A scaled nucleation model for ideal binary systems

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Abstract

A scaled binary nucleation model for ideal systems is presented and used to analyze the experimental hexanol–ethanol data of Strey and Viisanen at 260 K. A major feature of the scaled nucleation rate is the rate prefactor, \( J_0 \), which is only weakly \( T \) (and composition) dependent and here is approximated by a constant. The model gives surprisingly good agreement with the experimental activity plot, and the scaled model method for finding the critical cluster composition (with binary surface tension composition variation) provides a better fit to the experimental data than the revised classical model. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Binary nucleation plays a major role in many physical processes including atmospheric phenomena such as the generation of stratospheric aerosols catalyzing ozone depletion [1]. While the classical binary nucleation formalism [2–11] and a more recent approach using density functional theory [12] have had some success in predicting binary nucleation rates, a fully satisfactory theory does not exist. In this Letter we present an extension of a scaled unary nucleation model [13–15] to the nucleation of an ideal binary system. The scaled model approach, valid at temperatures \( T \ll T_c \), was developed for qualitative analysis of unary vapor-to-liquid nucleation data and as a guide for systems with limited experimental surface tension and vapor pressure data. However, the scaling law does predict the onset supersaturations of many systems [13,16,17] and the scaled nucleation rate formalism provides a temperature dependence consistent with experimental data. In particular, the nucleation rate data for toluene and nonane are well described by the scaled model [15]. The scaled binary (vapor-to-liquid) nucleation rate model presented here assumes a classical binary model energy of formation [2–11] but casts the surface energy term into a scaled form, similar to the unary case (and to the scaled form of Binder [18] near the critical point). The approach rewrites the classical binary model energy of formation in an equivalent one component form [4] using one variable to specify binary cluster composition (the mole fraction of one species, \( x \)) and the second variable to specify binary cluster size information (\( n \), the total number of molecules). Upon maximizing the free energy of formation with respect to \( n \), one obtains a composition-dependent critical cluster size. The critical composition is determined by maximizing the scaled supersaturation of Binder and Stauffer [19].

This model is described in Section 2 and the resulting formalism is applied to the hexanol–ethanol
data of Strey and Viisanen [20] in Section 3. We find that the scaled binary model gives better agreement with the experimental hexanol–ethanol data than the revised classical binary nucleation model [10,11]. With this simple scaled binary model for nucleation rates, we hope to establish a starting point for less tractable systems, such as those with surface enrichment effects. Finally, our intent is to extend the validity of the scaled formalism and provide a tool for quick analysis of binary nucleation phenomena—in particular for cases where limited physical binary data are available.

2. Scaled binary nucleation model

In this approach we adopt the scaled model formalism [15] in which the nucleation rate, \( J \), is given by

\[
J(P_1, P_2, T) = J_0 \exp[-\Delta \Phi^*]
\]

where

\[
\Delta \Phi^* = \frac{16 \pi}{3} \frac{\Omega(x^*)^3}{\ln S(x^*)^2} \frac{T_c(x^*)}{T} \left[ \frac{T_c(x^*)}{T} - 1 \right]^3
\]

and \( T, T_c \) and \( P_i \) are the temperature, critical temperature, and partial vapor pressure of species \( i \), respectively; \( x^* \) is the critical mole fraction of one species (say species 1) and \( S(x) \) is the effective binary system supersaturation ratio, given in Eq. (3). In the unary scaled models, \( J_0 = [2 \pi m k T / h^2]^{1/2} / \Delta t \approx \exp[60 \text{ cm}^{-3} \text{ s}^{-1}] \) where the first factor is the inverse thermal wavelength cubed and \( \Delta t = 1 \text{ s} \); \( m \) is the incident monomer mass, \( k \) is the Boltzmann constant and \( h \) is Planck’s constant. The reason for the simple prefactor is not obvious. However, its form can be derived in the unary case by adding the free energy differences for small \( n \)-molecule clusters, until one reaches the critical cluster size, \( n^* \) [15]. One finds that the temperature dependence normally encountered in the standard classical model is cancelled by the discrete size treatment of small clusters [15]. To complete the evaluation of \( J_0 \) one needs to incorporate the \( \tau \ln n \) term of Fisher [21].

Dillmann and Meier [22] whose model also treated small cluster effects.

In Eq. (2) \( T_c(x) \) is the composition-dependent critical temperature and \( S(x) \) is an effective supersaturation given by \([2,4,23-25]:\)

\[
S(x) = S_i(x)^x S_2(x)^{1-x},
\]

where \( S_i(x) = P_i/P_i^0(x) \), and \( P_i^0(x) \) is the equilibrium partial vapor pressure of species \( i \) above the binary solution with mole fraction \( x \). The \( \Omega(x) \) is the composition-dependent molecular excess surface entropy (in units of \( k \)) which one expects to be of the order of 2 for normal liquids and about 1.5 for liquids which associate. In order to use the binary scaled model for ideal systems where composition dependent data is lacking one needs a simple form for \( \Omega(x) \) and \( T_c(x) \). The following approximations use single component quantities, \( \Omega_i \) and \( T_c^i \), and incorporate the dependence of \( \Omega(x) \) on the binary liquid number density, \( \rho(x) \)

\[
\Omega(x) = \left[ \frac{\rho(1)}{\rho(x)} \right]^{2/3} \Omega_i + (1-x) \left[ \frac{\rho(0)}{\rho(x)} \right]^{2/3} \Omega_2;
\]

\[
T_c(x) \approx xT_c^i + (1-x)T_c^2.
\]

The \( \Omega_i \) can be extracted from the temperature derivative of the single component surface tension, \( \sigma_i \), using the pure component liquid number density, \( n_i \) and the approximate relationship \( \Omega_i(T_c^i - T) = \sigma_i/(k \rho_i^{2/3}) \). A good procedure for obtaining \( \Omega_i \) is to fit \( \Omega_i(T_c^i - T) \) to \( \sigma_i/(k \rho_i^{2/3}) \) over a range of \( T \) where experimental surface tension data exist.

In order to find the critical composition, \( x^* \), and the critical size, \( n^* \), one needs the cluster free energy of formation, \( \Delta \Phi(n, x) \), where \( n = n_1 + n_2 \) is the total number of molecules. The scaled binary energy of formation is assumed to have the same form as the classical model,

\[
\Delta \Phi(n, x) = A(x)n^{2/3} - n \ln S(x).
\]

One can compare Eq. (6) with the classical model by letting \( A(x)n^{2/3} = 4 \pi r^2 \sigma(x)/kT \) and \( n = 4 \pi r^2 \rho(x)/3 \). Using the unary scaled model as an example, a general scaled form for \( A(x) \) can be
obtained by replacing $\sigma(x)$ with $\sigma_0(x) [T_c(x) - T]$, and replacing $\sigma_0(x)/[k \rho(x)^{2/3}]$ with $\Omega(x)$:

$$A(x) = \left( \frac{36\pi}{3\ln S(x)} \right)^{1/3} \left[ \frac{T_c(x)}{T} - 1 \right].$$  \hspace{1cm} (7)

It is straightforward to determine $n^*(x)$ at the relative maximum of $\Delta \Phi(n, x)$ by setting $\partial \Delta \Phi(n, x)/\partial n = 0$ and solving for $n^*(x)$:

$$n^*(x) = \left[ \frac{2A(x)}{3\ln S(x)} \right]^{1/3}. \hspace{1cm} (8)$$

The resulting form for $\Delta \Phi[n^*(x), x]$ is:

$$\Delta \Phi[n^*(x), x] = \left[ \frac{s_0}{s(x)} \right]^2. \hspace{1cm} (9)$$

where we have cast $\Delta \Phi[n^*(x), x]$ into a form similar to the unary scaled energy of Binder and Stauffer [19] using $s_0 = 2/(3\sqrt{3})$ and the 'scaled supersaturation', $s(x)$

$$s(x) = \ln S(x)/A(x)^{3/2}. \hspace{1cm} (10)$$

From Eqs. (9) and (10) one can see that the saddle point of $\Delta \Phi[n^*(x), x]$ is located at the value of $x$ for which $s(x)$ is a maximum. Thus one can reduce the determination of the critical composition, $x^*$, to maximizing $s(x)$:

$$s(x^*) = \text{Max} \left[ \frac{\ln S(x)}{A(x)^{3/2}} \right]. \hspace{1cm} (11)$$

We note this is equivalent to Doyle's approach [6] in which the surface tension is allowed to vary. If the surface tension is held constant in Eq. (11), and if the binary system is ideal the maximization of $s(x)$ is equivalent to the thermodynamically consistent classical model procedure for determining $x^*$ pointed out by Wilemski [10,11]. Once $x^*$ is known one can determine $n^*_1$ from

$$n^*_1 = x^* n(x^*). \hspace{1cm} (12)$$

$$n^*_2 = (1 - x^*) n(x^*). \hspace{1cm} (13)$$

The approach outlined above employs the equivalent unary form for $\Delta \Phi(n, x)$. It also provides one with a determination of the critical cluster size from the equilibrium partial vapor pressures, $P_i^c(x)$, and the binary solution number density, $\rho(x)$, without the need to calculate partial molecular volumes. This affords a minor practical advantage. The transformation of the energy of formation into the variables $n$ and $x$ and the use of $S(x)$, is not a new idea [2,4]; however, we are not aware of a previous use of the maximization of the scaled supersaturation, $s(x)$, to find $x^*$. It is the case, however, that use of Eq. (8) and the maximization of $s(x)$ is mathematically equivalent to setting the partial derivatives of $\Delta \Phi(n_1, n_2)$ equal to zero and solving for $n_1^*$ and $n_2^*$.

Finally, we note that one can formulate a scaling law for $\ln S(x)$ similar to the unary case [13]. That is, whenever the binary nucleation rate is constant (as in an activity plot) one can write:

$$\ln S(x^*) = \frac{s_0}{[\ln (J_0/J)]^{1/2}} A(x^*)^{3/2}, \hspace{1cm} (14)$$

and when $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$ one has the same form as the scaling law in the unary case:

$$\ln S(x^*) = 0.53 \left( \frac{\Omega(x^*)}{\frac{T_c(x^*)}{T} - 1} \right)^{3/2}. \hspace{1cm} (15)$$

3. Application to the hexanol–ethanol system

The application of the above formalism to the nearly ideal hexanol–ethanol system is straightforward. For the determination of $A(x)$ and $S(x)$ we use the partial vapor pressures, binary surface tension and binary liquid density given by Strey and Viisanen in Table 1 of Ref. [20]. For ethanol and hexanol, we use $T_c^1 = 513.9 \text{ K}$ and $T_c^2 = 611 \text{ K}$, respectively. One could use $\sigma_0(x)/[k \rho(x)^{2/3}]$ to find $\Omega_1 = 1.47$ at $x = 0$ and $\Omega_2 = 2.05$ at $x = 1$ and adopt the approximate form for $\Omega(x)$ in Eq. (4). This gives a good approximation for the $\sigma(x)$ reported by Strey and Viisanen. However, in this test of the scaled model we choose the $\Omega(x)$ which reproduces the $\sigma(x)$ exactly. This choice allows a more direct comparison with the classical models. In particular, analysis of the method for determining $x^*$ and the role of the flux prefactor of the nucleation rate are of interest. From Eqs. (5) and (11) we find the scaled model prediction for $x = x^*$ for each experimental data point, corresponding to the triplet $(a_i, b_i, T)$ where $a_i = P_i/P_{i,0}$ is the experimental gas
The hexanol–ethanol data of Strey and Viisanen were taken in a fast expansion chamber operated to produce rates at constant temperature, $T = 260\text{K}$. The usefulness of this approach is that it permits the determination of the composition of the binary critical cluster from $\frac{\partial \ln(J)}{\partial \ln(a_i)}|_T = n_i$ [28–31]. In Fig. 1 are the scaled binary model and the revised classical binary model predictions for $n_1$ and $n_2$ in the critical nucleus, together with the experimental values. (In using the revised classical model [10,11], we assume here that the total cluster volume is equal to $n[ xu_1 + (1-x)u_2 ]$ where the $x$ is the mole fraction corresponding to the interior of the cluster and the $u_i$ are the partial molecular volumes.) This analysis probes specifically the form for the energy of formation and the methods for locating the saddle point. In Fig. 2 is an activity plot, showing the curves in $(a_1,a_2)$ space corresponding to $J = 10^7 \text{ cm}^{-3} \text{ s}^{-1}$ for both models and the experiment. The classical model results have been taken from the work of Wilemski and Wyslouzil [32] and differ somewhat from the classical model predictions presented by Strey and Viisanen [20].

We note that the scaled binary model prediction for $n_1$ and $n_2$ seems to provide a better description of the critical binary cluster compositions than the revised classical model. Similarly, the activity dependence of the scaled binary nucleation rate is in good agreement with the data and its overall fit is valid (and emerges in our present test of a binary system) then the kinetic prefactor for binary systems should have the same magnitude as in the unary nucleation case.
better than the revised classical model prediction. The classical model calculations were repeated using a derivative of the binary surface tension with respect to composition to determine \( x^* \). The resulting predictions for \( n_1 \) and \( n_2 \) are identical to the scaled binary model curves of Fig. 1. The resulting activity plot, however, was not significantly altered from that of the revised classical model, as is indicated in Fig. 2. This suggests that the differences between the classical models and the scaled model activity plot predictions in Fig. 2 arise primarily from the composition dependence of the classical model flux prefactor.

4. Conclusions and comments

The fixed 260 K temperature of the binary ethanol–hexanol data [20] offers a unique opportunity to examine the composition dependence of binary nucleation rate models for a nearly ideal binary system. In the present study we find that the simple scaled binary model using a constant prefactor, \( J_0 \), and the \( s(x) \) maximization procedure gives a better fit to the data than the thermodynamically consistent revised classical model \([10,11]\). Emerging from this comparison as intriguing issues are both the method for determining the critical cluster composition and the kinetic prefactor composition dependence.

Specifically, the present study suggests that inclusion of the surface tension composition variation in the determination of \( x^* \) (the so-called 'thermodynamically inconsistent' approach) produces an improved prediction for the ethanol–hexanol critical binary cluster composition. A possible explanation is that the thermodynamically consistent procedure of the revised classical model does not extrapolate simply to small \( n \)-particle clusters. This could also be a reflection of the difference between the interior and total composition which is not addressed by the revised theory, as used here. It is also possible that there is a cancellation of effects arising from missing terms in the classical energy of formation.

The present study also indicates that the scaled model prediction of the \( a_1 \) and \( a_2 \) dependence for a constant nucleation rate has the correct overall composition dependence. If this is indeed the case for a general ideal binary system, the scaling law of Eq. (14) should predict the activity plot. This suggests that (if the classical model is to agree with experiment) there must be missing terms in the energy of formation which cancel the classical model incident monomer flux composition dependence. We note some similarity between this situation and the troublesome temperature dependence of the unary classical model \([15]\). Unfortunately, the temperature dependence of the scaled binary nucleation rate (for which the scaled unary model is most noted) is not tested in this exercise since the experimental data are all taken near 260 K. A test of the temperature dependence is certainly in order and might shed more light on the role of the composition dependence in the classical binary model flux factor.

Finally, the simple scaled binary nucleation model presented here is not intended for a non-ideal binary system with surface enrichment effects. The model, in fact, produced poor agreement with the ethanol–water data of Viisanen et al. \([33]\). Clearly, some \( x \) dependence on surface enrichment has to be incorporated into \( A(x) \). We view the present scaled analysis of the hexanol–ethanol system as a first step in developing a scaled binary formalism of more universal character. Future work should address the role of surface enrichment, employing a modified \( A(x) \) (such as that of Stauffer and Binder \([34]\)), a specific cluster model \([35]\) or a renormalization of the surface tension, such as that proposed by Kalikmanov and van Dongen \([24,25]\).

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References