alpha\beta\gamma} L^{\alpha\beta\gamma}. \tag{4}$$

where τ is the line tension associated with a three-phase contact line (Boruvka and Neumann, 1977; Rowlinson and Widom, 1982) of length L. Again, in this equation it is assumed that the supercooling $T - T_0$ is not too large so that the enthalpy of fusion is almost constant in the temperature range between T and T_0.

The shape of the crystal will now differ from that in which all facets are in contact with the liquid. As shown in (Djikaev and Ruckenstein, 2008), the modified Wulff relations that take into account the effect of the line tension on the equilibrium shape of the crystal have the form

$$\frac{1}{h_1'}\left(\sigma_1^{\alpha\gamma} - \sum_{k\in\{\kappa\}} \tau_{\lambda k} \frac{\partial L_{\lambda k}}{\partial A_1}\right) = \frac{1}{h_2'}\left(\sigma_2^{\alpha\gamma} - \sum_{k\in\{\kappa\}} \tau_{\lambda k} \frac{\partial L_{\lambda k}}{\partial A_2}\right) = \ldots = \frac{1}{h_\lambda'}\left(\sigma_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} - \sum_{k\in\{\kappa\}} \tau_{\lambda k} \frac{\partial L_{\lambda k}}{\partial A_\lambda}\right) = \frac{m'}{2}, \tag{5}$$

where the prime marks quantities for the surface-stimulated mode, $\{\kappa\}$ is the set of facets adjacent to facet λ, $\tau_{\lambda k}$, and $L_{\lambda k}$ are the line tension and length of the edge formed by adjacent facets λ and k (as already mentioned, the droplet is assumed to be much larger than crystal clusters). Note that m' in Eq. (5) is a Lagrange multiplier analogous (but not identical) to m, both arising from the minimization (Defay et al., 1966; Gibbs, 1928; Curie, 1885) of the free energy of formation of a crystal cluster subject to the constraint $V^\gamma = const$ (see Djikaev and Ruckenstein, 2008, for more details) Consequently, Eq. (3) (the equivalent of Laplace's equation for crystals) becomes

$$P^\gamma - P^\alpha = m'. \tag{6}$$

Let us assume that the shape of an ice crystal cluster is known and it is a hexagonal prism. Hence, its state is completely determined by two geometric variables (provided that its density and temperature

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are given), e.g., the height of the prism and the length of a side of a (regular) hexagon (the base of the prism). However, owing to Wulff's relations, Eqs. (2) and (5), only one of these two variables is independent. Therefore, both works W^{vb} and W^{s} are functions of only one independent variable, say, variable a, the length of a side of the hexagon. The concrete form of the function $W^{ss}=W^{ss}(a)$ depends on the mutual orientation of the crystal cluster and droplet surface.

For instance, consider an ice cluster formed with one of its basal facets (assumed to be only partially wettable by water) at the droplet surface. Mark the basal facets with subscripts 1 and 2 and the prismal facets with subscripts $3,\ldots,8$ (as agreed above, facet 2, which is partially wettable by water, forms at the droplet surface and represents the crystal–vapor interface). Clearly, $\sigma_p^{\alpha\gamma}\equiv\sigma_3^{\alpha\gamma}=\cdots=\sigma_8^{\alpha\gamma}$, $A_p^{\alpha\gamma}\equiv A_3^{\alpha\gamma}=\cdots=A_8^{\alpha\gamma}$, $A_b^{\alpha\gamma}\equiv A_1^{\alpha\gamma}=A_2^{\alpha\gamma}$ (subscripts "b" and "p" mark quantities for the "basal" and "prismal" facets, respectively). In both the volume-based and surface-stimulated modes the base is an identical regular hexagon with the side length $a\equiv a_3=\cdots=a_8$, where a_i $(i=3,\ldots,8)$ is the length of the edge formed by the basal facet with prismal facet i.

Let us denote the volume of the crystal cluster in the volume-based and surface-stimulated modes by V^{γ} and V'^{γ}, respectively. In the first term on the RHSs of Eqs. (1) and (4) the number v of molecules in the crystal cluster can be represented as either $\rho^{\gamma}V^{\gamma}$ or $\rho^{\gamma}V'^{\gamma}$, respectively, where ρ^{γ} is the number density of molecules in phase γ (ice). The volume of an Ih crystal (shaped as a hexagonal prism) is equal to the product "*height of the prism*" × "*surface area of the base*". The surface area of the base (regular hexagon in the former and irregular in the latter) is proportional to a^2. In both cases, the height of the prism is linearly related to a according to Wulff's relations (2) and (5). Indeed, it can be found as the sum of the heights of two basal pyramids (i.e., pyramids with the basal facets as their bases). In the volume-based mode, the heights of both basal pyramids, according to Wulff's relations (2), are equal to $a(\sqrt{3}/2)(\sigma_b^{\alpha\gamma}/\sigma_p^{\alpha\gamma})$. This is also the height of that pyramid in the surface-stimulated mode whereof the base is *within* the droplet. On the other hand, the height of the pyramid built on the basal facet at the droplet surface is equal to $a(\sqrt{3}/2)(\sigma_b^{\beta\gamma}-\sigma^{\alpha\beta})/\sigma_p^{\alpha\gamma}$. Therefore, in the surface-stimulated mode

$$h'=a\frac{\sqrt{3}}{2}\frac{\sigma_b^{\alpha\gamma}+\sigma_b^{\beta\gamma}-\sigma^{\alpha\beta}}{\sigma_p^{\alpha\gamma}} \tag{7}$$

while in the volume-based mode

$$h=a\sqrt{3}(\sigma_b^{\alpha\gamma}/\sigma_p^{\alpha\gamma}) \tag{8}$$

(the effect of line tension on the shape of an equilibrium crystal is neglected as discussed in Djikaev and Ruckenstein, 2008). Thus, in both Eqs. (1) and (4) $v\propto\rho^{\gamma}a^3$. Likewise, one can show that all the surface tension and line tension terms on the RHSs of Eqs. (1) and (4) are proportional to a^2 and a, respectively. Therefore, the functions $W^{ss}(a)$ and $W^{vb}(a)$, reversible works of formation of a crystal cluster in the surface-stimulated and volume-based modes, can be written (tedious but simple algebra is omitted) as (Djikaev and Ruckenstein, 2008)

$$W^{ss}(a)=-S_3a^3+S_2a^2+S_1a,\quad W^{vb}(a)=-B_3a^3+B_2a^2+B_1a \tag{9}$$

with

$$S_3=\frac{9}{4}\rho^{\gamma}\Delta q\ln(\Theta)(\sigma_b^{\alpha\gamma}+\sigma_b^{\gamma\beta}-\sigma^{\alpha\beta})/\sigma_p^{\alpha\gamma},$$

$$S_2=\frac{3\sqrt{3}}{2}[2\sigma_b^{\alpha\gamma}+3(\sigma_b^{\gamma\beta}-\sigma^{\alpha\beta})],\ S_1=6\tau^{\alpha\gamma\beta}$$

and

$$B_3=\frac{9}{2}\rho^{\gamma}\Delta q\ln(\Theta)(\sigma_b^{\alpha\gamma}/\sigma_p^{\alpha\gamma}),\quad B_2=9\sqrt{3}\sigma_b^{\alpha\gamma},\ B_1=0$$

(there is no three-phase contact line in the volume-based mode of homogeneous crystal nucleation, hence $B_1=0$). One can find the radius a_* of the hexagonal base of the crystal nucleus as the positive solution to the equation $dW^{ss}(a)/da|_{a_*}=-3S_3a_*^2+2S_2a_*+S_1=0$, or alternatively, $dW^{vb}(a)/da|_{a_*}=-3B_3a_*^2+2B_2a_*+B_1=0$, which lead to $a_*=(2S_2+\sqrt{4S_2^2+12S_1S_3})/6S_3$ or $a_*=2B_2/3B_3$. The heights of the crystal nucleus (a hexagonal prism) are different in the surface-stimulated and volume-based modes, according to Eqs. (7) and (8).

2.2. Effect of the surface-stimulated mode on the kinetics of crystal nucleation

The classical expression for the rate of crystal nucleation conventionally used in atmospheric models as well as for treating experimental data, is derived by assuming that crystal nuclei form *within* the liquid (Defay et al., 1966; Pruppacher and Klett, 1997; Fletcher, 1962). However, under some conditions (Djikaev and Ruckenstein, 2008; Djikaev, 2008; Djikaev et al., 2002, 2003) the formation of a crystal nucleus with one of its facets at the droplet surface is thermodynamically favored over its formation with all the facets *within* the droplet. This effect can become important when the crystallizing liquid is in a dispersed state, which is the case with the freezing of atmospheric droplets (Pruppacher and Klett, 1997; Fletcher, 1962; Cox, 1971; Heymsfield and Miloshevich, 1993) and many experiments (Bertram and Sloan, 1998; Krämer et al., 1999; Duft and Leisner, 2004).

Assuming a monodisperse (or narrow enough Gaussian-like) distribution of liquid droplets, the average crystallization time of the ensemble equals that of a single droplet (this is a reasonable assumption in experiments because the droplet sizes are usually well controlled). Let us denote that time by t_1. For typical sizes of atmospherically relevant droplets the formation of a single crystal nucleus in a droplet immediately leads to the crystallization of the latter, i.e., the time of growth of a crystal nucleus to the size of the whole droplet is negligible compared to the time necessary for the first nucleation event in the droplet to occur (in experiments this can be achieved by using special techniques, Bertram and Sloan, 1998; Krämer et al., 1999; Duft and Leisner, 2004). Consequently,

$$t_1=1/I, \tag{10}$$

where I is the per-droplet (pd) nucleation rate, i.e., the total number of crystal nuclei appearing in the whole volume of the liquid droplet per unit time.

Even when the droplet surface stimulates crystal nucleation therein, the crystal nucleus has to start its initial evolution *homogeneously* as a subcritical cluster in a spherical layer adjacent to the droplet surface (sub-surface nucleation, SSN, layer, Djikaev, 2008). When this crystal becomes large enough (due to fluctuational growth usual for the nucleation stage), one of its facets hits the droplet surface and at this moment or shortly thereafter it becomes a nucleus owing to a drastic change in its thermodynamic state.

Any crystalline cluster that starts its evolution with its center in the SSN layer can become a nucleus once one of its facets that stimulates nucleation (say, facet λ), meets the droplet surface. However, to become a surface-stimulated nucleus, the subcritical cluster must evolve in such a way that its facet λ is parallel to the droplet surface at the time they meet. The orientation adjustment cannot be mechanical because this would require relatively long time scales, but may, or may not, occur by means of appropriate spatial distribution of density and structure fluctuations around the cluster.

In the framework of the SSN layer model, the pd-rate of crystal nucleation can be written as

$$I=I^{vb}+I^{ss}, \tag{11}$$

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where I^{vb} is the pd-rate of volume-based crystal nucleation (i.e., number of crystal nuclei that can form in the volume-based mode per unit time in the whole droplet) and I^{ss} is the pd-rate of surface-stimulated crystal nucleation (i.e., number of crystal nuclei forming in the surface-stimulated mode per unit time in the SSN layer). The rates I^{vb} and I^{ss} are simple functions of R,

$$I^{vb} = J_v \frac{4\pi}{3} R^3, \quad I^{ss} = J_v 4\pi R^2 \delta e^{-\Delta W_*/kT}, \tag{12}$$

where J_v is the rate of ice nucleation in the volume-based mode (Turnbull, 1950; Turnbull and Fisher, 1949), δ is the effective thickness of the SSN layer, and $\Delta W_* \equiv W_*^{ss} - W_*^{vb}$, with W_*^{vb} and W_*^{ss} being the free energies of formation of nuclei in the volume-based and surface-stimulated (with some representative facet at the droplet surface) modes, respectively. Thus, one can represent Eq. (11) in the form

$$\frac{I}{I^{vb}} = 1 + \kappa \frac{1}{R}, \tag{13}$$

where

$$\kappa = 3\delta e^{-\Delta W_*/kT}. \tag{14}$$

As will be seen below, κ depends on the line tension of the ice–water–vapor contact, τ. Note that on the RHS of Eq. (13) terms of the order of $(\delta/R)^2$ and $(\delta/R)^3$ (arising because volume-based nucleation takes place in a sphere of radius $R-\delta$ while surface-stimulated nucleation occurs in a spherical shell of thickness δ around that sphere) are omitted because δ is of the order of nucleus size which is usually much smaller than R.

3. Determination of the line tension of an ice–water–vapor contact

As clear from Eqs. (11)–(14), (1), and (2), the pd-rate of crystal nucleation, I, depends on the value of the tension $\tau \equiv \tau^{\alpha\beta\gamma}$ at the ice–water–vapor contact line. Thus, it appears that one can determine τ from experimental data on I, much like the liquid–vapor surface tension is estimated as a "kinetic parameter" adjusted to the experimentally obtained rates of ice nucleation in bulk supercooled water (Pruppacher and Klett, 1997). A theoretical basis for the procedure of determining τ is as follows.

For a given supercooling (i.e., given Θ), the rate J_v can be assumed to be known provided that the ice–liquid surface tension is known (see, e.g., Pruppacher and Klett, 1997, Chapter 7.2 and Pruppacher, 1995). The numerator on the LHS of Eq. (15) is the overall per-particle rate of crystal nucleation which is effectively measured in experiments on freezing of droplets (Krämer et al., 1999; Duft and Leisner, 2004). Thus, one can find a quasi-experimental dependence of the ratio I/I^{vb} on $1/R$. Using then the linear LMS fit of the experimental data (I/I^{vb} vs. $1/R$), one can determine the coefficient κ in Eq. (14).

For simplicity, let us consider the case where only two basal facets of an ice crystal contribute to the surface-stimulated mode of nucleation, so that the effective thickness $\delta \approx h'_b$. If the both the basal and prismal facets contribute to the surface-stimulated nucleation, one could estimate δ as a simple arithmetic mean, $\delta \approx (h'_b + h'_p)/2$, but this will have virtually no effect on the estimate for τ. (Recall that h'_b and h'_p are the heights of the pyramids whereof the bases are the basal or prismal facets, respectively, forming a crystal–vapor interface; they differ from each other by less than 25%, i.e., $h'_p/h'_b \approx 0.76$). According to Eqs. (14) and (9), the coefficient κ depends on τ because so does ΔW_*. The dependence of ΔW_* on τ has a simple linear form

$$\Delta W_* = Q_0 + Q_1 \tau, \tag{15}$$

where

$$Q_0 = -(S_3 - B_3)a_*^3 + (S_2 - B_2)a_*^2, \quad Q_1 = 6a_* \tag{16}$$

and $a_* = 2B_2/3B_3$. Thus, having found κ from experiments on crystallization of droplets, one can determine the line tension τ from

$$\tau = -\frac{1}{Q_1}\left[Q_0 + k_B T \ln\left(\frac{\kappa}{3h'_b}\right)\right] \tag{17}$$

with h'_b and a_* related by $h'_b = a_*(\sqrt{3}/2)(\sigma_b^{\beta\gamma} - \sigma^{\alpha\beta})/\sigma_p^{\alpha\gamma}$.

3.1. Numerical evaluations

The main problem in using the above procedure is the lack of systematic experiments on the crystallization of droplets. To accurately determine τ, experiments must be carried out under the same external conditions (temperature, pressure, composition of the ambient medium, etc.) on droplets of various sizes which should not be too large (in order for the surface-stimulation effect to be significant). At present, however, such systematic experiments are rather rare. Nevertheless, one can use the above procedure to roughly evaluate τ even from experimental results at one droplet size because the free term in the linear dependence of I/I^{vb} is known (equal to 1).

As an illustration, we used the experimental data reported in Krämer et al. (1999) and Duft and Leisner (2004) to evaluate the line tension of ice–(liquid)water–(water)vapor contact. In Krämer et al. (1999) homogeneous crystal nucleation rates were measured in single levitated water droplets of radius $R = 60 \pm 2\,\mu m$ in the range of temperatures between 236 and 237 K where the observed nucleation rates varied by two orders of magnitude. Homogeneous crystal nucleation rates in supercooled water droplets of radii 19 ± 0.25 and $49 \pm 0.5\,\mu m$ at $T = 237$ K were determined in Duft and Leisner (2004) by using the same technique. We considered the results reported for $T = 237$ K because this temperature is close to the temperature for which the data on the ice–water, ice–vapor, and water–vapor interfacial tensions are available (Pruppacher and Klett, 1997). The latter are needed to calculate I^{vb} in the denominator on the LHS of Eq. (13), as well as the coefficients $S_1, \ldots, B_3$ in the expressions for W^{ss} and W^{vb} in Eq. (9). The interfacial tensions were thus taken (Pruppacher and Klett, 1997) to be $\sigma_b^{\alpha\beta} \simeq 88$ dyn/cm, $\sigma_b^{\alpha\gamma} \simeq 23$ dyn/cm, $\sigma_p^{\alpha\gamma} \simeq 24$ dyn/cm, $\sigma_b^{\beta\gamma} \simeq 102$ dyn/cm, and $\sigma_p^{\beta\gamma} \simeq 111$ dyn/cm. The number densities of water and ice were taken $\rho^\alpha = (1\,N_A/18)\,cm^{-3}$ and $\rho^\gamma = (0.92N_A/18)\,cm^{-3}$ (where N_A is the Avogadro number), and the enthalpy of melting per molecule $\Delta q \simeq (333.55 \times 10^7 N_A/18)$ erg (the latter is needed for S_3 and B_3). The activation barrier ΔF_{act} that a water molecule overcomes (Turnbull, 1950; Turnbull and Fisher, 1949; Pruppacher and Klett, 1997) upon its transition across the ice–liquid interface (i.e., from its equilibrium position in the liquid state to its equilibrium position in ice) was evaluated according to Pruppacher and Klett, 1997 and Pruppacher (1995) (ΔF_{act} is needed to calculate I^{vb}).

Using these numerical values and experimental data for I provided in Krämer et al. (1999) and Duft and Leisner (2004) we evaluated the line tension τ of ice–water–vapor contact region to be positive: $\tau \sim 1.16 \times 10^{-11}$ N (from Krämer et al., 1999) and $\tau \sim 1.46 \times 10^{-11}$ (from Duft and Leisner, 2004). Both values (obtained by using Eq. (17)) fall well in the middle of the so far experimentally observed and theoretically predicted values for line tension in various systems. In calculating the former, κ was evaluated from Eq. (13) because droplets of only one radius were studied in Krämer et al. (1999), whereas the latter was calculated with κ obtained by fitting the experimental dependence I vs. R (provided in Duft and Leisner, 2004) with the polynomial of the form $A_2R^2 + A_3R^3$ whereof the coefficients A_2 and A_3, as clear from Eqs. (12) and (13), are expected to

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be $A_2 = (4\pi/3)J_v\kappa$ and $A_3 = (4\pi/3)J_v$. The fitting procedure also provided $J_v \simeq 2.7 \times 10^6\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ which is in excellent agreement with expectations (Duft and Leisner, 2004).

The sign of τ is not affected by the uncertainty in experimental data on I: when the value of the latter is changed by 50%, the value of τ changes by less than 10%. The uncertainly in measuring the droplet radii in experiments has even a smaller effect on τ. The most significant influence on τ thus extracted from experiments on droplet freezing is exerted by the value of $\sigma_b^{\alpha\gamma}$ and $\sigma_b^{\beta\gamma}$ used in calculating S_3 and B_3. For example, using a not unlikely value $\sigma_b^{\beta\gamma} \simeq 120\,\mathrm{dyn/cm}$ (see Pruppacher and Klett, 1997, Section 5.7.1) leads to a negative line tension, $\tau \sim -4\times10^{-12}$ N. Thus very accurate interfacial tensions are needed for the proposed method to provide accurate results for the ice–water–vapor line tension.

4. Concluding remarks

The line tension can play a major role in phase transition and phase equilibria in multiphase nanosize systems. Due to the ever increasing need in nanotechnologies, it is thus important to develop theoretical and experimental methods allowing one to clearly establish the magnitude and sign of line tension relevant to various (nano)technological applications.

At present, there are large discrepancies in both sign and magnitude of line tension data available from various theories, simulations, and experiments. This may reflect the diversity of systems studied. However, inconsistencies in experimental data provided by similar approaches and for similar systems can be caused by difficulties in sample preparation, inadequate experimental techniques, etc.

In this paper we have presented a theoretical basis for determining the line tension of a solid–liquid–vapor contact region by means of experiments on homogeneous crystallization of droplets. The underlying idea is based on our recent finding (Djikaev and Ruckenstein, 2008) that the line tension effect can give rise to an important contribution to the free energy of formation of a crystal nucleus in a surface-stimulated mode when one of its facets forms at the droplet surface and thus represents a “crystal–vapor” interface. It should be noted that no assumptions are required as for whether the surface-stimulated mode predominates the volume-based one or not, although the accuracy of the results for the line tension does increase with increasing predominance (of the former over the latter).

An accurate application of the proposed method requires systematic experimental data on the per-droplet rate of homogeneous crystal nucleation as a function of droplet size under otherwise identical external conditions (temperature, pressure, etc.). However, it can provide a rough estimate for the line tension even if the rate is known only for one droplet size. If experimental (per-droplet) rates for a series of droplet sizes are available, the proposed method allows one to independently extract not only the line tension but also the rate of volume-based crystal nucleation under given conditions. As an illustration the method has been used to treat experimental data on homogeneous crystal nucleation in droplets of 19, 49, and 60 μm radii at $T = 237$ K. The line tension of ice–(liquid)water–(water)vapor contact thus obtained is predicted to be positive of the order of 10^{-11} N which is consistent with the previously known data. The accuracy of the results for the line tension strongly depends on the accuracy of input data on the interfacial (solid–liquid and solid–vapor) tensions. By no means, however, this sensitivity should be considered as a flaw of the method developed for evaluating the line tension (the results extracted for the volume-based crystal nucleation rate are independent of the input for interfacial tensions).

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