

Analysis of water–ethanol nucleation rate data with two component nucleation theorems

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We generalize the second nucleation theorem to multicomponent systems. Nucleation theorems are used to extract the molecular composition and excess internal energy of the critical cluster from experimental nucleation rates in a water–ethanol mixture. The excess internal energy is found to depend only weakly on temperature and to be almost solely a function of the molecular numbers of water and ethanol in the cluster. We estimate the contribution of the kinetic pre-factor to our analysis, and find that it is small in the case of the first theorem, but significant for the second theorem. We find that capillarity approximation fails to predict the experimental critical size and excess energy in this highly nonideal system. © 2000 American Institute of Physics.
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I. INTRODUCTION

Characterizing the binding energy that holds matter together in a given atomic or molecular arrangement is a central theme of condensed matter and molecular physics. It contributes to our understanding of why certain microscopic structures are chosen under given conditions. Clearly, the framework for achieving this sort of understanding is to establish a theoretical model of intermolecular interactions, and to use it to calculate and compare suitable thermodynamic potentials for different structures. Recently it has become possible to perform *ab initio* calculations of these interactions, starting from a basic quantum-mechanical description of the electronic behavior in the system, though the computational costs are considerable.^{1,2} Alternatively, models can be built upon semiempirical potentials.^{3,4}

It is important to validate models using experimentally determined physical data. It is relatively easy to determine the energy of a bulk condensed phase by studying the calorimetry of the process of formation from its component parts, and this is valuable input to the development of models. The same information is often available for individual molecules. However, schemes that succeed in describing these special cases of condensed matter are perhaps suspect when applied to other cases like unusual bulk materials or surfaces, and much current research is directed at considering such systems.

Another unusual case is the molecular cluster. It has been possible for some years to create and isolate bound systems of some tens or hundreds of molecules, often using molecular beam experiments.^{5,6} The molecules in the cluster are held together by the same mechanisms that hold bulk and molecular structures together, but they have a very different environment compared with those other cases, and consequently the binding energy per molecule in the structure is

very different. If properties of such clusters could be determined experimentally, it would provide further stringent tests for the various theoretical models that have been developed to describe condensed matter.

Unfortunately, the calorimetry of the formation of molecular clusters is often poorly characterized, and this information is not usually available, except for simple cases and small clusters.^{7–9} But recent developments in the theory of nucleation of droplets from supersaturated vapors as well as the quality of experimental nucleation data offer new information that could revolutionize this situation.^{10–12} It has become possible to determine the thermodynamic properties (particularly the binding energy) of small clusters. The theorems have been successfully applied to clusters containing as few as six and as many as eighty molecules for a range of substances, by analyzing experimental droplet nucleation rate data. In these experiments, a supersaturated vapor is created and then the rate at which droplets nucleate from it is studied as a function of the supersaturation and temperature.^{13–15} This data can then be analyzed using the so-called nucleation theorems;^{10,16} relations between the rate of nucleation and the properties of the critical cluster, which is the size of cluster that is equally likely to grow or decay in the prevailing conditions. The main result of the analysis is a plot of cluster excess energy against cluster size in molecules. The excess energy is the difference between the energy of the cluster and the energy the constituent molecules would possess in a bulk liquid. It is loosely related to the number of unsatisfied intermolecular bonds at the surface of the cluster.

Until now, this analysis has been applied only to cases of single component vapor condensation, due to the lack of a key theoretical result, the second nucleation theorem for multicomponent nucleation. The first nucleation theorem for multicomponent systems has been developed and exploited in several earlier studies,^{17–20} most of which neglect the con-

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tribution of the kinetic factor in the nucleation rate. In Sec. II of this paper we derive the second nucleation theorem for multicomponent systems, and estimate the significance of the kinetic pre-factor in both the first and the second theorem. We apply the nucleation theorems in Sec. III to obtain information about small mixed molecular clusters of water and ethanol, using data from Schmitt *et al.*²¹ The results we obtain provide a picture of the binding behavior of small binary clusters. We discuss the implications of this microscopic information in Sec. IV, and give our conclusions.

II. SECOND NUCLEATION THEOREM FOR MULTICOMPONENT SYSTEMS

A. Basic thermodynamics

We adopt the Gibbs approach and model the formation of a molecular cluster from a vapor by referring it to the notional formation of a continuum liquid phase with bulk properties and definite spherical geometry. The difference between this model and the real properties of a small molecular cluster is expressed in terms of the properties of a surface phase, as will be seen.

We keep the terminology general, and starting with an ‘‘original’’ phase at pressure p_o consisting of a number of components labeled i , at fixed chemical potentials $\mu_{o,i}$, in a volume V , we reversibly and isothermally create within the system a droplet of ‘‘final’’ phase at pressure p_f occupying a volume V_f . To derive the second nucleation we need to evaluate the temperature derivative of the associated change in grand potential, or nucleation work. Following the notation of Oxtoby and Kashchiev¹⁶ the nucleation work W^* is given by

$$W^* = (p_o - p_f^*)V_f^* + \phi^*, \quad (1)$$

where ϕ^* is the total work of formation associated with the surface phase.

The asterisk refers to the critical cluster, which satisfies the following conditions:¹⁶

$$\mu_{o,i} = \mu_{f,i}^* = \mu_{s,i}^* \quad (\text{for all } i), \quad (2)$$

$$p_f^* = p_o + \left(\frac{\partial \phi^*}{\partial V_f^*} \right)_{T, \mu_{o,i}}, \quad (3)$$

where $\mu_{o,i}$, $\mu_{f,i}^*$, and $\mu_{s,i}^*$ are the chemical potentials of component i in the original, final and surface phases, respectively.

Now we take the derivative of Eq. (1) with respect to temperature holding the chemical potentials $\mu_{o,i}$ fixed for all species.

$$\left(\frac{\partial W^*}{\partial T} \right)_{\mu_{o,i}} = V_f^* \frac{\partial (p_o - p_f^*)}{\partial T} + \frac{\partial V_f^*}{\partial T} (p_o - p_f^*) + \left(\frac{\partial \phi^*}{\partial V_f^*} \right)_{T, \mu_{o,i}} \frac{\partial V_f^*}{\partial T} + \left(\frac{\partial \phi^*}{\partial T} \right)_{V_f^*, \mu_{o,i}}. \quad (4)$$

The second and third term vanish according to Eq. (3). The Gibbs–Duhem relation for the final phase reads

$$V_f dp_f - S_f dT = \sum_i n_{f,i} d\mu_{f,i}, \quad (5)$$

and for the original phase

$$V_o dp_o - S_o dT = \sum_i n_{o,i} d\mu_{o,i}, \quad (6)$$

where $n_{f,i}$ ($n_{o,i}$) is the number of molecules of type i that occupy the volume V_f (V_o) of uniform final (original) phase, and S_f (S_o) is the entropy of the final (original) phase. For the surface phase the Gibbs–Duhem relation reads

$$d\phi + S_s dT = - \sum_i n_{s,i} d\mu_{s,i} + \gamma dA, \quad (7)$$

where γ is the surface free energy per unit area, and the surface area of the cluster, A is a function of droplet volume V_f . $n_{s,i}$ is the surface excess number of particles and S_s is the entropy of the surface phase. When the temperature is kept constant this equation is also called the Gibbs adsorption isotherm. All the Gibbs–Duhem relations naturally hold for the special cases of a critical nucleus and the surrounding vapor. Keeping the chemical potentials of the original phase fixed, and requiring that the chemical potentials of the final and surface phases obey Eq. (2) gives the result

$$\left(\frac{\partial W^*}{\partial T} \right)_{\mu_{o,i}} = \frac{V_f^*}{V_o^*} S_o^* - S_f^* - S_s^*. \quad (8)$$

If we take the derivative of βW^* with respect to $\beta = 1/T$, we get

$$\begin{aligned} \left(\frac{\partial \beta W^*}{\partial \beta} \right)_{\mu_{o,i}} &= W^* - T \left(\frac{\partial W^*}{\partial T} \right)_{\mu_{o,i}} \\ &= (p_o - p_f^*)V_f^* + \phi^* - \frac{V_f^*}{V_o^*} T S_o^* + T S_f^* + T S_s^* \\ &= -p_f^* V_f^* + T S_f^* \\ &\quad + \sum_i n_{f,i}^* \mu_{f,i}^* + \phi^* + T S_s^* + \sum_i n_{s,i}^* \mu_{s,i}^* \\ &\quad + \left[-p_o V_o^* + T S_o^* + \sum_i n_{o,i}^* \mu_{o,i} \right] \\ &\quad - \left[-p_o V + \sum_i n_{\text{tot},i}^* \mu_{o,i} + T \left(1 + \frac{V_f^*}{V_o^*} \right) S_o^* \right], \end{aligned} \quad (9)$$

where $n_{\text{tot},i}^* = n_{f,i}^* + n_{o,i}^* + n_{s,i}^*$ is the total number of molecules of species i , and $V = V_f^* + V_o^*$ is the total volume. The combination of the terms in square brackets can be readily interpreted. The expression in the first square brackets is simply the energy of the original phase in the presence of critical cluster. The expression inside the second square brackets is the energy the original phase would have in the absence of the critical cluster, but at the same pressure p_o , chemical potentials $\mu_{o,i}$ and temperature T . The combination takes the form $\delta E_o = T \delta S_o - p_o \delta V_o + \sum_i \mu_{o,i} \delta n_{o,i}$ with $\delta V_o = -V_f^*$,

$\delta S_o = -V_f^*/s_o$ where $s_o = S_o^*/V_o^*$ is the constant entropy density, and $\delta n_{i,o} = n_{o,i}^* - n_{tot,i}$. So δE_o is the change in energy of the original phase caused by the loss of volume to the final phase cluster. We end up with the simple result

$$\left(\frac{\partial(W^*/T)}{\partial T}\right)_{\mu_{o,i}^*} = -(E_f^* + E_s^* + \delta E_o)/T^2 = -E_{\text{excess-original}}^*/T^2, \quad (10)$$

where E_f^* and E_s^* are the internal energies of the final and surface phases. The temperature derivative of the nucleation work divided by T is seen to be essentially the difference in internal energy between the system with the cluster and a homogeneous system of the original phase, which is written $E_{\text{excess-original}}^*$.

Using the Gibbs-Duhem relations keeping T constant yields in a similar fashion the first nucleation theorem¹⁶

$$\left(\frac{\partial W^*}{\partial \mu_{o,i}}\right)_T = -\Delta n_i^*, \quad (11)$$

where $\Delta n_i^* = (1 - \rho_{o,i}/\rho_{f,i}^*)n_{f,i}^* + n_{s,i}^* \approx n_{f,i}^* + n_{s,i}^*$, and the densities of the final and the original phase are $\rho_{o,i} = n_{o,i}^*/V_o^*$ and $\rho_{f,i} = n_{f,i}^*/V_f^*$, and the last approximate form applies for gas-liquid nucleation if the vapor is dilute ($\rho_o \ll \rho_f^*$).

B. Nucleation theorems for two component gas-liquid nucleation

In analyzing nucleation data for vapor-liquid nucleation, saturation ratios are more useful variables than the chemical potentials. The saturation ratio for component i is defined as $S_i = p_i/p_{i,\text{pure}}^s$, where p_i is the partial pressure of component i , and $p_{i,\text{pure}}^s$ is the saturation vapor pressure above a pool of liquid of pure substance i . The final phase is now liquid, and the original phase is vapor. Suffix v will now be used in place of suffix o , and suffix l will take the place of suffix f .

Using the first nucleation theorem we can transform the second theorem into the form

$$\left(\frac{\partial(W^*/T)}{\partial T}\right)_{S_1,S_2} = \frac{-E_{\text{excess-vapor}}^*}{T^2} - \frac{\Delta n_1^*}{T} \left(\frac{\partial \mu_{v,1}}{\partial T}\right)_{S_1,S_2} - \frac{\Delta n_2^*}{T} \left(\frac{\partial \mu_{v,2}}{\partial T}\right)_{S_1,S_2}. \quad (12)$$

If we make the usual assumption that the vapor phase is an ideal mixture of ideal gases, the chemical potential of component i in the vapor is given by $\mu_{v,i} = \mu_{v,i}^s(T) + kT \ln S_i$, where $\mu_{v,i}^s$ is the chemical potential of a saturated pure vapor and k is the Boltzmann constant.

The Gibbs-Duhem relation (6) for the pure vapor i and the Clausius-Clapeyron equation

$$\frac{dp_{i,\text{pure}}^s}{dT} = \frac{h_{v,i}^s - h_{l,i}^s}{T(v_{v,i}^s - v_{l,i}^s)}, \quad (13)$$

can be used to express the temperature derivative of the equilibrium chemical potential $\mu_{v,i}^s$ in the form

$$\frac{d\mu_{v,i}^s}{dT} = \frac{v_{v,i}^s(h_{v,i}^s - h_{l,i}^s)}{T(v_{v,i}^s - v_{l,i}^s)} - s_{v,i}^s \approx \frac{(h_{v,i}^s - h_{l,i}^s)}{T} - s_{v,i}^s, \quad (14)$$

Here $h_{v,i}^s$ and $h_{l,i}^s$ are the molecular enthalpies of saturated vapor and liquid, respectively, $s_{v,i}^s$ is the molecular entropy in the saturated vapor, and $v_{v,i}^s$ and $v_{l,i}^s$ are molecular volumes in the saturated vapor and equilibrium liquid, respectively, for pure species i . The last form follows when the liquid is much denser than the gas, $v_{l,i}^s \ll v_{v,i}^s$. Using $\mu_{v,i}^s = h_{v,i}^s - Ts_{v,i}^s$ for the equilibrium chemical potential and approximating $h_{l,i}^s \approx e_{l,i}^s$, where $e_{l,i}^s$ is the molecular energy in pure equilibrium liquid i , we get

$$\left(\frac{\partial(W^*/T)}{\partial T}\right)_{S_1,S_2} = \frac{-E_{\text{excess-vapor}}^*}{T^2} - \frac{\Delta n_1^*}{T^2}(\mu_{v,1} - e_{l,1}^s) - \frac{\Delta n_2^*}{T^2}(\mu_{v,2} - e_{l,2}^s). \quad (15)$$

Using the form implied by Eqs. (9) and (10) for $E_{\text{excess-vapor}}^*$ and assuming that $1 + V_f^*/V_o^* \approx 1$ and $V = V_f^* + V_o^* \approx V_o^*$, we end up with

$$\left(\frac{\partial(-W^*/kT)}{\partial T}\right)_{S_1,S_2} = \frac{1}{kT^2} \left[E_f^* + E_s^* - \sum_i (n_{l,i}^* + n_{s,i}^*) e_{l,i}^s \right] = \frac{E_{\text{excess-liquid}}^*}{kT^2}, \quad (16)$$

where $E_{\text{excess-liquid}}^*$ (which will hereafter be shortened to E_x^*) is the difference between the internal energy of the cluster and the energy the molecules would have as constituents of pure equilibrium liquids. Thus, both the surface contribution and the bulk mixing energy are included in the excess energy.

The first nucleation theorem in terms of saturation ratios S_i is given by

$$\left(\frac{\partial(-W^*/kT)}{\partial S_i}\right)_T = \frac{\Delta n_i^*}{S_i}. \quad (17)$$

C. The nucleation rate

For multicomponent systems an exact expression for the nucleation rate (analogous to the one used by Ford^{10,11} to obtain the derivatives of the nucleation rate in one component systems) is not available. Instead, we shall use a form suggested by approximate treatments,²²⁻²⁴ where the nucleation rate J takes the form

$$J = c_0^* \exp\left(-\frac{W^*}{kT}\right) R_{\text{av}}^* Z, \quad (18)$$

where $c_0^* \exp(-W^*/(kT))$ is the concentration of critical nuclei, R_{av}^* is the average growth rate of the critical nucleus, and Z is the Zeldovich factor.

For the cluster size distribution we use the form proposed by Wilemski *et al.*²⁵ [their Eq. (53)], which gives the coefficient c_0^* as

$$c_0^* = (\rho_{1,\text{pure}}^s)^{(1-x^*)} (\rho_{2,\text{pure}}^s)^{x^*}, \quad (19)$$

where $\rho_{i,\text{pure}}^s$ is the density of saturated pure vapor i , and $x^* = n_{i,2}^*/(n_{i,1}^* + n_{i,2}^*)$ is the mole fraction of component 2 in the critical cluster. The vapor phase is assumed to be ideal and thus $\rho_{i,\text{pure}}^s = p_{i,\text{pure}}^s/(kT)$.

According to Stauffer²³ the average growth rate has the form

$$R_{\text{av}}^* = \frac{\beta_1^* \beta_2^*}{\beta_1^* \sin^2 \varphi + \beta_2^* \cos^2 \varphi}, \quad (20)$$

where $\beta_i^* = S_i p_{i,\text{pure}}^s A^* / \sqrt{2kT\pi m_i}$ is the rate at which molecules of component i are added to the critical cluster, m_i is the mass of a molecule of type i , and A^* is the surface area of the critical cluster. The presented form for β_i^* is valid under the assumption that the mass and the volume of the critical cluster are much larger than those of a single molecule. φ is the direction of the nucleation flow in the $(n_{1,1}, n_{1,2})$ -plane and in the steepest descent approximation it is given by $\tan \varphi = x^*/(1-x^*)$. The pre-factor $J_0 \equiv c_0^* R_{\text{av}}^* Z$, therefore, takes the form

$$J_0 = \frac{Z S_1 S_2 A^* (p_{1,\text{pure}}^s)^{2-x^*} (p_{2,\text{pure}}^s)^{1+x^*} [x^{*2} + (1-x^*)^2]}{\sqrt{2\pi} (kT)^{3/2} [S_1 p_{1,\text{pure}}^s \sqrt{m_2} x^{*2} + S_2 p_{2,\text{pure}}^s \sqrt{m_1} (1-x^*)^2]}. \quad (21)$$

D. Derivative of the pre-factor with respect to supersaturation

First we want to see how much the pre-factor contributes to the derivative of $\ln J$ with respect to the supersaturations S_1 . We get

$$\left(\frac{\partial \ln J_0}{\partial S_1} \right)_{S_2, T} = \frac{1}{S_1} + \frac{1}{A^*} \frac{\partial A^*}{\partial S_1} + \frac{1}{Z} \frac{\partial Z}{\partial S_1} + \left(\frac{\partial x^*}{\partial S_1} \right)_{S_2, T} \left[\ln \frac{p_{2,\text{pure}}^s}{p_{1,\text{pure}}^s} + \frac{4x^* - 2}{2x^{*2} - 2x^* + 1} \right] - \frac{(1/S_1) + (2/x^*) (\partial x^*/\partial S_1)_{S_2, T} [1 + ((x^* - 1) S_2 p_{2,\text{pure}}^s \sqrt{m_1}) / (x^* S_1 p_{1,\text{pure}}^s \sqrt{m_2})]}{1 + [(x^* - 1)^2 S_2 p_{2,\text{pure}}^s \sqrt{m_1} / x^{*2} S_1 p_{1,\text{pure}}^s \sqrt{m_2}]}. \quad (22)$$

The derivative of the pre-factor with respect to S_2 reads

$$\left(\frac{\partial \ln J_0}{\partial S_2} \right)_{S_1, T} = \frac{1}{S_2} + \frac{1}{A^*} \frac{\partial A^*}{\partial S_2} + \frac{1}{Z} \frac{\partial Z}{\partial S_2} + \left(\frac{\partial x^*}{\partial S_2} \right)_{S_1, T} \left[\ln \frac{p_{2,\text{pure}}^s}{p_{1,\text{pure}}^s} + \frac{4x^* - 2}{2x^{*2} - 2x^* + 1} \right] - \frac{[(x^* - 1)^2 p_{2,\text{pure}}^s \sqrt{m_1} / x^{*2} S_1 p_{1,\text{pure}}^s \sqrt{m_2}] + (2/x^*) (\partial x^*/\partial S_2)_{S_1, T} [1 + ((x^* - 1) S_2 p_{2,\text{pure}}^s \sqrt{m_1}) / (x^* S_1 p_{1,\text{pure}}^s \sqrt{m_2})]}{1 + [(x^* - 1)^2 S_2 p_{2,\text{pure}}^s \sqrt{m_1}) / (x^{*2} S_1 p_{1,\text{pure}}^s \sqrt{m_2})]}. \quad (23)$$

Our aim is to estimate how significant the derivative of the pre-factor J_0 is compared to the derivative of $\exp(-W^*/(kT))$. Since the Zeldovich factor is known to be of the order of unity in two component systems, and it varies slowly with system conditions, we neglect the derivative of the Zeldovich factor.

To obtain the composition and surface area of the critical cluster and their derivatives we make use of the Kelvin equations (see, e.g., Refs. 26–28)

$$\Delta \mu_i(x^*, T, S_1, S_2) = \frac{-2\gamma(x^*, T) v_{l,i}(x^*, T)}{R^*}, \quad (24)$$

where $\Delta \mu_i = \mu_{v,i}(T, S_1, S_2) - \mu_{l,i}(p_v, x, T)$, γ is the surface tension and R^* the radius of the critical cluster. The surface area is given by $A^* = 4\pi R^{*2}$. If the liquid density is again assumed to be much larger than the vapor density, and the

vapor phase is assumed ideal, then the chemical potential difference takes the form $\Delta \mu_i = kT \ln(S_i/a_i)$, where the activity $a_i = a_i(x, T) = p_i^s(x, T)/p_{i,\text{pure}}^s(T)$ is the ratio of the saturation vapor pressure over a liquid solution with mole fraction x to the saturation vapor pressure over a pure liquid of component i .

The critical cluster composition is identified by solving the following equation, which can be obtained by taking the ratio of the Kelvin equations for components 1 and 2:

$$\Delta \mu_1(x^*, T, S_1, S_2) v_{l,2}(x^*, T) = \Delta \mu_2(x^*, T, S_1, S_2) v_{l,1}(x^*, T). \quad (25)$$

If we take the derivative of Eq. (25) with respect to S_1

keeping S_2 and T constant, we find an expression for the derivative of the composition of the critical cluster

$$\left(\frac{\partial x^*}{\partial S_1}\right)_{S_2,T} = \frac{v_{i,2}^*}{S_1} \left[- \left(\frac{\partial v_{i,2}}{\partial x}\right)_T^* \ln\left(\frac{S_1}{a_1^*}\right) + \left(\frac{\partial v_{i,1}}{\partial x}\right)_T^* \times \left(\frac{S_2}{a_2^*}\right) + \left(\frac{\partial a_1}{\partial x}\right)_T^* \frac{v_{i,2}^*}{a_1^*} - \left(\frac{\partial a_2}{\partial x}\right)_T^* \frac{v_{i,1}^*}{a_2^*} \right]^{-1}, \quad (26)$$

where $(\partial a_2/\partial x)_T^* \equiv (\partial a_2/\partial x)_T|_{x=x^*}$. The derivative of the surface area of the critical cluster can be obtained by taking the derivative of the Kelvin equation [Eq. (24)]; for example, for $i=2$:

$$\frac{1}{A^*} \left(\frac{\partial A^*}{\partial S_1}\right)_{S_2,T} = 2 \left(\frac{\partial x^*}{\partial S_1}\right)_{S_2,T} \left[\frac{1}{\gamma^*} \left(\frac{\partial \gamma}{\partial x}\right)_T^* \right] \quad (27)$$

$$+ \frac{1}{v_{i,2}^*} \left(\frac{\partial v_{i,2}}{\partial x}\right)_T^* - \frac{1}{a_2^* \ln(S_2/a_2^*)} \left(\frac{\partial a_2}{\partial x}\right)_T^* \quad (28)$$

We have assumed that the surface tension is a function of temperature and the mole fraction only, and does not depend on the size of cluster. This is essentially the capillarity approximation and we shall find ultimately that the resulting contribution to the nucleation theorems is small. We consider it likely that use of a curvature dependent surface tension would not change this situation.

E. Derivative of the pre-factor with respect to temperature

The contribution of the pre-factor to the temperature derivative of nucleation rate is

$$\begin{aligned} \left(\frac{\partial \ln J_0}{\partial T}\right)_{S_1,S_2} &= (2-x^*) \frac{L_1}{kT^2} + (1+x^*) \frac{L_2}{kT^2} - \frac{3}{2T} + \frac{1}{A^*} \left(\frac{\partial A^*}{\partial T}\right)_{S_1,S_2} + \frac{1}{Z} \left(\frac{\partial Z}{\partial T}\right)_{S_1,S_2} + \left(\frac{\partial x^*}{\partial T}\right)_{S_1,S_2} \left[\ln \frac{p_{2,pure}^s}{p_{1,pure}^s} + \frac{4x^*-2}{2x^{*2}-2x^*+1} \right] \\ &\quad - \frac{(L_1/kT^2) + (L_2/kT^2)((x^*-1)^2 S_2 p_{2,pure}^s \sqrt{m_1}) / (x^{*2} S_1 p_{1,pure}^s \sqrt{m_2})}{1 + [((x^*-1)^2 S_2 p_{2,pure}^s \sqrt{m_1}) / (x^{*2} S_1 p_{1,pure}^s \sqrt{m_2})]} \\ &\quad - \frac{(2/x^*) (\partial x^*/\partial T)_{S_1,S_2} (1 + ((x^*-1) S_2 p_{2,pure}^s \sqrt{m_1}) / (x^* S_1 p_{1,pure}^s \sqrt{m_2}))}{1 + [((x^*-1)^2 S_2 p_{2,pure}^s \sqrt{m_1}) / (x^{*2} S_1 p_{1,pure}^s \sqrt{m_2})]}. \end{aligned} \quad (29)$$

We have used the Clausius-Clapeyron equation [Eq. (13)] and the approximation $v_{v,i}^s / (v_{v,i}^s - v_{l,i}^s) \approx 1$ to express the derivatives of the saturation vapor pressures of pure substances in terms of latent heats of evaporation per molecule, $L_i = h_{v,i}^s - h_{l,i}^s$, for pure liquids. The remaining task is to obtain the temperature derivatives of the surface area and composition of the critical cluster by taking the derivatives of Eqs. (24) and (25).

For the mole fraction we get

$$\begin{aligned} \left(\frac{\partial x^*}{\partial T}\right)_{S_1,S_2} &= \left[- \frac{1}{v_{i,2}^* a_2^*} \left(\frac{\partial a_2}{\partial T}\right)_x^* + \frac{1}{v_{i,1}^* v_{i,2}^*} \left(\frac{\partial v_{i,1}}{\partial T}\right)_x^* \frac{S_2}{a_2^*} + \frac{1}{v_{i,1}^* a_1^*} \left(\frac{\partial a_1}{\partial T}\right)_x^* - \frac{1}{v_{i,1}^* v_{i,2}^*} \left(\frac{\partial v_{i,2}}{\partial T}\right)_x^* \ln \frac{S_1}{a_1^*} \right] / \\ &\quad \left[\frac{1}{v_{i,2}^* a_2^*} \left(\frac{\partial a_2}{\partial x}\right)_T^* - \frac{1}{v_{i,1}^* v_{i,2}^*} \left(\frac{\partial v_{i,1}}{\partial x}\right)_T^* \frac{S_2}{a_2^*} - \frac{1}{v_{i,1}^* a_1^*} \left(\frac{\partial a_1}{\partial x}\right)_T^* + \frac{1}{v_{i,1}^* v_{i,2}^*} \left(\frac{\partial v_{i,2}}{\partial x}\right)_T^* \ln \frac{S_1}{a_1^*} \right], \end{aligned} \quad (30)$$

and finally for the surface area

$$\begin{aligned} \frac{1}{A^*} \left(\frac{\partial A^*}{\partial T}\right)_{S_1,S_2} &= 2 \left\{ \frac{1}{\gamma^*} \left[\left(\frac{\partial \gamma}{\partial T}\right)_x^* + \left(\frac{\partial \gamma}{\partial x}\right)_T^* \left(\frac{\partial x^*}{\partial T}\right)_{S_1,S_2} \right] + \frac{1}{v_{i,2}^*} \left[\left(\frac{\partial v_{i,2}}{\partial T}\right)_x^* + \left(\frac{\partial v_{i,2}}{\partial x}\right)_T^* \left(\frac{\partial x^*}{\partial T}\right)_{S_1,S_2} \right] \right. \\ &\quad \left. - \frac{1}{T} - \frac{1}{a_2^* \ln(S_2/a_2^*)} \left[\left(\frac{\partial a_2}{\partial T}\right)_x^* + \left(\frac{\partial a_2}{\partial x}\right)_T^* \left(\frac{\partial x^*}{\partial T}\right)_{S_1,S_2} \right] \right\}. \end{aligned} \quad (31)$$

III. RESULTS

There are not many sources that present experimental binary nucleation rates at different temperatures. We analyzed the data of Schmitt *et al.*,²¹ who measured the supersaturations of ethanol (S_e) and water (S_w) required to pro-

duce nucleation rates of $10^3/(\text{cm}^3 \text{ s})$, $10^4/(\text{cm}^3 \text{ s})$ and $10^5/(\text{cm}^3 \text{ s})$ at temperatures 263, 273, 283, and 293 K. For consistency, we used the same fits for surface tension, activity coefficient, saturation vapor pressures of pure components and density as Schmitt *et al.* Latent heats of evapora-

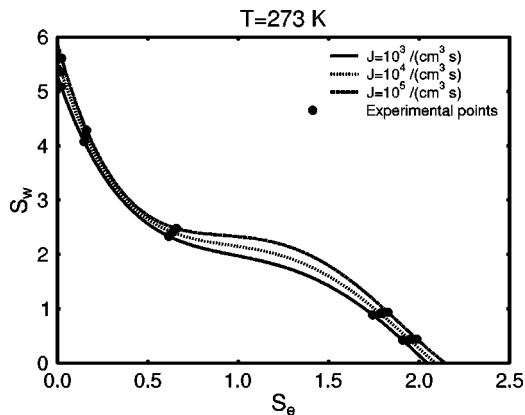


FIG. 1. The saturation ratio of water (S_w) as a function of the saturation ratio of ethanol (S_e) needed to produce a certain nucleation rate. The uppermost of the triple dots corresponds to $J=10^5/(\text{cm}^3 \text{ s})$, the middle one $J=10^4/(\text{cm}^3 \text{ s})$ and the lowest one $J=10^3/(\text{cm}^3 \text{ s})$. The figure shows the experimental points and our polynomial fits.

tion were taken from the work of Schmeling and Strey^{29,30} for ethanol and from Preining *et al.*^{31,32} for water. We fitted a fourth order polynomial $S_w(S_e, T, \ln J) = A + BS_e + CS_e^2 + DS_e^3 + ES_e^4$ to present S_w as a function of S_e at constant nucleation rate and temperature. The coefficients of the polynomial A , B , C , D and E were fitted up to second order as functions of $\ln J$ and T (for example $A(T, \ln J) = \alpha_1 + \alpha_2 \ln J + \alpha_3 \ln^2 J + \alpha_4 T + \alpha_5 T^2 + \alpha_6 T \ln J$), to obtain S_w as a function of temperature, nucleation rate and S_e . Figure 1 shows the experimental points and the polynomial fits at $T = 273 \text{ K}$.

The fourth-order polynomial produced the best polynomial fit to the data, and the fit remains monotonic over the whole range of experimental points. We used our fit to obtain the derivatives of $\ln J$ with respect to S_e , S_w , and T at experimental points. Clearly the disconnectedness of the data results in some uncertainty in the derivatives obtained from the fit, and all the presented results are subject to this uncertainty. We did not evaluate any results in the regions between the experimental points since we felt that the uncertainty would be too large. A physically more well-grounded fitting formula would be the scaled formula for binary systems presented by Hale *et al.*³³ However, this formula would require a knowledge of the bulk mole fraction x^* of the critical cluster which cannot be extracted from the experimental data. Thus we felt that a direct fit to the experimental points is more appropriate. The saturation ratios of water are clearly lower pure water than for the water–ethanol mixture. This causes problems in the parametric fit, and we chose to fit the pure water cases separately. For pure water we fitted $\ln J$ as a second order polynomial of S_w and the coefficients were fitted as third-order polynomials of T . The pure ethanol data of Schmitt *et al.*²¹ were not incorporated into this study.

The derivatives of the nucleation rate were interpreted using Eqs. (16) and (17) for the derivative of the exponential function in the nucleation rate, Eq. (18), together with the estimates of the derivatives of the pre-factor.

The molecular numbers in the critical cluster are given by

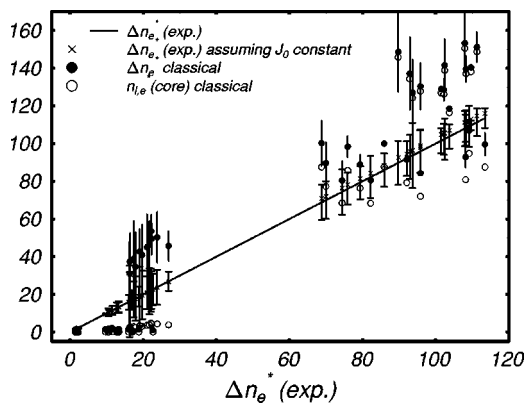


FIG. 2. The number of ethanol molecules in the critical cluster. The data is arranged as a function of the number obtained from experimental data. The solid line represents one to one correspondence. The error bars terminated by cross bars are related to the experimental values, and the ones without cross bars to the classical values.

$$\Delta n_i^* = \left(\frac{\partial \ln J}{\partial S_i} \right)_{S_j, T} S_i - \left(\frac{\partial \ln J_0}{\partial S_i} \right)_{S_j, T} S_i, \quad (32)$$

and the excess energy of the critical cluster (compared to the energy of its molecules in pure bulk liquids) is given by

$$E_x^* = \left(\frac{\partial \ln J}{\partial T} \right)_{S_i} kT^2 - \left(\frac{\partial \ln J_0}{\partial T} \right)_{S_i} kT^2, \quad (33)$$

where the derivatives of the pre-factor J_0 are estimated by the classical equations [Eqs. (22), (24), and (29)].

Figures 2 and 3 show the relative lack of importance of the pre-factor in evaluating numbers of molecules in the critical cluster. They also compare the classical predictions for these numbers and the ones obtained from experimental data. On the x axis is the number obtained from experimental data. The curve representing experimental data is of course a straight line indicating one to one correspondence. The points for Δn_i^* obtained assuming J_0 is constant shows that the contribution of the pre-factor is seen to be almost negligible, as expected. Although our estimates for the derivatives

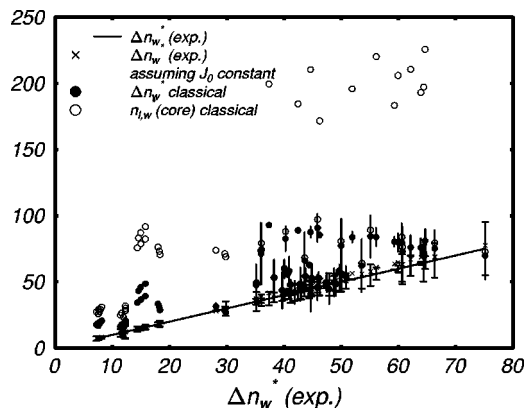


FIG. 3. The number of water molecules in the critical cluster. The data is arranged as a function of the number obtained from experimental data. The solid line represents one to one correspondence. The error bars terminated by cross bars are related to the experimental values, and the ones without cross bars to the classical values.

of the pre-factor are based on a clearly inadequate classical theory, we can safely conclude that uncertainty in the pre-factor is not important in using the first nucleation theorem. We have estimated the sensitivity of the results to the form of the fitting function by using third-order polynomials instead of fourth order polynomials [i.e., by setting $E(T, \ln J) \equiv 0$]. The resulting change in the excess numbers is indicated as error bars terminated by crossbars in Figs. 2 and 3. We see that the results are reasonably insensitive to the change in the fitting function.

In the classical theory the cluster reference state is modeled as a spherical droplet that has sharp Gibbs dividing surface between liquid and vapor phases. The difference between the number of molecules possessed by the true cluster and the reference state of uniform liquid encompassed by the dividing surface (referred to as the core) is the surface excess number. Two classical values of molecular number are presented in Figs. 2 and 3: one represents the number of molecules in the core of the cluster and the other is the total number of molecules including surface excess molecules. Once the mole fraction in the core is obtained from Eq. (25), the molecular numbers in the core can be solved from Eq. (24) using $V^* = 4\pi R^{*3}/3 = n_{l,1}^* v_{l,1}(x^*) + n_{l,2}^* v_{l,2}(x^*)$. The method for evaluating the surface excess numbers is described by Laaksonen *et al.*^{20,28} The total number represents the actual number of molecules belonging to the cluster; it is also the one that can be extracted from experimental data. The core numbers are purely hypothetical and depend on the choice of the dividing surface between the liquid and vapor phases. We take the dividing surface to be the surface of tension, as usual. The error estimates for the classical values are obtained by using slightly modified fits for surface tension, density and activities. It must be noted that the modifications to ethanol and water activities can not be performed independently, since the activities have to satisfy the Gibbs–Duhem equation. Not only the absolute values of these quantities, but also their temperature and composition derivatives must be modified to perform a relevant sensitivity analysis. At most, the uncertainty in activities was taken to be 10%, and the density as well as surface tension were modified by 5%.

For water, the classical theory generally overestimates the molecular numbers. The core numbers are far off the experimental results, but taking the surface excess into account improves the situation considerably. For clusters with only a few ethanol molecules the classical theory underestimates the number of ethanol molecules in the critical cluster severely, and for clusters having many ethanol molecules the predictions oscillate between underestimation and overestimation. The surface excess numbers for ethanol are generally much smaller than for water. These results point out the importance of surface excess numbers in surface active systems such as water–alcohol mixtures.

Viisanen *et al.*¹⁹ have analyzed their experimental data for water–ethanol mixtures at $T = 260$ K for $J = 10^7/\text{cm}^3 \text{ s}$. They present the molecular content of the nuclei as a function of normalized activity fraction defined as

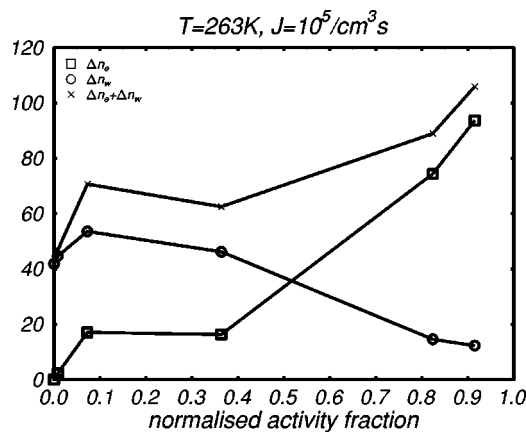


FIG. 4. Molecular content of critical clusters. The symbols show the number of ethanol and water molecules and the total number of molecules in the critical cluster. The solid lines are a guide to the eye.

$$x_{\text{norm}} = \frac{S_e/S_{e0}}{S_e/S_{e0} + S_w/S_{w0}}, \quad (34)$$

where S_{e0} and S_{w0} are the saturation ratios which lead to nucleation rate $J = 10^7/\text{cm}^3 \text{ s}$ for pure ethanol and water, respectively. Although the lowest temperature we studied is 263.15 K, we use the values S_{e0} and S_{w0} which are valid for $T = 260$ K, and are taken from Fig. 2 of Viisanen *et al.*¹⁹ The highest nucleation rate measured by Schmitt *et al.*²¹ is $J = 10^5/\text{cm}^3 \text{ s}$. To enable qualitative comparison with Viisanen *et al.*,¹⁹ Fig. 4 shows our deduced molecular content of the nuclei as a function of normalized activity for $T = 260$ K and $J = 10^5/\text{cm}^3 \text{ s}$. When comparing with Fig. 3 of Viisanen *et al.*,¹⁹ we conclude that our results agree well with the earlier ones.

Figure 5 shows a comparison between the classical prediction for the excess energy of the critical cluster and the experimental results. Also the contribution of the pre-factor is indicated. The energy is expressed in units kT_0 , where $T_0 = 273.15$ K. On the x axis is the number obtained from experimental data. The curve representing experimental data is of course a straight line indicating one to one correspond-

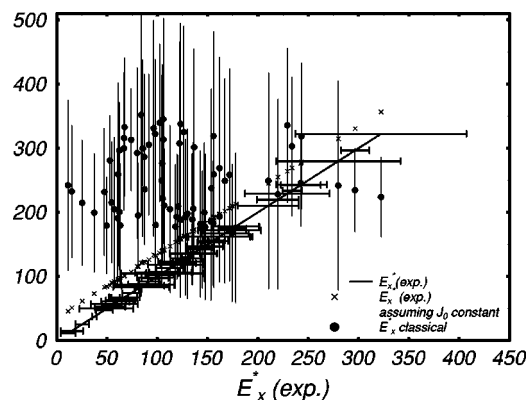


FIG. 5. The excess energy of the critical cluster. The data is arranged as a function of the number obtained from experimental data. The solid line represents one to one correspondence. The horizontal error bars terminated by cross bars are related to the experimental values, and the ones without cross bars to the classical values.

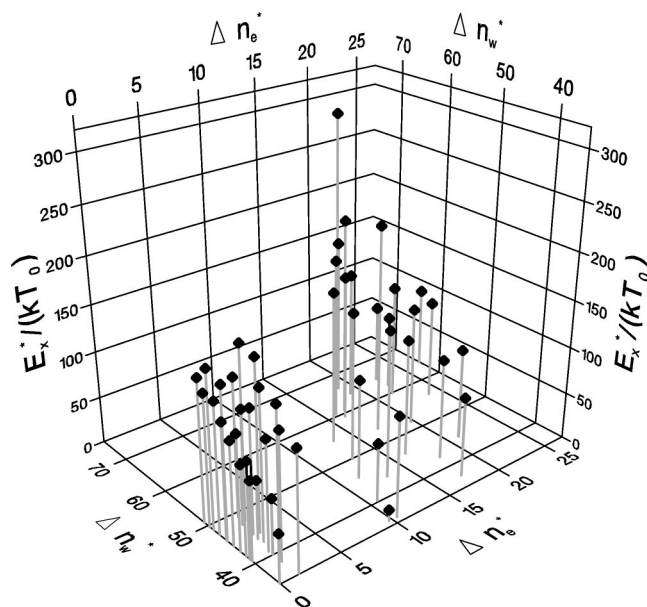


FIG. 6. The experimental excess energy of the critical cluster as a function of the number of ethanol and water molecules in the cluster, for water-rich clusters.

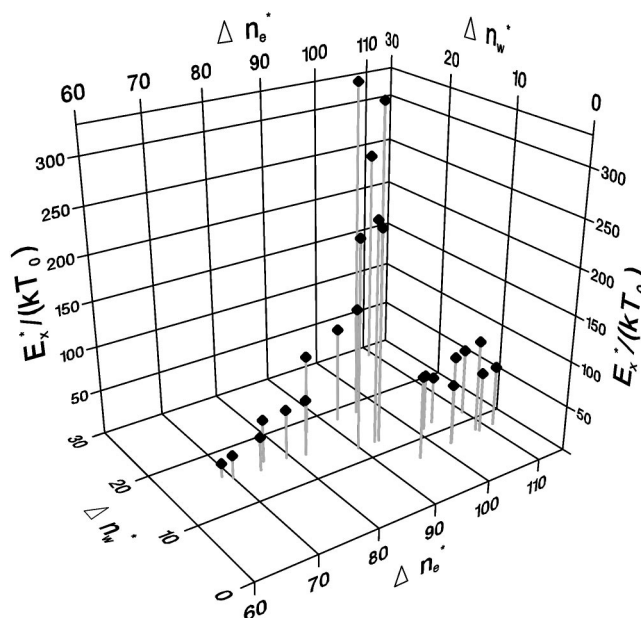


FIG. 7. The experimental excess energy of the critical cluster as a function of the number of ethanol and water molecules in the cluster, for ethanol-rich clusters.

dence. The contribution of the pre-factor is between $32 kT_0$ and $38 kT_0$ for all the cases, including pure water, and cannot simply be neglected.

The classical excess energy is evaluated using a temperature derivative of $W^*/kT = 4\pi R^{*2}\sigma^*/3$, where R^* is given by the Kelvin equation [Eq. (24)]. The error bars are produced as was done for the excess numbers. Vertical error bars are related to the classical values and are quite significant, since the excess energy as a derivative of the free energy is very sensitive to changes in the composition and temperature dependence of the activities. Horizontal error bars with end bars refer to experimental values and show that the energies are fairly insensitive to the specific form of the fitting function. It should be noted, that the experimental and classical energies compared in this Figure are not related to clusters of the same size: The experimental energy on the x axis corresponds to certain conditions (S_w, S_e, T), and the classical energy is the excess energy of a cluster that is considered critical in these conditions according to the classical theory. We found that the error in classical predictions consists of two factors: The critical size is in error, and so is the energy of a given size. It is seen that most often classical theory overestimates the excess energy of a critical cluster.

Figures 6 and 7 show the excess energy of the critical cluster as a function of the number of ethanol and water molecules in the cluster for a number of points derived from the experimental data. The clusters rich in water are shown in Fig. 6 and the ones dominated by ethanol in Fig. 7; it turns out that the data produce two separate groups of points. Data representing different temperatures were found to be consistent with a single surface and thus they are all combined into one picture.

Figures 6 and 7 give an indication of a fairly smooth energy surface describing various molecular compositions of the cluster. The dominating terms in Eq. (29) are the ones

involving latent heats. The surface area derivative produces a small correction, and all the other terms are almost negligible. The latent heats of evaporation for water and ethanol are quite close to each other, and so from Eq. (29) the major contribution of the pre-factor to the second nucleation theorem is fairly independent of the mole fraction of the critical cluster. This diminishes the error caused by the inaccurate prediction of critical cluster mole fraction by the classical theory.

IV. CONCLUSIONS

We have derived a multicomponent version of the second nucleation theorem which allows us to analyze experimental data on the nucleation of droplets from metastable mixtures of vapors. The result of this analysis is information on the binding energies of small clusters consisting of only a few molecules of each species. The theorem is based partly on thermodynamic identities, and partly on an approximate analysis of the growth kinetics of clusters. Together with the multicomponent first nucleation theorem^{16–20} we are then able to produce a plot of energy against molecular content of the cluster. This approach provides valuable and unique insight into the binding characteristics of small molecular clusters. We also present an estimate for the significance of the kinetic factor in the multicomponent nucleation theorems.

We have applied the analysis to data on the nucleation of droplets from a mixture of water and ethanol vapors.²¹ We extract information about clusters which happen to fall into two groups: those consisting mostly of water with a relatively minor component of ethanol, and vice versa. The largest cluster studied contained 143 molecules, 29 of which were water, and the smallest contained 0 ethanol and 35 water molecules. The temperatures of the surrounding vapor ranged from 263 to 293 K, so that the clusters are probably

liquidlike. We find that the contribution of the pre-factor is negligible for the first theorem, but in the case of the second theorem it has to be taken into account. We have compared the cluster energies with the predictions of the capillarity approximation, which imposes macroscopic droplet properties upon small molecular clusters. This model can only be considered a very rough approximation, but it is often used in theoretical studies of droplet nucleation. We have produced plots of energy against cluster content for comparison with our data. We find that the cluster properties extracted from the data differ from the capillarity predictions, though not by orders of magnitude. The critical cluster sizes obtained from experimental data agree well with the results of Viisanen *et al.*¹⁹

The picture of binding energies for various sizes and composition of water-ethanol molecular clusters we have presented is a first glimpse of the energetics of these tiny and ephemeral structures. This information, readily extracted from experimental nucleation rate data, can be used to test models of intermolecular interactions.

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