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Revised parametrization of the Dillmann-Meier theory of homogeneous nucleation

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The Dillmann-Meier theory of homogeneous nucleation in its original form contains an inconsistency which can be removed by taking into account imperfect vapor effects. The predicted nucleation rates of the corrected model are much larger than those of the original model. Agreement between theory and experiment can be restored, however, by a revised parametrization of the model, involving only one free parameter τ. Models suggest a range of possible values for this parameter, with $\tau=0$ yielding good agreement between predictions and data for n-nonane, water, and the lower alcohols. This value is characteristic of a class of nucleation models which includes the classical theory and a self-consistent derivative, modified to incorporate a size-dependent surface tension.

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I. INTRODUCTION

The condensation of liquid droplets from a condensible vapor is a familiar example of a phase transition which is responsible for the formation of clouds and mists in the atmosphere, and which also has practical importance in a number of industrial processes. The phenomenon has attracted much recent interest motivated by the striking discrepancies between measured nucleation rates and various model predictions [1]. These disagreements have been established by increasingly more accurate experimental techniques [2–10] for a wide range of condensation conditions and substances, and there is now a need for a theory to account for the data and to allow reliable extrapolation to different conditions.

Nucleation proceeds by the clustering of vapor molecules, by processes of accretion and disintegration, in a dynamical system which can be treated within statistical mechanics [11]. The important ingredient in this approach is the cluster binding energy as a function of i, the number of molecules in the cluster [12]. The failure of continuum thermodynamics, in the form of the classical theory of nucleation [13,14], to account for the measured nucleation rates, has demonstrated that the clusters taking part in the nucleation process cannot be considered as tiny versions of a bulk liquid droplet. The most satisfactory alternative approach, the evaluation of cluster free energies using numerical simulation based on intermolecular potentials [15], is not practical due to an inadequate knowledge of these potentials, and the correct interpretation of the results is still being developed [16,17]. A possible second-best strategy is to use a prescribed cluster model containing unknown parameters which can be chosen to reproduce known imperfect vapor properties. The structure of the model is uncertain but can be made to contain desirable features. The final predictions are only phenomenological, but are at least based on a sound physical model.

A model proposed by Dillmann and Meier [18,19] (henceforth referred to as the DM model) followed the approach just outlined. When compared with experiment, and adjusted to reproduce the correct critical properties and virial coefficients of the vapor, agreement in prediction of the nucleation rate was excellent for several substances. An inconsistency in the DM theory was, however, recently pointed out by Ford, Laaksonen, and Kulmala [20] and Delale and Meier [21]. Namely, the ideal gas law is used for monomers at one point of the derivation of the DM theory, even though the model is later calibrated against imperfect vapor properties. The removal of this inconsistency by the use of the virial

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equation of state affects the resulting equations. It was, furthermore, shown by Ford, Laaksonen, and Kulmala [20] that the predictions of the corrected theory differ significantly from those of the original DM theory. Delale and Meier [21], one the other hand, were able to restore the agreement with experiment to a large degree by introducing a parameter which describes the dependence of the mean surface area on the number of molecules in a cluster. For a spherical (liquid droplike) cluster its value is $\frac{2}{3}$. The strategy of Delale and Meier was to calculate this parameter at the critical point using the critical exponents as proposed by Fisher [22], and then to add a temperature dependence in the form of a power law. The values of the constants of this functional form were deduced using experimental nucleation rate measurements for various substances.

It is our purpose to show, in this paper, that the agreement between the corrected DM theory and the original DM model can actually be recovered by considerably simpler means than those employed by Delale and Meier [21]. This, however, involves the determination of one of the parameters of the DM theory from theoretical models rather than from experiments.

The corrected DM model is discussed in the next section. Experimental data used in the calculations for various substances are discussed in Sec. III, and predictions using a number of alternative parametrizations are discussed in Sec. IV. Finally, our conclusions are given in Sec. V.

II. THE CORRECTED DM THEORY

We start with an expression for the populations of i clusters [18,19]:

$$n_i=\exp[-K_i\Theta i^{2/3}-\tau\ln i+\ln q_0V+i(\mu_v-\mu_{v,\mathrm{coex}})/k_BT]\ , \tag{1}$$

where $\Theta=\sigma A_1/k_BT$, σ is the surface tension, $A_1i^{2/3}$ the cluster surface area, V the system volume, k_B Boltzmann's constant and T the absolute temperature. The coefficients q_0,τ and the K_i are adjustable parameters. The above equation is often written in terms of a free-energy change ΔG_i given by $n_i=n_1\exp(-\Delta G_i/(k_BT))$. The chemical potential μ_v in Eq. (1) is related to the monomer concentration n_1 according to

$$\mu_v=k_BT\ln n_1+f(T)\ , \tag{2}$$

where $f(T)$ is a function of temperature only. $\mu_{v,\mathrm{coex}}$ is the chemical potential of a vapor in equilibrium over a plane surface of condensate. Using the virial equation of state, the monomer concentration can be expressed as

$$n_1=\frac{pV}{k_BT}\left[1+\frac{Bp}{k_BT}+O(p^2)\right]\ , \tag{3}$$

where B is the second virial coefficient. Hence, the number density ρ is given by

$$\rho=\frac{1}{V}\sum_{i=1}^{\infty}in_i \simeq\frac{1}{V}\sum_{i=1}^{\infty}\exp\left[-K_i\Theta i^{2/3}-(\tau-1)\ln i+\ln(q_0V)+\frac{iB(p-p_s)}{k_BT}\right]\left[\frac{p}{p_s}\right]^i\ , \tag{4}$$

where p_s is the equilibrium vapor pressure. Equation (4) can equivalently be expressed as

$$\frac{p}{\rho}=\frac{p_s\exp(K_1\Theta+Bp_s/k_BT)}{q_0}\times\left[1-\frac{Bp}{k_BT}-\exp\left[K_1\Theta-K_2\Theta 2^{2/3}-(\tau-1)\ln 2-\frac{Bp_s}{k_BT}\right]\frac{p}{p_s}+O\left[\left[\frac{p}{p_s}\right]^2\right]\right]. \tag{5}$$

Comparison with the virial expansion

$$\frac{p}{\rho}=k_BT+Bp+O(p^2)\ , \tag{6}$$

leads to the identification of K_1 and K_2:

$$K_1=-\frac{1}{\Theta}\left[\ln\left[\frac{p_s}{q_0k_BT}\right]+Bp_s/k_BT\right]\ , \tag{7}$$

and

$$K_2=-\frac{1}{\Theta 2^{2/3}}\ln\left[\frac{-Bp_s}{k_BT}\exp(-K_1\Theta+Bp_s/k_BT)2^{\tau}\right]. \tag{8}$$

Equations (7) and (8) are then used to calibrate an expansion of the K_i in powers of $1/r$ (or equivalently, in $i^{-1/3}$), with r the cluster radius:

$$K_i=1+\sum_{j=1}^{\infty}\alpha_j(i^{-1/3})^j\ , \tag{9}$$

with α_j a set of unknown coefficients. The expansion represents a size-dependent surface tension. Since only K_1 and K_2 are known, the development can only proceed by limiting the expansion to two terms with coefficients α_1 and α_2 related to K_1 and K_2. This determines all the K_i, supposing the expansion in Eq. (9) limited to $i=1$ and 2 is sufficiently accurate.

Comparison of the above development with the DM theory shows that there is, besides the small Bp_s/k_BT terms in Eqs. (7) and (8), a factor of two missing from the logarithm in the expression for K_2 in the original DM model. This increases the resulting nucleation rate by reducing the nucleation barrier height, and alters the predictions of the model significantly.

Let us now look at the model parameters q_0, τ, and K_i.

It was shown by Ford *et al.* [20] that if K_i is given by the truncated form of Eq. (9), the model actually becomes independent of q_0 entirely, and the only remaining free parameter is τ. This rather surprising result would change if some other functional form was assumed to hold for K_i. Our intention, however, is not to consider other possibilities, but rather to find out how the variation of τ affects the predictions of the present theory.

Delale and Meier [21], following Dillmann and Meier [18,19], use Eq. (1) at the critical point to obtain values of τ and q_0 from the critical properties of the vapor. For instance, *n*-nonane critical properties yield $\tau=2.19$ and $q_0=1.87\times10^{26}\ \mathrm{m}^{-3}$. There are other ways of completing the parametrization, however, which do not rely on extrapolating the free-energy expression from the critical point to the droplet nucleation conditions, and we shall now explore these. Unfortunately, the parametrization loses its reliance solely on experimentally measurable quantities (such as the critical properties) and becomes model dependent.

III. THERMODYNAMIC DATA

With *n*-nonane, water, methanol, ethanol, propanol, and butanol we use the thermodynamic properties listed by DM [19], with the exception that the surface tension of *n*-nonane is calculated from Ref. [23]:

$$\sigma=24.7316-0.0992362\theta+8.38083\times10^{-5}\theta^2 \qquad (10)$$

in $\mathrm{mN\,m^{-1}}$, where θ is the temperature in degrees centigrade. The revised surface tension leads to a small enhancement of the rates calculated by DM [19].

The surface tensions and vapor pressures of pentanol and hexanol were taken from Schmeling and Strey [25], and the densities were determined by a linear fit to the data of Timmermans [26]. There is no data available for the second virial coefficients for these substances. The expression which DM use for the *n*-alcohols is

$$\frac{Bp_c}{RT_c}=\frac{9}{128}\left[1-\frac{6}{T_r^2}\right]-aT_r\exp(b/T_r)\ , \qquad (11)$$

where T_c and p_c are the critical temperature and pressure, T_r is the reduced temperature, and a and b are experimental constants. To estimate the second virial coefficients of pentanol and hexanol, we plotted the constants a and b of the lower alcohols against the number of carbon atoms in the molecule, and fitted curves through the data points in order to get extrapolated rough values of a and b for pentanol and hexanol. We then plotted the second virial coefficients of all the alcohols at various temperatures, and adjusted the pentanol and hexanol parameters until smooth curves could be drawn through the values of B for the homologous series at temperatures between 250 and 350 K. The resulting expressions are $B_{\mathrm{pent}}=87.9-527.5/T_r^2-8.0\times10^{-5}\ \exp(10.5/T_r)$, $B_{\mathrm{hex}}=88.2-529.2/T_r^2-1.0\times10^{-6}\ \exp(12.6/T_r)$, both in $\mathrm{cm^3/mol}$. The critical temperatures and pressures used were 588.2 K and 39.1 bar for pentanol and 611 K and 40.5 bar for hexanol [27].

The thermodynamic properties used for dibutylphtalate were taken from Okuyama *et al.* [29], except for the critical parameters and the second virial coefficient. The critical temperature and pressure were estimated with the Ambrose method (see [27]) to be 823.5 K and 17.3 bar. The dipole moment of dibutylphthalate (DBP) is 2.4 [28]; an estimation for the second virial coefficient was obtained using the Tsonopoulos method for polar materials:

$$\frac{Bp_c}{RT_c}=f_0(T_r)+\omega f_1(T_r)+f_2(T_r)\ , \qquad (12)$$

where

$$f_0(T_r)=0.1445-0.330/T_r-0.1385/T_r^2-0.0121/T_r^3-0.000607/T_r^8\ , \qquad (13)$$

$$f_1(T_r)=0.0637-0.331/T_r^2-0.423/T_r^3-0.008/T_r^8\ , \qquad (14)$$

and

$$f_2(T_r)=-0.003105/T_r^6\ . \qquad (15)$$

R denotes the gas constant, and the Pitzer factor ω is estimated to be 0.79. The thermodynamic properties used for toluene were taken from Schmitt, Zalabasky, and Adams [35].

IV. RESULTS AND DISCUSSION

Figure 1 illustrates the predicted nucleation rates for water according to a number of possible models, normalized by a set of experimentally measured values [10]. The original (inconsistent) DM model predictions are shown along with their corrected values, with the same parametrization. The remaining four models correspond to parameters q_0 and τ suggested by the theories of Reiss, Katz, and Cohen (RKC I and II) [11], the classical theory [13,14], and a form of the classical theory [24]. (Do not be mislead by the names attached to the predictions in Fig. 1: all models considered here possess a size-dependent surface tension and so are distinct from the

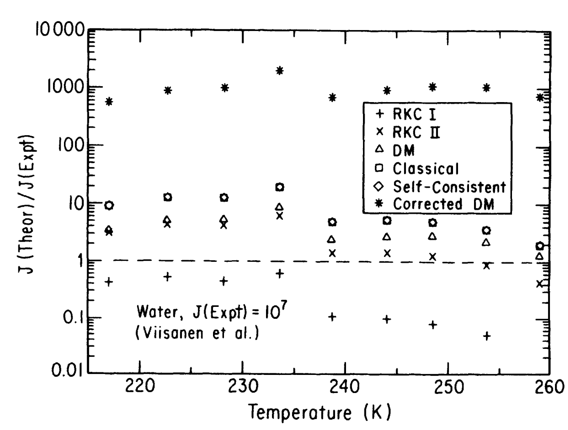

FIG. 1. Predicted nucleation rates for water for a range of temperatures, normalized by experimental data (Ref. 10). Each model corresponds to a different parametrization, described in the text.

TABLE I. Parameters τ and q_0 provided by various models. On the left are analytic expressions, where available: The asterisk denotes a numerical value based on critical properties [18,19]. On the right are example values for *n*-nonane at 219 K and $S=200$. v_0 is the liquid volume per molecule.

	General case		Parameters for *n*-nonane at 219 K and $S=200$	
model	τ	q_0	τ	q_0/m^{-3}
Classical	0	p/k_BT	0	2.7×10^{22}
RKC I	$-\frac{3}{2}$	$(6/\pi)^{3/2}p/k_BT$	$-\frac{3}{2}$	7.1×10^{22}
RKC II	$-\frac{1}{2}$	$(12/\pi)^{3/2}/v_0$	$-\frac{1}{2}$	2.7×10^{28}
Consistent	0	p_s/k_BT	0	1.4×10^{20}
DM	*	*	2.19	1.9×10^{26}

originals.) The "self-consistency corrected" model is a variant of classical theory, in which q_0 is given by p_s/k_BT rather than by p/k_BT. Note, that this ensures that $K_1=0$ (to lowest order in B), which is required in some models which interpret $K_i\Theta i^{2/3}$ as the surface term in a cluster potential energy [12]. It must be stressed that in all the calculations, the K_i depend on i, determined by Eq. (9). RKC I and II and the classical theory normally use $K_i=1$ for all i, so the calculations in Fig. 1 differ from the usual RKC I, II and classical predictions. We take from each model a value of τ and q_0 and these are listed for comparison in Table I, both in analytic form, where available, and numerically for n nonane at 219 K and $S=200$ as an example. The predictions increase with τ, as expected, and furthermore, the classical and consistent model predictions coincide, bearing out the q_0 independence established by Ford, Laaksonen, and Kulmala [20].

A few comments on the physical origin of the various choices of q_0 and τ are perhaps necessary, and since q_0 does not affect the predictions here, we concentrate on τ. Fisher considered the ln$i$ term in the droplet free energy to represent an entropy change corresponding to the phase change. In RKCI I and II, the ln$i$ term appears after a statistical mechanical derivation of the free energy, taking into account both the position and momentum degrees of freedom of the atoms, and the constraints of the cluster definition. The latter affects the value of τ, suggesting that here, too, the term represents entropy, or more exactly, the enumeration of equivalent states. Different approaches to the problem give rise to different values of τ.

It is seen from Fig. 1 that the corrected theory yields nucleation rates close to the experimental rates of Viisanen, Strey, and Reiss [10], when τ is given a value between $-\frac{3}{2}$ and 0. The predictions of the original DM theory are close to those of the "RKC II" model ($\tau=-\frac{1}{2}$) at the lower end of the temperature range, and approach those of the "classical" model at higher temperatures. Based on the information of Fig. 1 we conclude, that the predictive success of the DM theory is recovered to a large extent by setting $\tau=0$ within the framework of the corrected theory. The predictions are, in the case of Fig. 1, even better with $\tau=-\frac{1}{2}$. However, we prefer to set τ to zero, because this simplifies the model somewhat, which is convenient in a phenomenological theory. Besides, the predictions with other substances and at different nucleation rates are not necessarily better with the $\tau=-\frac{1}{2}$ model. This is illustrated in Fig. 2, which shows the predictions of the original DM theory and the $\tau=-\frac{1}{2}$ and $\tau=0$ models for *n*-nonane nucleation rates, normalized by two experimental datasets at $I=1$ $\text{cm}^{-3}\text{s}^{-1}$ and $I=10^4$ $\text{cm}^{-3}\text{s}^{-1}$ [4]. The predictions of

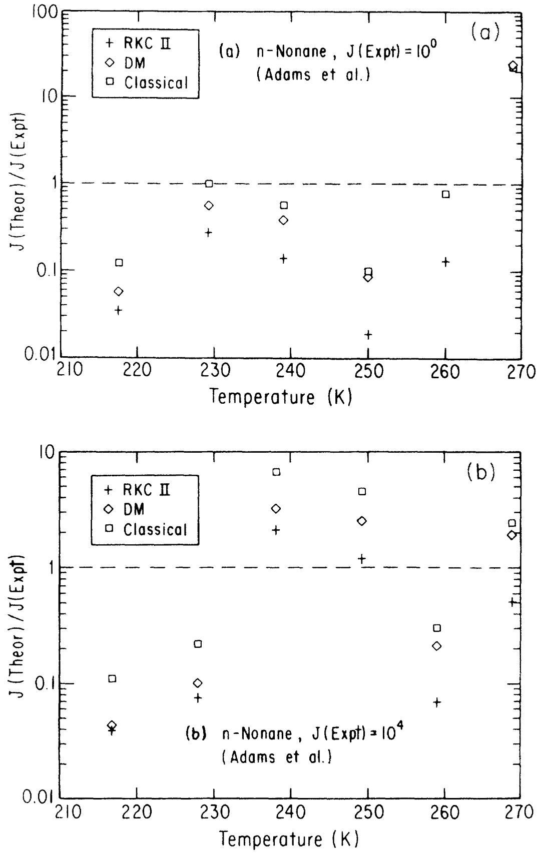

FIG. 2. Predicted nucleation rates for n nonane for a range of temperatures, normalized by experimental data with nucleation rates of 1(a) and 10^4 $\text{cm}^{-3}\,\text{s}^{-1}$ (b) Ref. [4].

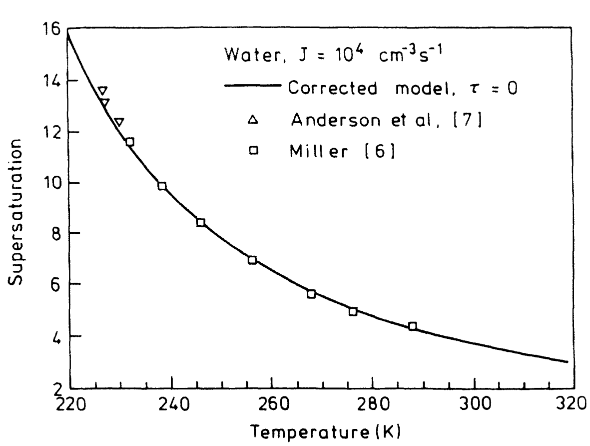

FIG. 3. Comparison of experimental critical supersaturations for water (Refs. [6] and [7]) and the correct theory with $\tau=0$.

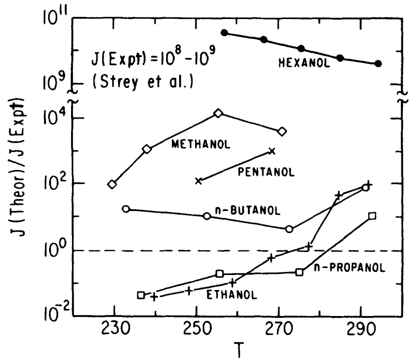

FIG. 4. Predicted nucleation rates for the homologous alcohol series for a range of temperatures, normalized by experimental data (Ref. [5]).

the model with $\tau=0$ turn out to be the closest to the measured rates in most cases. In the remaining calculations we shall use this model only, and refer to it as the revised DM model.

It should be noted that not all of the experimental data of *n*-nonane nucleation is consistent (see, e.g., Kalikmanov and van Dongen [30]), and, thus, the predictions of the original and the revised DM model are in disagreement with the dataset of Wagner and Strey [2] (see Ford, Laaksonen, and Kulmala [20]). Whether or not the revised DM model can really predict nucleation rates of *n* nonane can only be decided in the future, with further experimental data.

Fortunately, there are substances for which the various datasets of measured nucleation rates are consistent. Figure 3 shows the critical supersaturations for water nucleation at a rate of 10^4 cm^{-3} s^{-1} for a range of temperature, together with a curve calculated using the revised DM model. The fit is excellent, lending further support to the use of the classical theory parameters together with the corrected theory. Once again, the predictive success of the revised model is as good as that of the original one (see DM [19]). In fact, we find that the nucleation rate predictions of the revised model are always very close to the predictions of the original model, regardless of the substance or nucleating conditions.

Figure 4 illustrates a set of comparisons between theory and experiment for the homologous *n*-alcohol series at experimental nucleation rates between 10^8 and 10^9 cm^{-3} s^{-1} [5]. It is seen from Fig. 4 that the higher the alcohol, the higher is the ratio between theoretical and experimental nucleation rates, with methanol as an exception. It must be noted that the experimental values for methanol measured by Strey, Wagner, and Schmeling [5] seem to be misplaced in the figures of DM [19] and Delale and Meier [21]—a calculation of *J*(theor)/*J*(expt) using the original DM theory yields results very close to those shown in Fig. 3. However, the experimental data of methanol at nucleation rates close to unity measured with a diffusion chamber [8,9] show much better agreement with theory than the expansion chamber data of Strey, Wagner, and Schmeling [5], as shown by Fig. 5. It is possible that the quality of the diffusion chamber data is better than the quality of the expansion chamber data as far as methanol is concerned, because of the lack of the association heat effects in the diffusion chamber (see, e.g., Ref. [5]).

Another feature that Fig. 4 reveals (if pentanol, with only two datapoints, is left out) is that the slope of the curves diminishes from methanol upwards in the homologous series, becoming negative for hexanol. The overall predictability of the theory is good with ethanol, propanol, and butanol. The fact that the second virial coefficients of pentanol was estimated using data for lower alcohols may lead to the two–three order-of-magnitude disagreement between theory and experiment seen in Fig. 4. With hexanol the disagreement between theory and experiment is about ten orders of magnitude. To remove this discrepancy just by altering *B* would require the use of the second virial coefficient expression of *n* butanol instead of the one estimated for hexanol (the difference between the actual values of *B* calculated using the two expressions is over an order of magnitude at the temperature range considered here). On the other hand, one could regard τ as an adjustable parameter, although this is far less satisfactory, and fit the theoretical rates to the experimental values. However, in that case one would have to use $\tau \approx -10$, a value which is far less than suggested by any model, and besides, the temperature dependence would be wrong.

Figure 6 shows the logarithm of critical supersatura-

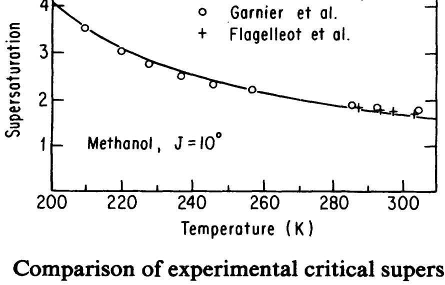

FIG. 5. Comparison of experimental critical supersaturations for methanol (Refs. [8] and [9]) and the corrected theory with $\tau=0$.

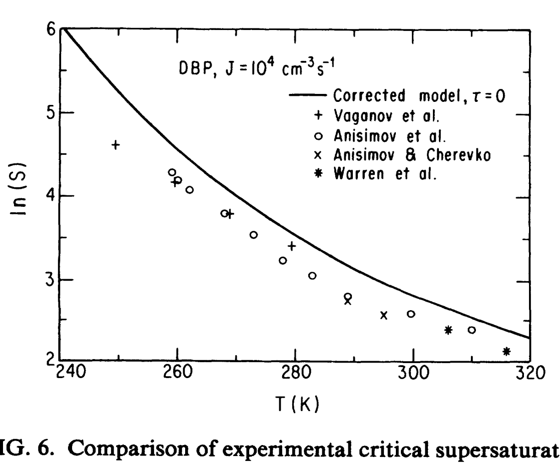

FIG. 6. Comparison of experimental critical supersaturations for DBP (Refs. [31], [32], [33], and [34]) and the corrected theory with $\tau=0$.

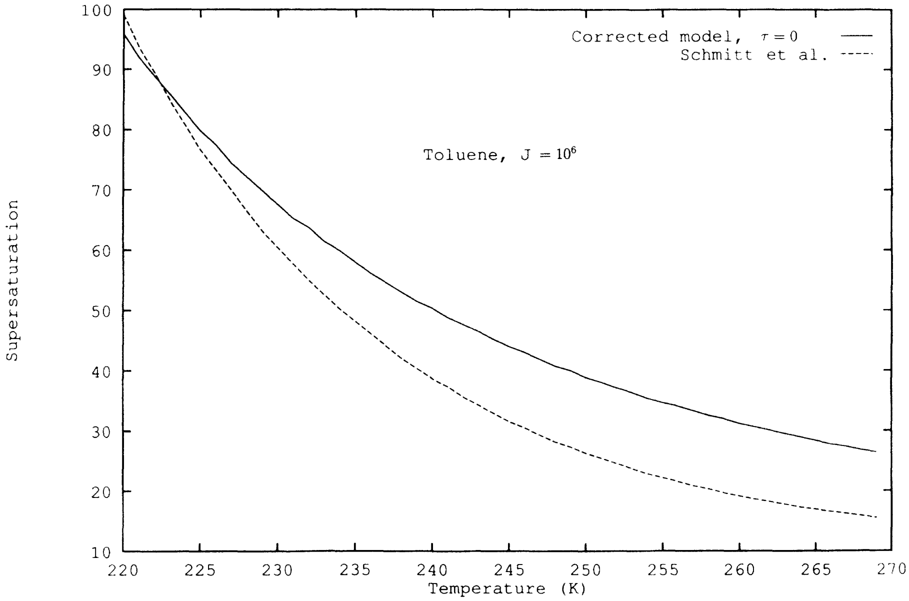

FIG. 7. Comparison of experimental critical supersaturations for toluene, calculated using the empirical nucleation rate expression of Schmitt, Zalabasky, and Adams (Ref. [35]), and the corrected theory with $\tau=0$.

tion against temperature for nucleation of DBP at a constant rate of 10^4 cm^{-3} s^{-1}. The solid line is calculated using the revised theory. The experimental supersaturations are by about a factor of two lower than the theoretical ones, which corresponds to a difference of about six orders of magnitude in nucleation rate. Again, if τ is regarded as a fitting parameter, it would have to be assigned a value of about $+10$ in order to achieve agreement between theory and experiment. The question of the correctness of the theoretical temperature dependence remains somewhat unclear. The theoretical curve would appear to show crossover behavior compared with the individual measurement series of both Vaganov, Kodenev, and Rubakhim [31] and Anisimov, Hämeri, and Kulmala [32]. However, the crossover temperatures of these two series are some 30° C apart.

Figure 7 shows the logarithm of critical supersaturation against temperature for nucleation of toluene at a constant rate of 10^6 cm^{-3} s^{-1}. The solid line is calculated using the revised theory. The dashed line represents experimental supersaturations calculated using an experimental nucleation rate equation given by Schmitt, Zalabasky, and Adams [35]. As with DBP, the curves indicate crossover behavior. However, unlike with DBP, the experimental supersaturations are lower than the theoretical ones at high temperatures, and lower at high temperatures.

One can conclude from these calculations that a successful description of the experimental data of several substances can be obtained using the Dillmann-Meier approach to evaluate the K_i within a free-energy model with $\tau=0$. The free energy, therefore, looks somewhat like the classical theory, or a model based on the self-consistency corrected classical theory which requires the value of K_1 to become zero, but, in fact, the adjustment to the K_i makes the predictions rather different to these other models. Surprisingly, many of the differences between the models disappear when the parametrization using the imperfect properties of the vapor is made.

It appears that the model described above can predict the nucleation rates of water, lower alcohols, and n-nonane (although with methanol and n-nonane this is not quite certain at this point, since different experimental datasets are not consistent with each other). With a large polar molecule (DBP) the model predicts nucleation rates which are much too low at most parts of the experimental range, whereas with hexanol the model predicts nucleation rates several orders of magnitude too high. Wright and El-Shall [36] have found that two strongly polar molecules, acetonitrile and nitromethane, behave in the same manner as we find for hexanol, i.e., they calculated, using the original DM theory, critical supersaturations that were a factor of two lower than the experimental ones. Interestingly, Smolik and Zdimal [37] found crossover behavior resembling that of DBP with bis(2-ethyl-hexyl)sebacate (DEHS), another strongly polar molecule, as the original DM theory predicted the critical supersaturations of DEHS to be too low at high temperatures and vice versa. Finally, we are somewhat surprised to find that our model does not account satisfactorily for the nucleation behavior of toluene, a nonpolar molecule.

Wright and El-Shall [36] associated the unsuccessful predictions of the original DM theory with the polarity of the molecules they studied. While this may well be correct, our calculations with toluene suggest that the theoretical predictability of the DM theory (be it the original or the revised version) can be weak also with some nonpolar molecules. However, we would like to note that one feature of the theory noted by Wright and El-Shall seems to hold true also in our calculations. Consider the factor K_i, which can be interpreted as the size-dependence factor of surface tension for clusters with i molecules. The work of Sinanoglu [38] indicates, that K_i should be greater than unity for polar molecules and less than unity for nonpolar molecules; this is also what DM [19] found with the substances they studied. Wright and El-Shall, on the other hand, found that the K_i^* (the star denoting the critical cluster) of acetonitrile and nitromethane are below unity. Of the polar molecules studied in this work, K_i^* (calculated with $q_0=p/k_BT$) exhibits values above one with water, methanol, ethanol, and *n*-propanol. With *n*-butanol and pentanol K_i^* is slightly below one, and with hexanol it has values close to 0.6 at the critical cluster sizes. With DBP K_i^* exhibits values below one at the lower end of the temperature range studied here, where the experimental and theoretical critical supersaturations are furthest off; at the higher end of the temperature range K_i^* is slightly above one. With the two nonpolar molecules, K_i^* is below one for *n*-nonane. With toluene, K_i^* is below unity at low temperatures and above at high temperatures. It would thus seem that the unsuccessful predictions of the theory with some substances are related to the fact that the K_i calculated for them do not behave as expected from Sinanoglu's work [38]. It would perhaps be worthwhile to investigate why the K_i does behave as expected for some substances and not for others: in the DM theory it is assumed that K_i can be represented as an expression based on K_1 and K_2 only, which can be regarded as a questionable assumption at best.

V. CONCLUSIONS

The phenomenological model of homogeneous nucleation proposed by Dillmann and Meier (DM) [18,19] contains an inconsistency which emerges when the equation of state is calculated by two different routes [20]. The inconsistency can be resolved by including imperfect vapor effects in the model, showing that the route chosen in the original development is incorrect. The corrected nucleation rates are much larger than the old predictions, unfortunately spoiling the agreement with experiment with most of the substances studied. This can be restored, however, by abandoning the parametrization of the model using the critical properties of the vapor. This approach can be called into question, anyway, since it relies on the same expression for the free energy applying at the critical point as well as at nucleation conditions. The two parameters τ and q_0 which were set by this procedure are now set according to models.

However, an examination of the theory reveals that one of these parameters, q_0, is actually irrelevant and cancels out when the correct virial behavior of the vapor is imposed. The remaining parameter is τ, the coefficient of the $\ln i$ term in the model free energy. Various theories suggest values of τ between $-\frac{3}{2}$ and 0: the DM model used a value of about 2.2, based on a model of the free energy at the critical point. More generally, but less satisfactorily, once could consider τ as a fitting parameter not corresponding to any particular theory. However, the comparisons with experimental data for water and lower alcohols given here have suggested that $\tau \approx 0$ provides a good fit to the measured critical supersaturations for *n* nonane, water, and the lower alcohols. This would indicate a free-energy function motivated by classical theory or a derived consistent version of it.

The model has a number of drawbacks which have been ignored in the development. At best, it is phenomenological, since it is based on an assumed free-energy expression with only a limited number of possible terms. The most questionable assumption is the form chosen for K_i, the coefficient of the surface term. The expansion of Eq. (9) limited to only two terms is really only reliable for large i and can merely be regarded as a hypothesis for small i, where it is fitted against known vapor properties. The form chosen for K_i would appear to affect the predictions in an arbitrary way. Nevertheless, the success of the model supports the approximation, and an investigation into why this is so must be left to the future.

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