Energetics of small *n*-pentanol clusters from droplet nucleation rate data

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We use nucleation theorems to extract the excess internal energy of small molecular clusters of
n-pentanol from experimental droplet nucleation rates. Corrections to the theorems are derived, in
order to take into account the nonideality of the vapor phase, but these have only a small effect on
our results. Experimental datasets from different groups provide information about clusters of
different sizes at a range of temperatures. The analysis shows that there are significant and intriguing
deviations from the predictions of the capillarity approximation. © *2000 American Institute of
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I. INTRODUCTION

Identifying short-lived physical states which mediate a transformation between more easily characterized initial and final states is a familiar problem in fields as diverse as chemical reaction kinetics,[1,2] and nuclear and particle physics.[3] In condensed matter physics, the problem arises in the phenomenon of nucleation: the conversion of a metastable phase, such as a supersaturated vapor, into a thermodynamically stable state such as a liquid.[4] The intermediaries in this transformation are small, quasibound, molecular clusters. Theories of the population dynamics of these clusters, together with ideas concerning their general thermodynamic properties, lead us to conclude that the principal intermediate state in a droplet nucleation event is the so-called critical cluster.[8] This is a cluster of a size that is equally likely to grow or decay under the conditions prevailing in the supersaturated vapor. It is the analog of the excited compound nucleus in nuclear physics, or the activated complex, or transition state, in chemical kinetics.

By a careful analysis of the rate of phase transformation, specifically the number of droplets appearing per unit time and per unit volume from a supersaturated vapor, the properties of this critical molecular cluster can be determined. The dependence of the rate of droplet nucleation on vapor pressure yields the size of the cluster, and the dependence on temperature yields its energy. Such studies are analogous to the determination of the order of a reaction, and its activation energy, in chemical kinetics. The analysis of droplet nucleation rates to provide this information has only recently been undertaken;[8,9] the theoretical tools for the analysis are called nucleation theorems,[5–9] and they are quite general results based on the thermodynamics of cluster formation. The main result of the analysis is a plot of the excess internal energy of a critical cluster against its size (number of molecules). The excess internal energy is the difference between the energy of the cluster, and the corresponding energy the component molecules would possess if they were part of a bulk con-

densed phase under the same conditions; it is loosely related to the surface energy. Analysis of various substances has provided information about clusters containing only a few tens of molecules.

In this paper we analyze several experimental datasets for the nucleation of *n*-pentanol droplets. This substance has been the subject of a coordinated research program by a number of experimental groups. In the course of this work, we have examined one of the assumptions made in a recent derivation of the nucleation theorems,[8] namely, that the vapor phase is ideal. The corrections to the theorems are described in the next section. We go on in Sec. III to describe our methods of analysis, and what they tell us about small molecular clusters of *n*-pentanol. We give our conclusions in Sec. IV.

II. CORRECTIONS TO NUCLEATION THEOREMS FOR NONIDEAL VAPORS

Two nucleation theorems have recently been derived,[5–9] which relate the derivatives of the nucleation rate, with respect to supersaturation and temperature, to the size and internal energy, respectively, of the critical cluster. According to a statistical mechanical derivation by Ford[8] the first theorem reads

$$\left(\frac{\partial \ln J}{\partial \ln S'} \right)_T = 1 + i^*, \tag{1}$$

where J is the nucleation rate, T is the temperature, and i^* is the size (number of molecules) of the critical cluster. The monomer supersaturation S' is defined as $S' = \rho_1 / \rho_1^s$, where ρ_1 and $\rho_1^s = \rho_1^s(T)$ are the monomer number concentrations in the supersaturated and saturated vapor, respectively.

Similarly, the second nucleation theorem is given by

$$\left(\frac{\partial \ln J}{\partial T} \right)_{S'} = \frac{1}{kT^2} [L - kT + E_x(i^*)], \tag{2}$$

where L is the latent heat of condensation per molecule, and $E_x(i^*)$ is the excess internal energy of the critical cluster. Terms of the order of ρ/ρ_l and smaller have been neglected

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in deriving this result, where ρ and ρ_l are the molecular densities of the vapor and liquid phase, respectively.

Experimental data are usually presented in terms of the vapor supersaturation, defined as $S = P/P_s$, where P and $P_s = P_s(T)$ are the pressures of the supersaturated and saturated vapor, respectively. Only for an ideal gas does S' reduce exactly to S. In order to analyze nucleation rate data to extract the critical cluster properties, we therefore need to convert the theorems to a form involving S rather than S'. For the first theorem we write

$$\left(\frac{\partial \ln J}{\partial \ln S'}\right)_T = \left(\frac{\partial \ln J}{\partial \ln S}\right)_T \frac{S'}{S}\left(\frac{\partial S}{\partial S'}\right)_T = \left(\frac{\partial \ln J}{\partial \ln S}\right)_T \frac{\rho_l}{P}\left(\frac{\partial P}{\partial \rho_l}\right)_T. \tag{3}$$

We need to know something about the cluster size distribution to be able to evaluate the last derivative on the right-hand side. For this purpose we use the following truncated virial equation of state,

$$P = kT\rho(1 + B\rho), \tag{4}$$

where $B = B(T)$ is the second virial coefficient, which depends on temperature only. The number of dimers in the vapor can be related to the second virial coefficient, assuming that the deviations from ideal behavior arise from the presence of dimers in addition to the dominant monomers in the vapor. In a more general case larger clusters also contribute, but we neglect this. The molecular density can then be written as $\rho = \rho_1 + 2\rho_2$ and the pressure as $P/(kT) = \rho_1 + \rho_2$, leading to $B = -\rho_2/\rho^2$ and $\rho_1 = \rho + 2B\rho^2$, where ρ_2 is the number concentration of dimers.

Using the virial approximation we then obtain from Eq. (3), the following form for the first theorem:

$$\left(\frac{\partial \ln J}{\partial \ln S}\right)_T = (1 + i^*)(1 + B\rho + \mathcal{O}(B\rho)^2). \tag{5}$$

To reformulate the second nucleation theorem, we start from the identity

$$\left(\frac{\partial \ln J}{\partial T}\right)_{S'} = \left(\frac{\partial \ln J}{\partial T}\right)_S + \left(\frac{\partial \ln J}{\partial \ln S}\right)_T \left(\frac{\partial \ln S}{\partial T}\right)_{S'}, \tag{6}$$

and use the relations between ρ, B, and ρ_1 presented above Eq. (5), to express $S = P/P_s$ in terms of $S' = \rho_1/\rho_1^s$,

$$S = \frac{4B\rho_1^s S' - 1 + \sqrt{1 + 8B\rho_1^s S'}}{4B\rho_1^s - 1 + \sqrt{1 + 8B\rho_1^s}}, \tag{7}$$

which can be simplified using Taylor expansions, to give

$$S = \frac{S'(1 - B\rho_1^s S') + \mathcal{O}(B\rho)^2}{(1 - B\rho_1^s) + \mathcal{O}(B\rho)^2}$$

$$= S'(1 - (S' - 1)B\rho_1^s) + \mathcal{O}(B\rho)^2. \tag{8}$$

Now we can evaluate the last derivative on the right-hand side of Eq. (6) and use the first nucleation theorem, Eq. (5), for $(\partial \ln J/\partial \ln S)_T$ to get the following form for the second nucleation theorem:

$$\left(\frac{\partial \ln J}{\partial T}\right)_S = \frac{1}{kT^2}[L - kT + E_x(i^*)] + (i^* + 1)\left(\frac{\rho}{\rho(P_s)} - 1\right)$$

$$\times \left(\frac{\partial B}{\partial T}\rho(P_s) + \frac{BL}{kT^2\Delta v} - \frac{BP_s}{kT^2} + \mathcal{O}(B\rho)^2\right). \tag{9}$$

The Clausius–Clapeyron equation $dP_s/dT = L/(T\Delta v)$ has been used to express the derivative of the vapor pressure in terms of the molecular latent heat L and the difference in the molecular volumes $\Delta v = 1/\rho(P_s) - 1/\rho_l$. $\rho(P_s)$ is the molecular density of the saturated vapor.

Corrections made by using Eqs. (5) and (9), instead of the versions based on an ideal vapor, would be meaningless if the experimental data were not in fact provided in terms of the pressure ratio supersaturation S. We mention this since sometimes it is the vapor mass density ρ that is measured; this is compared with a density at saturation ρ_s to express the vapor supersaturation. If this were the case, another pair of nucleation theorems would be needed, and their derivation would follow a similar procedure to that detailed above.

III. ANALYSIS OF EXPERIMENTAL DATA

A. Fitting the data for *n*-pentanol

The two nucleation theorems allow us to calculate the size and excess energy of a critical cluster if we know the dependence of the nucleation rate on temperature and supersaturation. The most effective way to obtain this dependence from the experimental data is to fit a function $J(S,T)$ to the data. Then the derivatives $(\partial \ln J/\partial \ln S)_T$ and $(\partial \ln J/\partial T)_S$ can be used, in conjunction with the nucleation theorems, to produce expressions for i^*, the number of molecules in the critical cluster, and E_x^*, its excess energy; a relation between i^* and E_x^* follows from these expressions. In our analysis we use the original forms of the nucleation theorems, ignoring the nonideal gas corrections; this will be justified later. We write E_x^* as shorthand for $E_x(i^*)$, the excess energy evaluated at size i^*.

We chose to fit the data on *n*-pentanol with a function of the form,

$$\ln J = a - \frac{b(c/T - 1)^3}{(\ln S)^2}, \tag{10}$$

where a, b, and c are fitting parameters. This fitting function was motivated by the work of Hale, who found that a phenomenological expression which took a form similar to this was surprisingly effective in correlating nucleation rates for a variety of substances.[10,11] We use it since it permits a better fit to the experimental data than other functions that we tried; in fact, given the scatter in the available data, a fitting function which is definitively better than this one seems unlikely to be identified.

Three sets of experimental data on the nucleation of *n*-pentanol were used. The data of Ždímal and Smolík[12] and Rudek *et al.*[13] (which we regard as one set) were obtained using thermal diffusion cloud chambers, the data of Hrubý *et al.*[14] were collected using an expansion cloud chamber, and the data of Luijten *et al.*[15] were gathered using the pulse

TABLE I. Values of the fitting parameters a, b and c for the three datasets.

Reference	a	b	c (K)
Hrubý et al.	68.5	101	591
Ždímal and Smolík, Rudek et al.	54.4	16.1	830
Luijten et al.	76.5	394	485

expansion method. Collectively the sets of data cover a range of temperatures from 240 K to 320 K, supersaturations from 3.3 to 27, and resultant nucleation rates (in $m^{-3}\,s^{-1}$) from 10^2 to 10^{17}. Table I shows the values of a, b and c for the three sets of data. Figure 1 demonstrates that Eq. (10), with the parameters as in Table I, provides a good fit to the data; the limitations of the fitting function are revealed by the fact that the fit is not perfect.

B. The energetics of critical clusters in *n*-pentanol

By finding the derivatives of Eq. (10) with respect to $\ln S$ and T and applying the two nucleation theorems, one can derive the following expressions for E_x^* and i^* in terms of S and T:

$$i^* = \frac{2b(c/T-1)^3}{(\ln S)^3} - 1, \tag{11}$$

$$E_x^* = \frac{3bck(c/T-1)^2}{(\ln S)^2} - L + kT. \tag{12}$$

We use these expressions to find a relation between i^* and E_x^*. Since both of these quantities are functions of S and T, there will not be a unique relation between them; we can write

$$E_x^* = f(S,T,\gamma)(1+i^*)^\gamma - L + kT, \tag{13}$$

and the relation between the critical cluster size and excess energy will depend on γ, which can take any value. However, since the excess energy is analogous to the surface

FIG. 2. The excess energy as a function of critical cluster size. Solid lines, calculations from the experimental data, each valid within the range of (S, T) values covered by its respective dataset. Dashed lines, predictions of classical nucleation theory.

energy of a macroscopic system, we expect $E_x^* \propto i^{*2/3}$ in the limit of a large critical cluster. Therefore we set $\gamma = 2/3$, which yields the expression

$$E_x^* = \frac{3b^{1/3}ck}{2^{2/3}}(1+i^*)^{2/3} - L + kT. \tag{14}$$

The latent heat of condensation per molecule, L, can be calculated using the Clausius–Clapeyron equation, together with an empirical expression for the saturation vapor pressure P_s as a function of temperature. For *n*-pentanol, we use[16]

$$P_s = 133.324 \exp(90.08 - 9788/T - 9.90\ln T), \tag{15}$$

where the pressure is expressed in Pa and the temperature T in K; therefore the latent heat is given by

$$L = 9788k - 9.90kT. \tag{16}$$

Figure 2 shows the curves of E_x^* as a function of i^* (in units of kT_0, where $T_0 = 273.15$ K) which were produced from each of the three sets of data. It should be noted that these $E_x^*(i^*)$ curves are not very sensitive to small changes in the fitting function.

A comparison is also made with the results of classical nucleation theory, for which we use the following formula for the nucleation rate, based on the original classical rate modified[8] by a factor of ρ_l/ρ,

$$\ln J_{cl} = \ln\left(\sqrt{\frac{2\sigma}{\pi m}}\frac{SP_s}{kT}\right) - \frac{16\pi}{3}\frac{\sigma^3}{\rho_l^2(kT)^3(\ln S)^2}, \tag{17}$$

where σ is the surface tension (in N m^{-1}) and m the mass of a molecule. Combining this with the two nucleation theorems and the Clausius–Clapeyron equation, we find
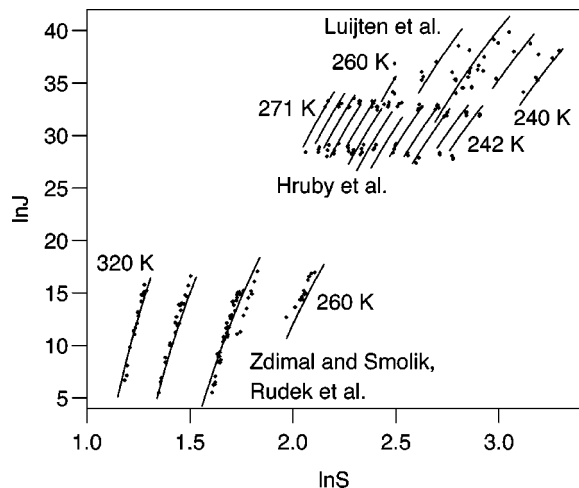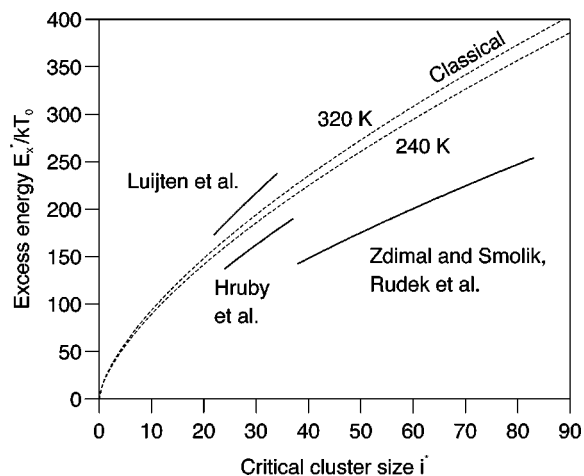

FIG. 1. Comparison of experimental data and the functions fitted to them. Dots, experimental data. Lines, predictions of the fitting functions for $\ln J$ along isothermal lines corresponding to the experimental data.
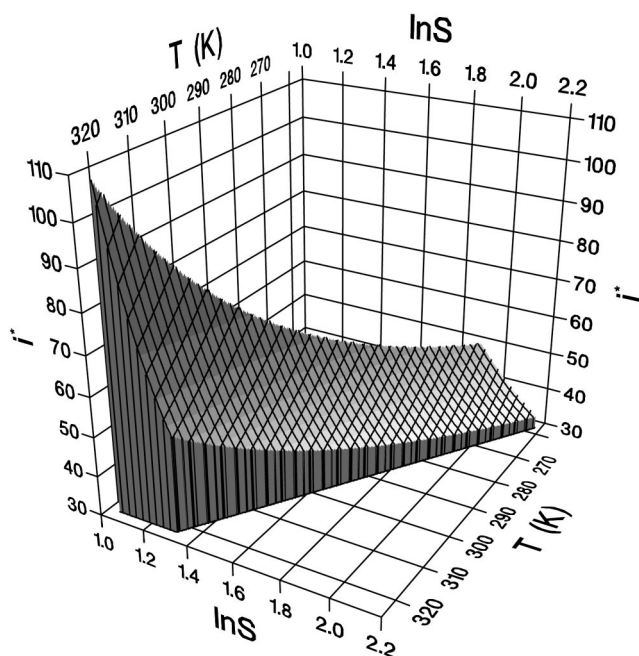
FIG. 3. The critical cluster size as a function of temperature and supersaturation, calculated from the data of Ždímal and Smolík and Rudek *et al.* and valid within the *(S,T)* range covered by those data.

$$E^*_{\text{xcl}} = kT^2 \left(\frac{1}{2\sigma} \frac{d\sigma}{dT} - \frac{(36\pi)^{1/3}}{3} \left(\frac{3}{\sigma} \frac{d\sigma}{dT} - \frac{2}{\rho_l} \frac{d\rho_l}{dT} - \frac{3}{T} \right) \right.$$

$$\left. \times \frac{\sigma}{kT\rho_l^{2/3}} i^{*2/3} \right), \tag{18}$$

where E^*_{xcl} represents the classical excess energy evaluated at the classical critical size i^*_{cl}. For the temperature dependence of σ and of the liquid molecular density ρ_l, we use the following correlations,[13]

$$\sigma = 10^{-3}[26.85469 - 0.07889(T - 273.15)], \tag{19}$$

$$\rho_l = 10^3 N_A (3.06 + 21.90Z^{1/3} - 95.46Z^{2/3} + 218.1Z$$

$$- 210.5Z^{4/3} + 74.37Z^{5/3}), \tag{20}$$

where N_A is Avogadro's number and $Z = 1 - T/T_c$; the critical temperature T_c is taken to be 588.15 K.

Figures 3 and 4 show the critical cluster size and the excess energy, respectively, as a function of S and T, calculated from the data of Ždímal and Smolík[12] and Rudek *et al.*[13] and covering the region of the (S,T) plane investigated by them. Similar plots could be produced for the other sets of data.

It is notable that Eq. (10), unlike an arbitrary function $J(S,T)$, leads to a situation where, if we set γ equal to 2/3 on the physical grounds mentioned above, the first and most significant term in Eq. (13) does not depend on the supersaturation or temperature other than through i^*; that is, $f(S,T,2/3)$ is actually independent of S and T. This means that, if the less significant $-L + kT$ term is disregarded, there is a one to one correspondence between the number of molecules in a critical cluster and its excess energy. A given i^* will always be associated with the same E^*_x, irrespective of
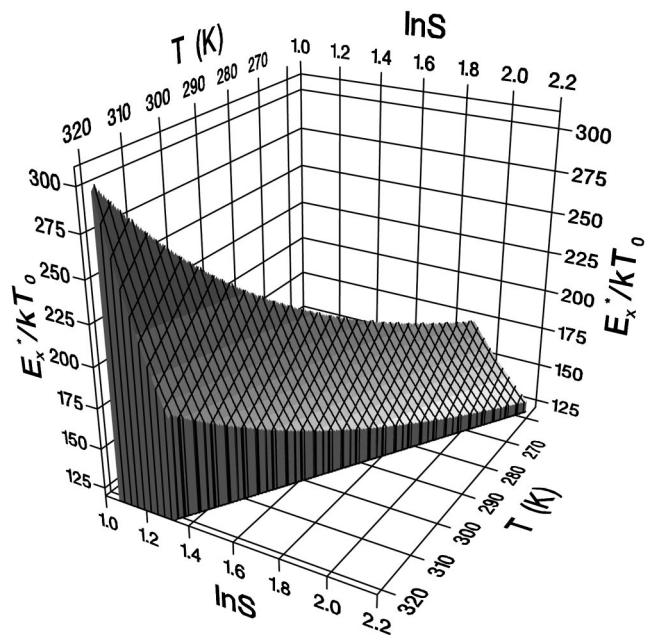

FIG. 4. The excess energy of the critical cluster as a function of temperature and supersaturation, calculated from the data of Ždímal and Smolík and Rudek *et al.* and valid within the *(S,T)* range covered by those data.

the values of S and T which produced it. If γ were set to a different value, this would still be true, but the point would be obscured by the appearance of explicit T- and S-dependence in E^*_x. (It is useful to bear in mind that we are seeking information on the excess energy $E_x(T,S,i)$ for a general cluster size i, given data on $E^*_x = E_x(T,S,i^*(T,S))$ for a T- and S-dependent critical size $i^*(T,S)$. The value of γ determines how much of the T- and S-dependence is explicitly present in the expression for E^*_x, and how much is locked up in i^*.)

The fact that the Hale function can be made to fit the experimental data shows that, over the small region of the (S,T) plane which is covered by a single set of experimental measurements, this one to one correspondence between i^* and E^*_x is approximately correct. From a physical point of view, too, we would expect this to be the case, since the excess energy is closely related to the number of dangling bonds on the surface of a cluster. This depends on the number of molecules in the cluster, but not strongly on the temperature or pressure (provided the cluster is compact, which it is at temperatures well below the critical temperature).

In general, however, the correspondence does not hold. This is demonstrated by the inconsistency between the three different $E^*_x(i^*)$ curves in Fig. 2, which use sets of data from different regions of the (S,T) plane.

These excess energy curves, then, should be regarded as approximations which are valid on restricted regions of the (S,T) plane. Without such an approximation, it would be hard to produce a graph such as Fig. 2. Introducing the approximation enables us to gain insight into the energetics of the critical cluster.

C. Correction terms in the nucleation theorems

In order to evaluate the importance for this work of the nonideal terms in the nucleation theorems, we need B, the

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second virial coefficient of *n*-pentanol. Since data for this do not appear to be available in the literature, we use instead the second virial coefficient of *n*-butanol. We follow a correlation for B as a function of temperature which was introduced by Tsonopoulos,[17,18] based on an earlier one by Pitzer and Curl.[19] This gives

$$B = \frac{kT_c}{P_c}(f^{(0)}(T_r) + \omega f^{(1)}(T_r) + f^{(2)}(T_r)), \tag{21}$$

where T_c is the critical temperature (563 K for *n*-butanol), $P_c = 4.423 \times 10^6$ Pa is the critical pressure, $T_r = T/T_c$, $\omega = 0.590$ is an acentric factor, and

$$f^{(0)}(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8}, \tag{22}$$

$$f^{(1)}(T_r) = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8}, \tag{23}$$

$$f^{(2)}(T_r) = \frac{0.0878}{T_r^6} - \frac{0.0408}{T_r^8}. \tag{24}$$

We have reservations about the use of this correlation here, since it is based on experimental data in the range 380–440 K, while we wish to apply it in the range 240–320 K. This extrapolation is hard to justify, and it should be noted that it leads to B values around 240 K which are more than an order of magnitude larger than those recommended at 380 K. However, since the literature does not contain data quantifying the nonideality even of *n*-butanol in the desired temperature range, extrapolating the Tsonopoulos correlation is currently the best way of proceeding.

The nonideal gas correction term to the first nucleation theorem is not significant for this work, since $B\rho \ll 1$. For example, at $T = 273.15$ K and $\ln S = 2$, we find $B \approx -2 \times 10^{-26}$ m³ and $\rho \approx 10^{23}$ m⁻³, so $B\rho \approx -2 \times 10^{-3}$. The second nucleation theorem can be written as

$$\left(\frac{\partial \ln J}{\partial T}\right)_S = D_{id} + D_{corr}, \tag{25}$$

where $D_{id} = (L - kT + E_x^*)/kT^2$ is the ideal gas term and D_{corr} is the correction term which, if we introduce the approximation $\Delta v \approx 1/\rho(P_s)$ and also the ideal gas approximation $\rho \approx P/kT$, and substitute Eq. (11) for i^*, becomes

$$D_{corr} = \frac{2b(c/T-1)^3}{(\ln S)^3}(S-1)\frac{P_s}{kT^2}\left(B\left(\frac{L}{kT} - 1\right) + T\frac{\partial B}{\partial T}\right). \tag{26}$$

In order to quantify the importance of the correction term, we consider the ratio $R_{corr} = D_{corr}/(D_{id} + D_{corr})$. Using Eq. (10), we write

$$D_{id} + D_{corr} = \frac{3bc(c/T-1)^2}{(T\ln S)^2}. \tag{27}$$

Therefore, the ratio is
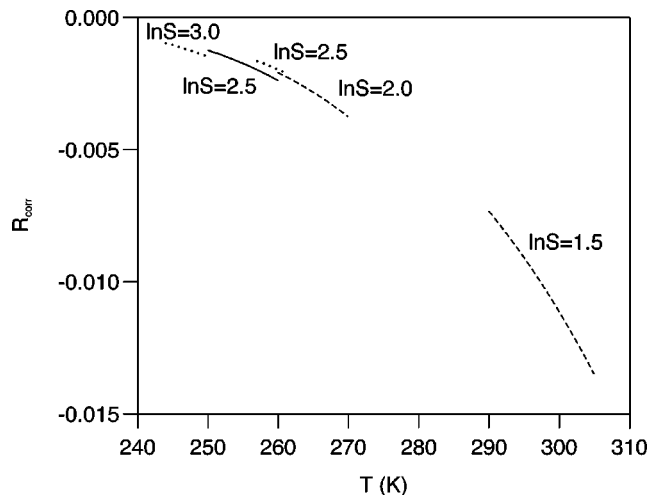

FIG. 5. The ratio $R_{corr} = D_{corr}/(D_{id} + D_{corr})$, quantifying the importance of the correction term in the second nucleation theorem. Solid line, Ref. 14; dashed lines, Refs. 12,13; dotted lines, Ref. 15.

$$R_{corr} = \frac{2(c/T-1)}{3ck\ln S}(S-1)P_s\left(B\left(\frac{L}{kT} - 1\right) + T\frac{\partial B}{\partial T}\right). \tag{28}$$

Figure 5 shows that R_{corr} is very small for a range of S and T representative of experimental conditions, justifying the neglect of the correction term in this investigation of the energetics of *n*-pentanol. However, it might prove necessary to include the correction term in calculations involving different substances or different (S,T) regimes.

The magnitude of R_{corr} increases with increasing S and T. One might expect the correction term to become less important with increasing temperature, since the magnitude of B decreases and, physically, a vapor becomes more ideal. However, increasing the temperature at constant supersaturation involves increasing the pressure, which leads to less ideal behavior and outweighs the effect of the change in B, with the result that the correction term becomes more significant as the temperature increases.

IV. CONCLUSIONS

Experimental data on the nucleation of droplets from supersaturated vapors can provide us with detailed information about the energies of small molecular clusters. The theoretical tools which allow us to uncover this information are the recently derived nucleation theorems, which are relations between the derivatives of the nucleation rate and properties of the critical cluster. Such an analysis has been made possible by the availability in recent years of high quality experimental data.

In this paper we have extended an earlier derivation of the theorems to account for nonideality of the vapor phase. In practice, the corrections are small, largely due to the low vapor densities used in experimental studies. We estimate that the neglect of nonideality leads to an error in the derived cluster excess energy of less than 2%.

We have analyzed data from a number of experimental studies of the nucleation of droplets of *n*-pentanol. The availability of data on a single substance from different experi-

mental groups provides the opportunity for a detailed investigation of the size dependence of the excess energy, since each dataset can potentially explore critical clusters of different sizes. Indeed, we have been able to estimate the excess energy for clusters with sizes ranging from 22 to 83 molecules.

A convenient three-parameter function, based on the Hale scaling formula, has been fitted to each set of measured nucleation rates. This simplifies the evaluation of the required derivatives, and produces an excess energy curve versus cluster size for each dataset. The excess energy curve derived from the most recent data, those of Ždímal and Smolík[12] and Rudek et al.,[13] lies well below the curve predicted by classical theory, as can be seen in Fig. 2. However, data from Hrubý et al.[14] and Luijten et al.,[15] obtained at lower temperatures, lead to curves rather closer to classical theory.

This is a manifestation of the decrease, as the temperature is increased, of the ratio of the measured nucleation rate to the rate predicted by classical nucleation theory, since $\partial \ln (J/J_{cl})/\partial T = (E_x^* - E_{xcl}^*)/kT^2$, from Eq. (2). This behavior has been commented upon many times, most recently by Rudek et al.[13] The difference between E_x^* and E_{xcl}^* is not due only to the difference between i^* and i_{cl}^*: our analysis suggests that as the temperature increases, the excess energy per molecule of the clusters falls, while classical theory does not predict this behavior. What remains to be done is to identify a physical model which accounts for such a reduction.

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