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Some issues of thermodynamic consistency in binary nucleation theory

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The "generalized" Kelvin equations used to determine the critical nucleus composition in some binary nucleation theories are shown to be thermodynamically inconsistent. Also, the surface tension calculated by the method of Flageollet-Daniel, Garnier, and Mirabel [J. Chem. Phys. **78**, 2600 (1983)] is shown to be thermodynamically consistent with respect to the dynamic surface tension, contrary to the recent assertion of Spiegel, Zahoransky, and Wittig.

INTRODUCTION

Binary nucleation theory has received considerable attention in the past several years. Four theories or methods are presently available for practical computations. The theories differ in the way the critical nucleus composition is determined and interpreted and, consequently, in the way the free energy of critical nucleus formation is calculated. The early theory of Reiss¹ and Doyle² assumes a uniform droplet composition and uses the macroscopic surface tension with two generalized (but, as will be shown, thermodynamically inconsistent) Kelvin equations that contain compositional derivatives of the surface tension. The Kelvin equations determine the critical nucleus composition and are thus crucial to the evaluation of the critical free energy. This theory is known to be inadequate for describing binary nucleation in water-rich aqueous alcohol or acetone mixtures for which surface enrichment effects occur in bulk liquids.³⁻⁶ The three newer theories⁷⁻¹¹ provide different ways of overcoming this theoretical inadequacy in relatively successful fashion. Despite the lack of agreement regarding the conceptual basis for binary nucleation theory,⁷⁻¹² the ability to account computationally for experimental results is now good, and this provides some measure of confidence in predicting the behavior of systems not yet studied experimentally.

Details of these new approaches can be found in the original papers,⁷⁻¹¹ and only key aspects will be noted here. The theories share an important trait: the explicit recognition that the macroscopic surface tension intrinsically embodies the effects of surface enrichment occurring in a bulk system. Each of the new theories modifies either the use of the macroscopic surface tension or the way in which the critical composition is determined or both, depending on whether or not surface enrichment is assumed to be present in the nucleating cluster.

The approach developed by Flageollet-Daniel, Garnier, and Mirabel⁷ (FDGM) uses a lattice model to explicitly account for differences between the cluster interior and surface compositions. The cluster surface tension is the macroscopic surface tension of a solution whose composition is equal to that of the cluster interior. The revised classical theory I developed,^{8,9} following the observation of Renninger *et al.*,¹³ relies only on the macroscopic surface tension but uses thermodynamically consistent Kelvin equations to determine the interior cluster composition, implicitly ac-

counting for surface enrichment. The third theory, proposed by Rasmussen¹⁰ and Spiegel, Zahoransky, and Wittig¹¹ (SZW) assumes that surface enrichment is negligible in the cluster and invokes the use of the dynamic surface tension of a freshly formed interface instead of the macroscopic surface tension of an equilibrium interface.

The dynamic surface tension is appropriate for systems in which compositional gradients have not yet developed. At first glance its use is an appealing tactic because it seemingly eliminates the conceptual inconsistency of using a model that explicitly ignores surface enrichment with a macroscopic surface tension that automatically includes it. This approach is also quite successful computationally in accounting for condensation onset activities of aqueous alcohol mixtures observed in shock tubes,¹¹ diffusion cloud chambers,⁵ and supersonic nozzles.¹⁴ An example of this is given in Fig. 1 where results⁵ for 1-propanol/water mixtures are compared with predictions made using the four theoretical approaches described above. The curve labeled "standard" is based on the original Reiss-Doyle theory^{1,2} with the equilibrium surface tension. The "dynamic" curve results from the Reiss-Doyle theory with the dynamic surface tension.^{10,11} The "revised" curve represents calculations using

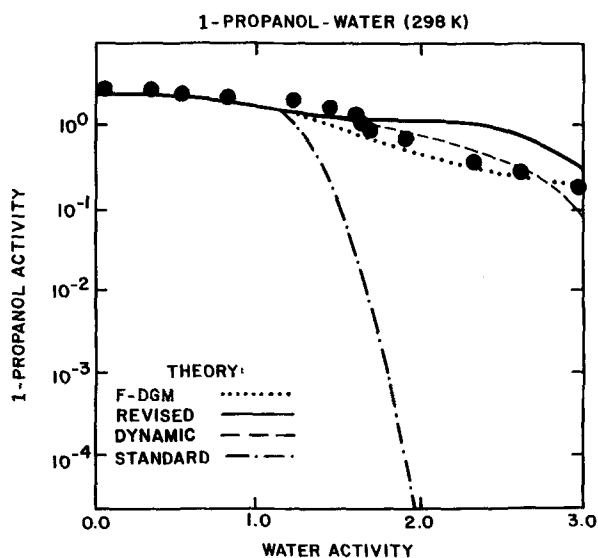


FIG. 1. 1-Propanol/water onset activities at nucleation rate of $1 \text{ cm}^{-3} \text{ s}^{-1}$ compared with predictions of theories discussed in the text. FDGM curve and experimental points (●) from Ref. 7.

the equilibrium surface tension as described in Ref. 9. The FDGM curve is calculated using the surface monolayer lattice model described in Ref. 7.

THERMODYNAMIC INCONSISTENCY OF GENERALIZED KELVIN EQUATIONS

From the standpoint of predictive success at high water activities, the use of the dynamic surface tension results in a significant improvement over the standard theory. Despite this improvement, the theory still suffers from an internal thermodynamic inconsistency because, as in the original theory,^{1,2} the critical cluster composition satisfies the two generalized Kelvin equations containing the compositional surface tension derivative. These equations have been questioned^{8,9,12,13} and defended¹⁵⁻¹⁷ previously on various grounds, but the following simple demonstration should convincingly establish their thermodynamic inconsistency. The result holds even if the composition is determined by numerically inspecting the free energy surface, as is commonly done, rather than by explicitly solving the two Kelvin equations because these two methods are numerically equivalent.

The free energy of cluster formation is conventionally written as

$$\Delta G = n_1 \Delta \mu_1 + n_2 \Delta \mu_2 + 4\pi r^2 \sigma, \quad (1)$$

where n_i is the number of molecules of species i in the cluster, r is the (spherical) cluster radius, σ is the surface tension appropriate to the theory being used, and $\Delta \mu_i$ is the difference between the droplet phase and gas phase chemical potentials of a molecule of species i . It is important to note that both the liquid and gas phase chemical potentials are evaluated at the same pressure, P_g , of the gas phase. The critical cluster composition locates a saddle-point on the free energy surface at which the cluster is in unstable equilibrium with the gas phase. This point may be found either by numerically evaluating ΔG directly or by solving the two generalized Kelvin equations that arise when the two first derivatives of ΔG with respect to n_1 and n_2 are set equal to zero. It should be obvious that these two procedures are mathematically equivalent. These two equations can be written as²

$$\Delta \mu_1 + \frac{2\sigma v_1}{r} - \frac{3xv}{r} \frac{d\sigma}{dx} = 0, \quad (2)$$

$$\Delta \mu_2 + \frac{2\sigma v_2}{r} + \frac{3(1-x)v}{r} \frac{d\sigma}{dx} = 0, \quad (3)$$

where v is the average molecular volume, v_i is the partial molecular volume of species i , and x is the average mole fraction of species 2.

The condition of unstable equilibrium for the droplet of critical composition implies the equality of the gas phase chemical potential and that of the droplet phase at the droplet's actual pressure P_d , i.e.,

$$\mu_i^d(P_d) = \mu_i^g(P_g). \quad (4)$$

Now, with the conventional assumption of an incompressible droplet phase, the standard relationship for the pressure dependence of μ_i , $(\partial \mu_i / \partial P)_{T, n_i} = v_i$, may be used to express $\Delta \mu_i$ as

$$\Delta \mu_i = \mu_i^d(P_g) - \mu_i^g(P_g) = v_i(P_g - P_d) \quad (5)$$

and this expression may, in turn, be used to rewrite Eqs. (2) and (3) as

$$P_g - P_d + \frac{2\sigma}{r} = \frac{3xv}{v_1 r} \frac{d\sigma}{dx}, \quad (6)$$

$$P_g - P_d + \frac{2\sigma}{r} = \frac{-3(1-x)v}{v_2 r} \frac{d\sigma}{dx}. \quad (7)$$

Because the pressure drop between the droplet and gas phases must be the same regardless of which equation is used to determine it, Eqs. (6) and (7) imply that

$$[(1-x)v_1 + xv_2] \frac{d\sigma}{dx} = 0. \quad (8)$$

Since neither the average molecular droplet volume [$v = (1-x)v_1 + xv_2$] nor, in general, the compositional surface tension derivative is zero, this equation is physically contradictory. Thus, despite its impressive computational success, the dynamic surface tension approach is marred by its reliance on thermodynamically inconsistent Kelvin equations and the corresponding composition. It should also be clear that numerical evaluation of ΔG does not avoid this inconsistency since it gives results identical to those found by solving Eqs. (2) and (3).

The thermodynamically consistent composition can be obtained easily by solving Eq. (5) for ΔP to obtain

$$\frac{\Delta \mu_1}{v_1} = \frac{\Delta \mu_2}{v_2}. \quad (9)$$

This equation is the same one found in the so-called revised theory⁹ in a somewhat different manner. The use of this equation in binary nucleation theory actually goes back to the early work of Neumann and Döring.¹⁸

THERMODYNAMIC CONSISTENCY OF FDGM SURFACE TENSION

The use of the dynamic surface tension by SZW¹¹ seems to be motivated partly by their comment that the FDGM⁷ surface tension is thermodynamically inconsistent, but this seems to be based on a misinterpretation of the FDGM theory. FDGM have themselves contributed to this confusion by originally presenting their calculated cluster surface tension as a function of average cluster composition for various cluster sizes. When the FDGM surface tension is considered to be a function of the average cluster composition, the SZW remark is apparently true, because the FDGM surface tension then appears to be larger than the dynamic surface tension at many compositions. However, from the point of view of a large droplet,^{8,9,12} the surface tension should be regarded as a function of the interior (i.e., bulk) composition, not the average composition of the droplet. When this is realized, the FDGM surface tension is then seen to be lower than the dynamic surface tension because of the enhancement of the surface composition with the lower tension component that occurs for any interior composition. Thus, the apparent inconsistency vanishes.

Furthermore, when surface tension is plotted against the interior composition, all of the FDGM surface tension curves for different cluster sizes collapse to a single curve

that is identical to that of the equilibrium bulk mixture. Thus, FDGM have actually developed a clever, explicit method for determining the interior droplet composition appropriate to clusters of different size and average composition. This interior composition is used to evaluate the bulk chemical potentials, surface tension, and partial molar volumes whose use results in quite successful predictions of nucleation onset conditions.

I do not wish to imply by default that either the FDGM or revised theory is completely free of inconsistencies or problems. Deeper analysis of these theories has recently begun,¹² but more work remains to be done. Also, instances of unphysical behavior predicted by the revised theory were discussed in recent papers.^{9,17}

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