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Composition of the Critical Nucleus in Multicomponent Vapor Nucleation

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Figure 1 shows the libron linewidth from 1.5 to 200 K can be explained entirely by the cubic anharmonic energy relaxation model. Neglecting the temperature dependence of the B coefficients apparently does not result in appreciable error. This is not the case for the temperature dependent phonon frequency, which has a strong density dependence.[3,4] The d_8N libron linewidths, which were not previously studied, agree within experimental error with the h_8N data; thus neutron scattering measurements of the dispersion and density of states of d_8N may be used to interpret h_8N data. By contrast deuteration drastically affects vibron line shapes in naphthalene.[8,9]

Della Valle et al. have hypothesized that the extreme complexity of their method may be avoided by assuming all B coefficients to be equal.[1] We find the temperature dependence calculated in this approximation to be in good agreement with the data in Fig. 1. Equality of these coefficients implies phonon lifetimes will decrease rapidly with increased phonon frequency. We observe this effect in h_8N and d_8N, and also in anthracene, perdeuteroanthracene, and α-perylene, substances with the naphthalene crystal structure. In the latter three substances we observe that the lowest A_g libron has a lifetime of ∼ 100 ps at 10 K and a temperature dependence quite similar to naphthalene. In a recent picosecond CARS study of librons in l-alanine,[10] a hydrogen bonded crystal, the lifetimes of seven librons were measured and

also decreased rapidly with frequency. The lifetimes and the decrease were in quantitative agreement with a model assuming equal B coefficients which, surprisingly, were nearly equal to the values for naphthalene. These results imply that a simplified version of the DV calculation with constant B coefficients may be applicable to libron relaxation in a wide variety of molecular crystals.

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Composition of the critical nucleus in multicomponent vapor nucleation

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Onset conditions for the nucleation of water-rich binary liquid droplets in gas mixtures are poorly predicted by classical binary nucleation theory.[1–4] This disagreement is due, at least in part, to the calculation of critical cluster compositions using equations that are inconsistent with macroscopic thermodynamics in the large cluster limit. In this letter, I outline a consistent thermodynamic model of mixed nucleus formation. Calculations using this new model indicate that agreement between theory and experiment is much improved.

In classical nucleation theory,[5] macroscopic thermodynamic concepts are used to evaluate the free energy of formation of small nuclei of the new phase. Although open to fundamental criticism, this approach, nevertheless, has had much practical success for single component nucleation[6–8] and provides a basis for treating multicomponent nucleation.[9,10]

In classical nucleation theory for a binary mixture,[9,10] the cluster free energy $\Delta G(n_1,n_2)$ is conventionally written as

$$\Delta G = n_1\Delta\mu_1 + n_2\Delta\mu_2 + A\gamma, \tag{1}$$

where $\Delta\mu_i (= \mu_i^l - \mu_i^v)$ is the difference in chemical potential for a molecule of species i in solution (l) and in the vapor (v), n_i is the number of molecules of species i in the nucleus, A is the area of the (spherical) cluster, and the surface tension γ is, following usual practice, assumed to be that of an equilibrium flat interface.

Of considerable importance are the composition and size of the critical nucleus in unstable equilibrium with the supersaturated vapor. In a single component system, the size of the critical nucleus is determined by an equation that is formally identical to the well-known Gibbs–Thomson equation for the change in droplet vapor pressure with radius. This is both reasonable and consistent since macroscopic thermodynamics is being used for the cluster free energy.

One would anticipate a similar situation to hold for the multicomponent system. Here the critical composition locates a saddle point of ΔG in the multidimensional composition space. For a binary system, this point is defined by the solution to the two equations

$$[d\Delta G(n_1,n_2)]_{n_i} = 0 \quad (i = 1,2; \text{const.} \; T, P), \tag{2}$$

where the subscript n_j indicates a variation with that species number held constant. Carrying out the variations indicated by Eq. (2), one would expect to find the corresponding Gibbs–Thomson equations for multicomponent drops. These equations, to a sufficiently accurate approximation,[11,12] have the form

$$\Delta\mu_i + \frac{2\gamma v_i}{r} = 0, \qquad (3)$$

where r is the droplet radius and v_i is the partial molecular volume of species i.

In fact, as Doyle[10] showed, the equations that actually result include a surface tension derivative term:

$$\Delta\mu_i + \frac{2\gamma v_i}{r} + \frac{3(1 - X_i)v}{r}\frac{d\gamma}{dX_i} = 0, \qquad (4)$$

where v is the average molecular volume and X_i is an average mole fraction. In systems whose surface tension has a strong composition dependence, this extra term has great importance in determining the composition of the critical nucleus.

The inconsistency between Eqs. (3) and (4) was recently pointed out by Renninger et al.[13] who maintained the correctness of Eq. (3). In response, Doyle[14] defended Eq. (4). This conflict can be resolved by reconsidering the underlying cluster model.

The problem is that the model used for the mixed nucleus is oversimplified. In the model, the "surface" of the nucleus is idealized as a region of zero thickness. The composition is assumed to be uniform throughout the droplet with no allowance for the surface enrichment effects known to occur in macroscopic systems (when $d\gamma/dX_i \neq 0$). Thus the surface tension derivative is not compensated by terms involving the surface concentrations (i.e., the Gibbs adsorption equation is not used).

This deficiency can be removed by distinguishing between bulk and surface molecules in the cluster, as if the cluster were a large droplet. The cluster thermodynamics is then treated in accordance with standard methods for systems involving surfaces by setting

$$n_i = n_i^b + n_i^s, \qquad (5)$$

where b and s denote bulk and surface. Now use Eq. (5) in evaluating Eq. (2). The result is

$$0 = (\Delta\mu_j + \gamma(\partial A/\partial n_j)_{n_i})(dn_j)_{n_i}$$
$$+ n_1^b d\mu_1^l + n_2^b d\mu_2^l \qquad (6)$$
$$+ n_1^s d\mu_1^l + n_2^s d\mu_2^l + A d\gamma \quad (\text{const. } T, P),$$

which reduces to Eq. (3) when the Gibbs–Duhem identity $0 = n_1^b d\mu_1^l + n_2^b d\mu_2^l$ and the Gibbs adsorption isotherm $-A d\gamma = n_1^s d\mu_1^l + n_2^s d\mu_2^l$ are used. The two resulting equations [Eq. (3) with $i = 1, 2$] determine the chemical potentials of species 1 and 2 in the droplet needed to maintain unstable equilibrium with the vapor. These chemical potentials, in turn, determine a "bulk" cluster composition (again, invoking the picture of a large droplet) that should be used to consistently evaluate the remaining macroscopic thermodynamic properties (surface tension, density, etc.). (Microscopically, surface tension is a function of surface composition, but the latter is directly related to the bulk composition

which is always used in reporting measurements.)

In order to evaluate the composition variables n_i^b and n_i^s an additional equation is required. For example, one might follow Guggenheim[15] and write $A = n_1^s a_1 + n_2^s a_2$, where a_i is a (partial) molecular area. Guggenheim[15] has shown that this equation yields physically acceptable values for the surface concentration variables on a flat interface. Despite this, for a highly curved interface, a poor choice for the a_i can easily lead to unphysically large or small values for the n_i^s and n_i^b (and even to negative values), so care must be taken in any attempted evaluation.

Fortunately, it is unnecessary to compute actual values for the numbers of bulk and surface molecules in order to evaluate the quantities of primary theoretical interest: the free energy ΔG^* and the radius r^* of the critical nucleus. These quantities can be evaluated using only the bulk mole fractions x_i $(\equiv n_i^b/\Sigma n_i^b)$ found by solving Eq. (3). To see this, multiply Eq. (3) by x_i and sum over i. Then r^* immediately emerges as

$$r^* = -2\gamma\Sigma x_i v_i/\Sigma x_i \Delta\mu_i.$$

Substitute this expression into Eq. (3) (for $i = 1$, say). This leaves one independent equation to be solved for the free composition variable, say x_1. To obtain ΔG^* substitute in Eq. (1) for $\Delta\mu_1$ and $\Delta\mu_2$ using Eq. (3). The result can be written as $\Delta G^* = (4\pi/3)(r^*)^2\gamma^*$ if the droplet volume is expressed in the usual way as $V = 4\pi r^3/3 = \Sigma n_i v_i$. (Similar considerations apply for n component systems; formally identical expressions for r^* and ΔG^* arise.)

My preliminary estimates indicate that droplet compositions and surface tensions calculated with the proposed model differ significantly from those calculated in the standard way via Eq. (4) and the changes are in the direction of bringing theory and experiment closer together for systems in composition regions with large surface tension gradients. For example, at 293.2 K for a water vapor activity of 1.67 and an ethanol vapor activity of 0.7, Eq. (4) gives an ethanol mole fraction of about 0.19 with a corresponding surface tension of 30.7 dyn/cm. In order to bring theory and experiment into agreement, Mirabel and Katz[2] found that an effective value for the surface tension of 40.2 dyn/cm would be needed. For the two activities noted, Eq. (3) results in an ethanol mole fraction of about 0.06 with a corresponding surface tension of 43.7 dyn/cm. These differences arise because for water-rich mixtures, the large magnitude of $d\gamma/dX_i$ in Eq. (4) drives the cluster composition to be as rich in ethanol (the lower surface tension component) as possible. A bulk solution with a composition given by Eq. (4) has a greater surface enrichment in ethanol and, thus, a lower surface tension than one whose composition is given by Eq. (3). By explicitly ignoring surface enrichment, the model giving rise to Eq. (4) results in a lower surface tension and an implicit overenrichment than does the model underlying Eq. (3). Judging from this example, the revised thermodynamic scheme proposed here holds promise of providing much better agreement between theory and experiment when surface tension derivatives are large. Under conditions for which $d\gamma/dX_i$ is small, the results of Eqs. (3) and (4) are only slightly different. For systems with $d\gamma/dX_i = 0$, the new model reduces exactly to the old.

Considering that critical nuclei generally contain, at most, a few hundred molecules, the validity of these more refined thermodynamic methods may be questioned. The pragmatic defense is simply that thermodynamics has proven surprisingly successful in other applications where its validity also would be doubted.[16,17] Furthermore, since the necessity of modeling the cluster thermodynamics using macroscopic concepts is openly admitted, proceeding with the more refined model at least guarantees consistency with well established results[11,12,18] for large droplets and flat interfaces.

It is true that use of the Gibbs adsorption isotherm and the equilibrium surface tension implies that equilibrium surface enrichment occurs for the cluster. While this cannot be directly proven or disproven by experiment at present, there are no obvious dynamical constraints preventing it. (Inverse monomer–cluster collision frequencies and intracluster translational diffusion times are comparable.) Until such time as experiments or definitive calculations can be performed to determine cluster compositions and surface enrichment, determining the better model will have to be done largely by seeing which gives better agreement with experimental values of gross observables such as onset conditions. On this basis, the present model is a significant improvement over the conventional one[1–4,9,10] for systems with large surface tension gradients.

I thank Professor P. Mirabel for a useful discussion.

Recently, Flageollet-Daniel, Garnier, and Mirabel[19] proposed an alternative model that also gives improved agreement with experiment. However, their approach is more complicated than the one presented here.

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ERRATA

Erratum: Determination of dipole coupling constants using heteronuclear multiple quantum NMR [J. Chem. Phys. 77, 2870 (1982)]

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The scaling of heteronuclear Hamiltonian by the SHRIMP sequence of Sec. V is incorrectly described. The scaling factor is not unity, but rather $1/\sqrt{3}$. This change has no effect on the interpretation of the experiments presented or on the conclusions generally.

The following changes correct the text:

On p. 2879, delete the last sentence of the first paragraph of Sec. V A, which begins, "The scaling of $\mathcal{H}_{IS}$....". In the next sentence, the clause following "$\mathcal{H}_{IS}$" should be deleted and replaced by "with minimum scaling, while still removing $\mathcal{H}_{II}^{D}$ and retaining a secular average Hamiltonian."

In the first sentence of Sec. V B, the phrase "without scaling down" should read "with minimum scaling of." In Eq. (26), the first term on the right-hand side should be multiplied by the factor 1/3. This includes the scaling factor $\|\mathcal{H}_{I\text{-}S}\|/\|\mathcal{H}_{IS}\| = 1/\sqrt{3}$ and also the factor $\|I_{zi}S_{z}\|/\|I_{i}\cdot S\| = 1/\sqrt{3}$.

Finally, on p. 2882 in the last sentence of the second paragraph of the conclusion, the word "eliminates" should read "minimizes".

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