

Are the (Solid–Liquid) Kelvin Equation and the Theory of Interfacial Tension Components[†] Commensurate?

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The theory of interfacial tensions, ITC theory, developed over the last half-century from contact angle and wetting studies, has proven to be reliable in many fields of physical and biophysical chemistry. However, interfacial tensions for curved solid surfaces in liquids, estimated in various ways from the Kelvin equation (itself, of course, a very successful theory), give very different results from those estimated by ITC theory. That is, a clear distinction must be made between the *Kelvin equation parameter* (KEP) of classical freezing theory and the *contact angle parameter* (CAP) of ITC theory. The difference between KEPs and CAPs is to some degree caused by the incorrect application of addition rules, Antonow's rule, for example, but a more profound discrepancy remains even when correct addition rules are used. One source of a discrepancy in measures of solid–vapor surface tension has been known since Gibbs, but has often not been acted upon, and does not appear to have been routinely quantified. Discrepancies in solid–liquid interfacial tensions have not, to my knowledge, been identified and discussed quantitatively in such detail before. In this paper, solid–liquid CAPs, from ITC theory, and KEPs, from freezing theory, are given for water and for naphthalene. Naphthalene is apolar and so is independent of certain aspects of ITC theory. Both substances show a large discrepancy between their KEP and their CAP. The effects of the discrepancy on the freezing of water ice are described. Several possible reasons for the discrepancy are discussed. Of the reasons for the discrepancy that have been identified, order-of-magnitude quantification suggests that only strain in the solid lattice or gross systematic differences between macroscopic and molecular level contact angles are potentially large enough to account for it. If there is a lattice strain component in KEPs and the capillarity approximation is to be retained in freezing studies, there may be an additional stochastic effect in freezing, which will determine the magnitude of the interfacial tension of nucleating clusters and which will be very difficult to calculate from first principles.

Introduction

Like all phase change kinetics, the kinetics of freezing is poorly quantified: it will be argued below that we are in even poorer shape than we realized.

Take the freezing of aqueous droplets, for example, which happened to be the starting point for these investigations and which turns out to be a useful testing ground. Water ice clouds are important in determining the radiative balance of the Earth (Ramanathan et al., 1989) and as catalysts in ozone depletion chemistry (WMO, 1994). Solid sulfuric and nitric acid hydrate ice clouds occur sporadically in the stratosphere (Dye et al., 1992; Pueschel et al., 1992) and are also important in ozone depletion chemistry. However, theories of the formation of ice clouds are highly uncertain, largely because of shortcomings in the classical theory of freezing. The classical theory gives the volume free energy change, ΔG^c , on forming a cluster of solid, of volume V and area A , from liquid as

$$\begin{aligned}\Delta G^c &= \frac{V}{v_m} \Delta G_f + A \sigma_{sl} \\ &= \frac{4\pi r^3}{3v_m} \Delta G_f + 4\pi r^2 \sigma_{sl}\end{aligned}\quad (1)$$

where ΔG_f is the molar bulk free energy change on formation of the solid (J mol^{-1}), v_m is the molar volume, r is the radius of the cluster, and σ_{sl} is some measure of the free energy associated with building the surface of the cluster which, for reasons that will become obvious below, is referred to as the *Kelvin equation parameter* (KEP).

Recent attempts to improve the treatment of ice cloud formation in stratospheric models have included more detailed estimates of KEPs in the classical equations for nucleation and freezing (Peter et al., 1991; Luo et al., 1994; MacKenzie et al., 1995), but all of these attempts have relied on outdated ideas about contact angle theory (see below). When modeled using theory rather than empirical fits, ice cloud formation in the troposphere is generally treated in the way outlined by Pruppacher and Klett (1978) and also uses outdated ideas about contact angle theory (e.g., Jensen et al., 1994). (In what follows, I will refer to the *surface tension* of a liquid or solid against its vapor; to the *interfacial tension* between two condensed materials; and to *interfacial tensions* in the general case.)

[†] The nomenclature is of my own making and is, I hope, a useful shorthand. In the literature, ITC theory is usually labelled by some combination of its major authors: F.M. Fowkes, R.J. Good, L.A. Girifalco, M.K. Chaudhury and C.J. van Oss. It is occasionally referred to as 'the theory of surface tension components', but no widely accepted name seems to exist. I would venture to suggest the more general *interfacial tension components* (ITC) theory.

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The purpose of this paper is to bring together some characteristic data on interfacial tensions that have been produced by freezing studies and by contact angle studies, to investigate the differences that are apparent, and so to decide whether the solid–liquid Kelvin equation is incommensurate with ITC theory, at least as the theories are currently used. By “incommensurate”, I mean that the theories both lay claim to the same physical parameter, solid–liquid interfacial tension, but will not, in general, assign the same value, or even a vaguely similar value, to that parameter. Some experimental methods employ a combination of the Kelvin equation and Young’s equation (see below) to investigate interfacial tensions: the pore-freezing method (Ishikiriya et al., 1995) and the capillary condensates method (Christenson, 1995) for example. These methods tend to generate values which are of the same order as those from freezing studies, but their use of Young’s equation usually requires some unsubstantiated assumption about the size of a contact angle. The grain boundary groove method (Walford and Nye, 1991; Mader, 1992) uses a version of Young’s equation to calculate the ratio of the solid–liquid interfacial tension to the grain boundary interfacial tension and does not give values of solid–liquid interfacial tension without some additional, and hard to verify, assumptions regarding the grain boundary interfacial tension. In this paper, the focus is on classical freezing studies and contact angle studies because these two methods for determining interfacial tensions are genuinely independent. Water and naphthalene, two systems of widely different polarities, are used to demonstrate that the conclusions drawn from the discussion below appear to be general.

There is another method for estimating interfacial tensions, which can be called “bond counting” (*e.g.*, Pruppacher and Klett, 1978; Doremus, 1985; Luo et al., 1994). In this method, the interfacial tension, γ is related to the enthalpy of phase change, ΔH_{pc} , and a theoretical estimate of the number of intermolecular bonds broken in the phase change. In the simple case of breaking half the intermolecular bonds of a molecule to bring it from the bulk to the surface:

$$\gamma = \Delta H_{pc}/2N_A A \quad (2)$$

where A is the area occupied by a molecule at the interface. This technique gives the upper limit to the interfacial tension of an ideal crystal, since it does not take into account any reorganization of molecules at the surface. The equation also neglects any additional terms in the interfacial tension of a real crystal that are due to lattice defects (see below). Corrections to estimates of interfacial tension by bond counting are necessary because, for liquids, the method gives results very different to measurements, and the corrections seem designed to engineer an agreement between the bond counting estimate and some other estimate of the interfacial tension (*e.g.*, Pruppacher and Klett, 1978, section 5.7). We will not use bond counting estimates below.

Theories and Sample Calculations

Classical Freezing Theory. The free energy of a cluster (eq 1) passes through a maximum with respect to r at the critical cluster radius, r^* ,

$$\frac{d(\Delta G^c)}{dr} = \frac{4\pi(r^*)^2}{v_m} \Delta G_f + 8\pi r^* \sigma_{sl} = 0 \quad (3)$$

$$\Rightarrow r^* = \frac{-2\sigma_{sl}v_m}{\Delta G_f} \quad (4)$$

$$\Rightarrow r^* = \frac{-2\sigma_{sl}T_0v_m}{\Delta H_f(T - T_0)} \quad (5)$$

which is the solid–liquid Kelvin equation. The substitution, $\Delta G_f = \Delta H_f(T - T_0)/T_0$ (where ΔH_f is the molar enthalpy of freezing and T_0 is the normal melting temperature) uses the fact that $\Delta G_f = 0$ at T_0 and assumes that the enthalpy and entropy of fusion are constant over the range (T, T_0) . Notice that σ_{sl} must be positive for r^* to be positive. Then, from eq 1,

$$\Delta G^c = \frac{(16\pi/3)\sigma_{sl}^3v_m^2}{\Delta H_f^2(T - T_0)^2/T_0^2} \quad (6)$$

is the expression for the free energy of formation of a nucleation germ, *i.e.*, the smallest stable cluster of molecules which can form the new phase.

The full classical expression for the homogeneous freezing rate of a liquid droplet is then

$$I_f = A \exp\left(\frac{-\Delta G^c}{kT}\right) \quad (7)$$

$$\Rightarrow I_f = n \left(\frac{kT}{h}\right) \exp\left(\frac{-\Delta G_a}{kT}\right) \exp\left(\frac{-(16\pi/3)\sigma_{sl}^3v_m^2}{kT\Delta H_f^2(T - T_0)^2/T_0^2}\right) \quad (8)$$

where n is the molecular concentration in the liquid phase, h is Planck’s constant, k is Boltzmann’s constant, and ΔG_a is the diffusion-activation energy across the phase boundary (see: Hirschfelder et al., 1954; Pruppacher and Klett, 1978).

The use of the Kelvin equation to nucleating clusters, *i.e.*, the classical capillarity approximation, has been shown to be remarkably accurate for vapor–liquid nucleation, holding for critical germs of 1-butanol that are as small as about 1 nm radius (Strey, 1994). It is not possible to carry out similar validations of classical freezing theory because the only independent estimates of solid–liquid interfacial tensions are from ITC theory, and it is shown below that the results from the two theories are widely different.

The Components of Interfacial Tension. ITC theory can be summarized by the following propositions (Good, 1993; van Oss, 1994 and references therein):

(i) The free energy of adhesion between two phases is the geometric mean of the two phases’ free energies of cohesion:

$$\Delta G_{ij} = -\sqrt{\Delta G_{ii}\Delta G_{jj}} \quad (9)$$

(ii) The free energy of cohesion of a phase, i , is twice its interfacial tension against vacuum, γ_i ($\approx \gamma_{iv}$, the interfacial tension against vapour):

$$\Delta G_{ii} = -2\gamma_i \quad (10)$$

(iii) Interfacial tensions in contact angle studies are due, ultimately, to intermolecular bonding. Tensions originate from hydrogen (AB) bond components and Landau–Lifshitz van der Waals (LW) bond components which, because they are unrelated interactions, act independently, *i.e.*,

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (11)$$

(iv) From the geometric mean rule (above), Landau–Lifshitz van der Waals (LW) bond components interact according to the following:

$$\gamma_{ij}^{LW} = (\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}})^2 \quad (12)$$

(v) Hydrogen (AB) bond components interact in a pairwise, donor-acceptor fashion,

$$\gamma_{ij}^{AB} = 2(\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_j^+ \gamma_i^-} - \sqrt{\gamma_i^+ \gamma_j^-} - \sqrt{\gamma_i^- \gamma_j^+}) \quad (13)$$

where γ_j^+ is the electron-accepting component and γ_i^- is the electron-donating component of the bonding in phase i . Equation 13 shows that the cohesive (ii) interactions, which tend to minimize the contact across the surface, compete with adhesive (ij) forces.

(vi) The “force balance” definition of interfacial tensions, *i.e.*, Young’s equation, and the “work done to produce unit surface” definition, *i.e.*, the Dupré equation, are equivalent:

$$\gamma_{lv}(\cos \theta) = \gamma_{sv} - \gamma_{sl} \quad (14)$$

$$\Delta G_{sl} = \gamma_{sl} - \gamma_{sv} - \gamma_{lv} \quad (15)$$

$$\Rightarrow \gamma_{lv}(1 + \cos \theta) = -\Delta G_{sl} \quad (16)$$

so that γ_{sl} can be eliminated. The subscripts sl, lv, and sv refer to solid–liquid, liquid–vapor, and solid–vapor interfaces, respectively. Substituting for ΔG_{sl} using eqs 10–13, the system can be then defined in terms of a system of simultaneous equations for γ_i^{LW} , γ_i^+ , and γ_i^- , which can be determined using data from liquid–liquid contact angle measurements of immiscible liquids, and from solid–liquid contact angle measurements of different liquids on a single solid surface.

Ultimately, the following definitions are produced:

$$\gamma_{lv}(1 + \cos \theta) = 2(\sqrt{\gamma_{sv}^{LW} \gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^+ \gamma_{lv}^-} + \sqrt{\gamma_{sv}^- \gamma_{lv}^+}) \quad (17)$$

$$\gamma_{sv} = \gamma_{sv}^{LW} + 2\sqrt{\gamma_{sv}^+ \gamma_{sv}^-} \quad (18)$$

$$\gamma_{sl} = (\sqrt{\gamma_{lv}^{LW}} - \sqrt{\gamma_{sv}^{LW}})^2 + 2(\sqrt{\gamma_{sv}^+ \gamma_{sv}^-} + \sqrt{\gamma_{lv}^+ \gamma_{lv}^-} - \sqrt{\gamma_{sv}^+ \gamma_{lv}^-} - \sqrt{\gamma_{sv}^- \gamma_{lv}^+}) \quad (19)$$

and all the terms in Young’s equation can be found. For apolar substances, like naphthalene, only the (LW) terms appear in eqs 17–19. The way in which these interactions can contribute to the tension of a particular interface are shown in Figure 1 (van Oss et al., 1988). The figure depicts clearly the idea that the interfacial tension between two condensed materials is a physicochemical phenomenon originating in intermolecular bonding, which is additive only when the individual components of the interfacial tensions are recognized. Notice that, from eq 19, γ_{sl} can be negative if the adhesive forces across the interface are greater than the cohesive forces in the surface of each phase. This treatment of interfacial interactions has enabled a single explanation to be given of many, hitherto incompatible, contact angle measurements (van Oss et al., 1988) of polymer solubilities (van Oss et al., 1990) and of hydrophobic interactions (van Oss and Good, 1991). It is not to the purpose here to give an exhaustive account of the theory: a full-length description and defense is given in van Oss (1994).

ITC theory has been developed because Young’s equation (eq 14) contains two unknowns and so requires additional information before it can be solved. [The special case of Young’s equation, Antonow’s rule

$$\gamma_{lv} = \gamma_{sv} - \gamma_{sl} \quad (20)$$

is not generally valid, although it is still used, with very little justification, in studies based on the Kelvin equation (e.g., MacKenzie et al., 1995; Christenson, 1995), usually to eliminate

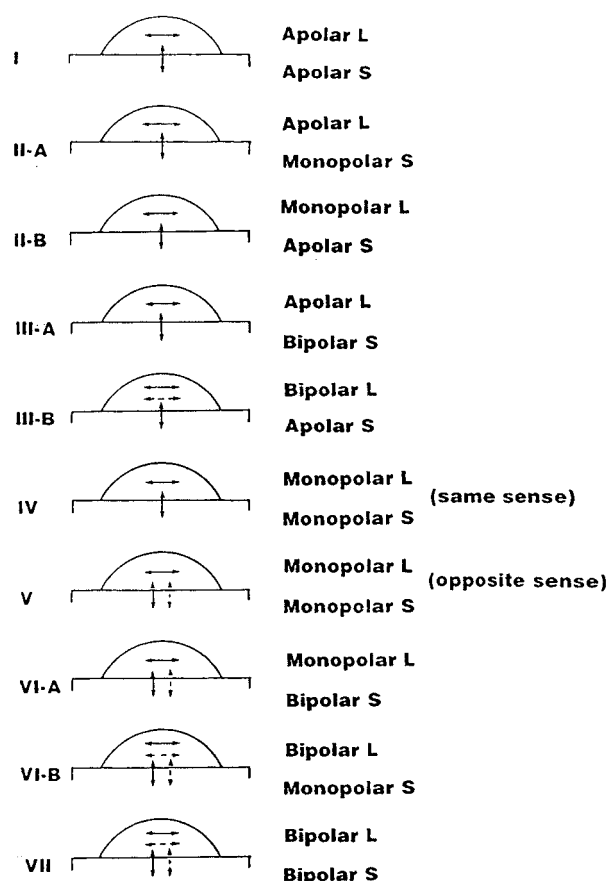


Figure 1. Schematic representation of the interactions that play a role in the shape of liquid drops on solid surfaces. LW interactions are shown by solid double-headed arrows. AB interactions are indicated by dashed double-headed arrows. Horizontal arrows indicate cohesion; vertical arrows indicate adhesion. From van Oss et al., 1988; reprinted with permission from *Langmuir*.

TABLE 1: Interfacial Tension Values for Water Substance, at 0 °C, in mJ/m², Calculated Using Classical Freezing Theory (KEP) and ITC Theory (CAP)

interface	KEP	CAP
liquid–vapor	75.7	75.7
solid–liquid	25.9	0.04
solid–vapor	97.0	69.2

the contact angle, θ , when it is one of three unknowns in Young’s equation.] It has been firmly established, but not universally recognized, that eq 14 cannot estimate interfacial tensions of one system from measurements on another, particularly in the manner of MacKenzie et al. (1995). The full Young–Dupré equation (eq 17) is the proper prognostic form that relates the measurable quantities, θ and γ_{lv} , to intrinsic properties of the materials. The full Young–Dupré equation implies that, to characterize any unknown surface, contact angles between the surface and three different liquids, each of which is itself completely characterized, must be measured.

The Effect of Incommensurability. Van Oss et al. (1993) have used ITC theory to investigate the water ice system. Their results are tabulated in Table 1 alongside KEPs derived from freezing theory. Liquid–vapor surface tensions are unaffected by the change in theory and can be measured using standard physicochemical techniques. The freezing theory value of the solid–liquid interfacial tension is taken from Turnbull (1950); the freezing theory value of solid–vapor surface tension is calculated from Young’s equation and a contact angle of 20° (Ketcham and Hobbs, 1969; van Oss et al., 1992). Both solid–vapor and solid–liquid interfacial tensions are different in the

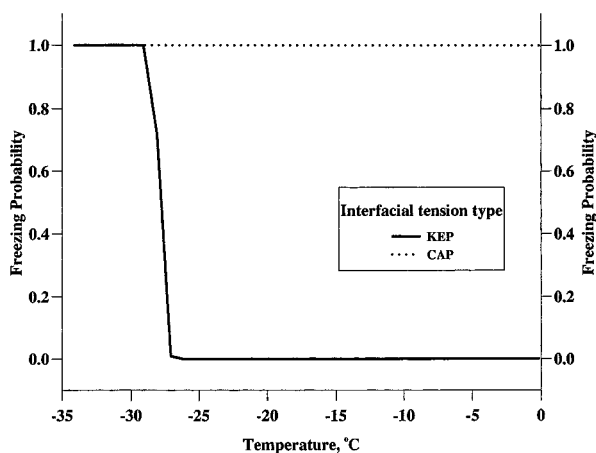


Figure 2. Probability that a water droplet of 50 μm radius will freeze in 1 s, as a function of temperature. At 273 K, the two lines correspond to the two values of γ_{sl} given in Table 1. The KEP is temperature-dependent, as discussed in the main text. The value of interfacial tension calculated by ITC theory does not reproduce the well-known supercooling of nucleus-free water.

two theories, as must be the case for both datasets to satisfy Young's equation. The solid–vapor values vary by 30% of the freezing theory value. The solid–liquid values vary by a factor of almost 10^4 .

Freezing Temperatures: σ_{sl} and γ_{sl} . Substituting the CAP from ITC theory for the KEP from classical freezing theory in calculations of the freezing of water is shown in Figure 2. The calculations were carried out using eq 8 and using either the Turnbull equation (Turnbull, 1950)

$$\sigma_{\text{sl}} = \frac{0.32\Delta H_f}{N_{\text{Av}}^{1/3} \nu_m^{2/3}} \quad (21)$$

(where ΔH_f is the molar enthalpy of fusion) or the CAP given in Table 1. The Turnbull equation gives a temperature dependent KEP which, at 273 K, is the value for the freezing theory given in Table 1. The figure shows the freezing probability, $P = 1 - \exp(-(4/3)\pi r^3 I_f t)$, for a water drop of radius, $r = 50 \mu\text{m}$, to freeze in time, $t = 1 \text{ s}$.

With the CAP derived by van Oss et al. (1988), no supercooling is calculated, whereas the freezing theory estimate produces a supercooling of $\sim 27 \text{ K}$. Observations and experiments have long since established that a supercooling of $\sim 30 \text{ K}$ is required for homogeneous freezing (see, for example, Pruppacher and Klett, 1978). It is not surprising, however, that the KEP gives a better fit to the experimental data, since it is itself derived from freezing calculations.

The problem is even more severe for aqueous solutions, such as the sulfuric acid and nitric acid solutions encountered in the atmosphere, which are likely to have negative CAPs according to ITC theory (C. J. van Oss, private communication). Negative CAPs, which indicate that the solid surface is unstable with respect to dissolution into the overlying liquid, are a simple upshot of eq 19 but are unphysical according to the solid–liquid Kelvin equation (see eq 5).

There is another aspect of the problem: it is very difficult to derive KEPs from freezing experiments, because heterogeneous freezing can occur instead of homogeneous freezing (Laaksonen et al., 1995; Huang and Bartell, 1995). This introduces an uncertainty into estimates of KEPs, which is one of the reasons that attempts have been made to use estimates from Young's equation corroboratively.

Discussion

There are substantial discrepancies between the solid–liquid interfacial tension values from ITC theory and those measured using classical freezing theory. The discrepancies extend to the sign of the interfacial tension as well as to its magnitude. Because the nineteenth century beginnings of contact angle theory gave coincidentally reasonable agreement with the values of KEPs required to reproduce some nucleation results, the temptation in the past has been to acknowledge the trouble with equating σ_{sl} and γ_{sl} , while simultaneously using Young's equation, bond counting, and Antonow's rule to extend the application of freezing theory *ad hoc*. This is an understandable strategy, but one that is now highly questionable, given what we know about interfacial tensions.

It is not novel to state that solid–vapor surface tensions are problematic, but literature discussions of the problems with defining solid–liquid interfacial tensions are neither common nor exhaustive (e.g., Doremus, 1985, p 64ff). In the nucleation/freezing literature, arguments usually center on whether the macroscopic interfacial tension is an accurate measure of the interfacial tension of the highly curved germs, or whether the free energy change on forming the germ contains other terms in addition to the interfacial tension term (for reviews of the extensive literature, see: Oxtoby (1992) and Laaksonen et al. (1995)). In the wetting/adhesion literature, the difference between *surface stress* and the *work done in forming a unit of the surface of discontinuity* in solid surface tensions has been known since Gibbs (see: Berg, 1993, p 68) but has often been overlooked or discussed only qualitatively.

The various theories for the size-dependence of interfacial tension all predict a decrease in tension with particle size (Pruppacher and Klett, 1978) and so cannot explain why the KEP for water is 4 orders of magnitude *larger* than its CAP. Introducing extra terms in the free energy expression for clusters (Lothe and Pound, 1962; Reiss, 1977) requires an increase in the KEPs for clusters, relative to that used by classical theory, to maintain the agreement between experiment and theory (Ruth et al., 1988). Again, this is a change in the opposite sense to the change required to make KEPs and CAPs commensurate.

Along with the uncertainties regarding the definition of σ_{sl} in classical freezing theory, there are several other ways in which one might try to rationalize the discrepancies between the interfacial tension values: (i) uncertainties in the observables; (ii) lattice strain in the solid cluster; (iii) metastable cluster formation; (iv) temperature-dependent or size-dependent interfacial tension; (v) Water as an anomalous substance; or (vi) σ_{sl} and γ_{sl} as different qualities of an interface. These possibilities are discussed, in turn, below.

Uncertainties in the Observables. The two principal observables in contact angle studies are liquid–vapor surface tensions and solid–liquid contact angles themselves. Liquid–vapor surface tensions can be measured by standard techniques to adequate precision and are compiled in standard reference texts. Contact angles are much less straightforward to measure because of hysteresis effects and surface contamination (see: e.g., Good, 1993). Using Young's equation and the observables alone, the difference between γ_{sv} and γ_{sl} can be found, but not the individual terms. The discrepancy between ITC theory and classical freezing theory estimates of interfacial tension is not due to uncertainty in the observables, therefore, unless there is some bias in the three measured contact angles which are used by ITC theory to estimate γ_{sv} . For example, when only apolar interactions are considered, the square root dependence in eq 17 means that, for γ_{sv} to decrease by 30%, $(1 + \cos \theta)$ is required to decrease by 50%, which in turn suggests an increase

in the contact angle of roughly 30–60°. An error of this magnitude is not likely in measurements of the macroscopic contact angle, although it is conceivable that there is a difference of this magnitude between the macroscopic contact angle and that pertaining at a molecular level, if the ice surface is not in equilibrium with the vapor of the liquid whose contact angle is being tested (Good, 1993). There is no information in van Oss et al. (1993) by which this possibility can be tested, but it would be surprising if contact angle measurements, made at different times and in different places by different groups, were all reproducibly subject to such an error.

Lattice Strain in the Solid Cluster. If liquid surface tensions and contact angles are not the cause of the discrepancies, then it is likely that the discrepancies arise from differences in the surface tension associated with the solid. The physical meaning of the γ_{sv} term in ITC theory and its antecedents has been much debated (e.g., S.C.I., 1967). It is unlikely that contact angle measurements give information on the solid phase below the interface and likely that the measurements are made on surface that, even when clean, have “relaxed” by minimizing the number of unused bonds (Fowkes et al., 1990; van Oss et al., 1996). Now, the definition of interfacial tension can be written (Lester, 1967):

$$\gamma^{\text{tot}} = \partial G^{\text{tot}} / \partial A \quad (22)$$

where the total free energy, G^{tot} , of the interface is made up of “bulk” and truly interfacial components,

$$G^{\text{tot}} = VG^v + AG^i \quad (23)$$

so that we have

$$\gamma^{\text{tot}} = G^i + A \frac{\partial G^i}{\partial A} + V \frac{\partial G^v}{\partial A} \quad (24)$$

One might then identify γ_{sv} with G^i and σ_{sv} with γ^{tot} for the following reason: in macroscopic liquids, the second and third terms on the right hand side are necessarily zero, but for solids they need not be. Hence γ and σ will agree for liquids but not for solids. These derivatives with respect to interface area constitute the contribution of the strain field in the solid to the interfacial tension (Lester, 1967; Doremus, 1985; Berg, 1993). But of what does this strain field consist? It must be made up of the combination of higher energy sites in the surface layers. The highest energy sites will be defects, and vacancies will be the highest energy sites of all. For water ice, we can guess the energy of a vacancy quite simply, it is the energy of two hydrogen bonds. The energy of a hydrogen bond in water ice is about 25.5 kJ mol⁻¹ (4×10^{-20} J/bond), which is roughly half the enthalpy of sublimation, as one would expect.

From eq 24, a residual interfacial tension can be defined:

$$\gamma^{\text{res}} = \gamma^{\text{tot}} - G^i = A \frac{\partial G^i}{\partial A} + V \frac{\partial G^v}{\partial A} \quad (25)$$

which, for the water ice system, is about 25 mJ m⁻² if the interfacial energy estimates from contact angles and from freezing theory are used. If, as is suggested below, G^i is not size-dependent, then one can solve for G^v by integration:

$$V \int_{G^v(\text{mon})}^{G^v(r^*)} dG^v = \gamma^{\text{res}} \int_{A(\text{mon})}^{A(r^*)} dA \quad (26)$$

where the limits of the integration are the values of G^v and A at the critical radius, r^* , and for a water monomer, mon. By definition, $G^v(\text{mon}) = 0$ because there can be no lattice strain in a monomer; and since $A(r^*) \gg A(\text{mon})$ we get

$$G^v(r^*) = \frac{A(r^*)}{V(r^*)} \gamma^{\text{res}} \quad (27)$$

which turns out to be roughly 5×10^7 J m⁻³, or 900 J mol⁻¹, for a cluster of radius 1.5 nm. Comparing this to the hydrogen bond energy suggests that breaking about 4% of the hydrogen bonds would account for the residual interfacial tension. This corresponds to a vacancy density of 2% v/v or a density of lower energy defects which is considerably higher. Such a defect density seems unlikely, but the author knows of no studies which have examined the defect density of nucleating crystals.

Metastable Cluster Formation. Huang and Bartell (1995) have demonstrated that small water ice clusters have a cubic crystal structure rather than the stable hexagonal structure, which supports the deductions made by Takahashi and co-workers, based on snow crystal habits (Takahashi and Kobayashi, 1983; Takahashi, 1982; Kobayashi et al., 1976) and which constitutes a change to the accepted molar bulk free energy, ΔG_f . However, the energy difference between the hexagonal and cubic states is small: $\Delta H(I_c \rightarrow I_h) \approx -160$ J mol⁻¹ (Huang and Bartell, 1995). From eq 5,

$$(T_0 - T) = \frac{2\sigma_{sl}T_0v_m}{\Delta H_f r^*} \quad (28)$$

which states that, for a constant supercooling, $\sigma_{sl}/\Delta H_f r^*$ is a constant. Changing σ_{sl} from 30 mJ m⁻² to 0.04 mJ m⁻² and ΔH_f from 6000 J mol⁻¹ to 5840 J mol⁻¹ requires r^* to change from 1.5 nm to 2 pm which, given a water monomer radius of about 200 pm, is clearly unphysical.

Temperature-Dependent or Size-Dependent Interfacial Tension. The effect of temperature-dependence on CAPs derived by ITC theory is largely unknown (van Oss, 1994). However, the definition, $\gamma_i = -1/2 \Delta G_{ii}^{\text{coh}}$, eq 10, implies that τ_i will, in general, be dependent upon temperature. This aspect of the theory has received little attention to date, but it is clear that it will be important in highly supercooled systems such as cloud droplets. It is unlikely, however, that the temperature-dependence could account for a change in γ_{sl} of a factor of 10⁴. In fact, this would not bring the theories into line, because allowing the interfacial tension of water ice to change, from 0.04 mJ m⁻² at 273 K to 30 mJ m⁻² at 243 K would make freezing less likely as the temperature is decreased, in direct conflict with the observations.

From the application of ITC theory to problems on the molecular scale, such as “hydrophobic” interactions (van Oss, 1994, chapter 14), we can deduce that ITC theory is not strongly size-dependent. This is to be expected because the theory comprises the description of interfacial forces in terms of the various types of intermolecular bonding. The likely size-dependence of KEPs has been discussed above and is in the opposite sense to that required for ITC theory to become commensurate with the Kelvin equation.

Water as an Anomalous Substance. Perhaps the discrepancy between estimates of γ_{sl} is unique to water and the result of its unique properties? Or perhaps the discrepancy is due to lacunae in the treatment of polar interactions in ITC theory? Both these hypotheses can be tested by looking at a second test substance, which has a different intermolecular bonding structure. The ITC theory components of naphthalene are compared with water in Table 2 (van Oss, 1994). Data from freezing studies of naphthalene are also available in the literature (Jones, 1973): the two datasets are compared in Table 3. Once again there are large discrepancies between the estimates, of about the same magnitude as the discrepancies for water for which

TABLE 2: Interfacial Tension Components for Liquid Water and Liquid Naphthalene, at 20 °C, in mJ/m²

component	water	naphthalene
γ^{LW}	21.8	39.4
γ^+	25.5	0
γ^-	25.5	≈ 1

TABLE 3: Interfacial Tension Values for Naphthalene, at 20 °C, in mJ/m², Calculated Using Classical Freezing Theory (KEP) and ITC Theory (CAP)

interface	KEP	CAP
liquid–vapor	39.4	39.4
solid–liquid	27.2	0.06
solid–vapor	66.6 ^a	42.7

^a From Antonow's rule. Bond counting gives $\gamma_{\text{sv}} \approx 52 \text{ mJ m}^{-2}$, and hence $\theta \approx 51^\circ$. It is known from experiment that molten naphthalene wets its solid completely.

neither the nature of water nor the treatment of polar interactions in ITC theory can be responsible. The intermolecular bonds in naphthalene are dispersive and slightly weaker than the hydrogen bonds in water, so again, defect densities amounting to $\sim 10\%$ v/v of the total crystal bonding are required to bring the ITC theory estimate into line with the estimate from freezing theory.

σ_{sl} and γ_{sl} as Different Qualities of an Interface. As much by a process of elimination as by any more rigorously deductive reasoning, one arrives at the possibility that σ_{sl} and γ_{sl} are qualitatively different, more different even than suggested in the subsection Lattice Strain in the Solid Cluster. One possibility is that σ_{sl} is dominated by an entropy term (Spaepen, 1994) which is either absent in γ_{sl} , or is balanced in γ_{sl} by an enthalpy term of almost equal magnitude. One can certainly calculate entropy terms from ITC theory, but these cannot be the same as those calculated by Spaepen, because both enthalpic and entropic theories of KEPs come to about the same value for σ_{sl} at the melting temperature. This is because both enthalpic and entropic theories are tied to freezing experiments and because $\Delta H = T\Delta S$ at the melting temperature. Recall that the values for γ_{sl} calculated by ITC theory are for the melting temperature. Furthermore, the temperature-dependence of σ_{sl} , according to an entropic model, is positive, so that again, it is not possible that the entropic theory can reconcile σ_{sl} and γ_{sl} if their definitions are taken at face value.

Conclusions

The problem of interfacial tensions has long been recognized in nucleation/freezing studies (e.g., Reiss, 1977) but not in the sense discussed here. Nucleation/freezing studies have used interfacial tension arguments when no other data were available (Luo et al., 1994; MacKenzie et al., 1995) or when there is disagreement between estimates of σ_{sl} (Pruppacher and Klett, 1978). Similarly, γ_{sl} values have been compared directly with KEPs (e.g., van Oss et al., 1992) without reference to the problems of definition. Previously, there have been enough degrees of freedom in the interfacial tension determinations, enough uncertainty in the freezing kinetics, and few enough interdisciplinary studies, to allow freezing theory and interfacial tension theory to share the same parameter without any obvious contradiction. Now, however, developments in interfacial tension theory mean that the results from both theories cannot continue to be taken at face value.

Of the reasons for the discrepancy discussed here, only lattice strain seems of the appropriate magnitude (although systematic disequilibrium in contact angle measurements cannot be ruled out). The appearance of such a large strain term in the interfacial tension of a nucleating cluster, if true, would have

several interesting implications. The inclusion of strain in crystals is a stochastic process which will be a strong function of the experimental setup and which will be stochastic even in a given setup. There will be, therefore, an inevitable spread in σ_{sl} values calculated even from a single experimental setup and an even larger spread in values calculated from different setups. It is tempting to suggest that this goes some way to explaining why a single value of σ_{sl} has been so difficult to obtain (e.g., Pruppacher and Klett, 1978; Huang and Bartell, 1995). By the same token, of course, the value of σ_{sl} to use in models of freezing will depend on the scenario to be modeled in a way which will be difficult to predict. Note, too, that if the discrepancy is caused by lattice strain, any agreement between interfacial tensions from freezing studies and those estimated from bond counting will be coincidental, since bond counting does not take lattice strain into account explicitly.

It is not possible to state categorically that the solid–liquid Kelvin equation and the theory of interfacial tension components are incommensurate, but the arguments above do seem to suggest that it is likely. The immediate upshot of this need be nothing more earth-shattering than a regularizing of nomenclature and data sources so that γ_{sl} (contact angle parameters) and σ_{sl} (Kelvin equation parameters) are not confused, but it would be surprising if physical chemists were satisfied with that alone. Resolving the discrepancy finally will require an improvement in our understanding of the meaning of the terms σ_{sl} in the Kelvin equation and the term γ_{sl} in ITC theory. Ultimately, of course, there are the possibilities that the capillarity approximation will be shown to be a poor approximation in the case of freezing, even though it has been shown to be a reasonable approximation in liquid–vapor nucleation (Strey, 1994), or that macroscopic contact angles, even when reproducible, are very different to microscopic, molecular level, contact angles.

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