Modification of the Dillmann–Meier theory of homogeneous nucleation

I. J. Ford
Theoretical Studies Department, AEA Industrial Technology, B424.4, Harwell Laboratory, Didcot, Oxon, OX11 0RA, United Kingdom

A. Laaksonen and M. Kulmala
Department of Physics, University of Helsinki, Siltavuorenpenger 20D, SF-00170 Helsinki, Finland

A model proposed by Dillmann and Meier[1,2] (referred to below as DM) offers a phenomenological description of the homogeneous nucleation of liquid droplets from a condensable vapor. It uses a free energy function containing parameters which are chosen to reproduce known vapor properties such as virial coefficients and the pressure and density at the critical point. When compared with experiment, agreement is excellent for several substances. The purpose of this paper is to point out an inconsistency within the model which can be corrected by a consideration of the imperfect behavior of a real vapor.[3] This, however, leads to a revised model which is less successful.

DM start with an expression for the populations of i-clusters:[1,2]

$$n_i = \exp[-K_i \Theta i^{2/3} - \tau \ln i + \ln q_0 V + i(\mu_v - \mu_{v,\text{coex}})/kT],\tag{1}$$

where $\Theta = \sigma A_1/kT$, σ is the surface tension, $A_1 i^{2/3}$ the cluster surface area, V the system volume, k Boltzmann's constant, T the absolute temperature, and q_0, τ and the K_i are adjustable coefficients. The above equation can be written in terms of a free energy change ΔG_i given by $n_i = n_1 \times \exp[-\Delta G_i/(kT)]$. The chemical potential μ_v in Eq. (1) is related to the monomer concentration n_1: $\mu_v = kT \ln n_1 + f(T)$, where $f(T)$ is a function of temperature only. $\mu_{v,\text{coex}}$ is the chemical potential of a vapor in equilibrium over a plane surface of condensate. DM make the approximation:[1,2] $\mu_v = kT \ln p + h(T)$, where p is the vapor pressure and $h(T) = f(T) + kT \ln(V/kT)$, so that

$$n_i = \exp[-K_i \Theta i^{2/3} - \tau \ln i + \ln q_0 V + i \ln(p/p_s)], \tag{2}$$

where p_s is the equilibrium vapor pressure. The development proceeds by expanding the number density $\rho = (1/V)\Sigma_{i=1}^{\infty} i n_i$, in powers of p. This leads to

$$\frac{p}{\rho} = p_s \Bigg/ \left(\sum_{i=1}^{\infty} \exp[-K_i \Theta i^{2/3} - (\tau-1)\ln i + \ln q_0] \right.$$
$$\left. \times (p/p_s)^{i-1} \right)$$
$$\simeq \frac{p_s \exp(K_1 \Theta)}{q_0} \left\{ 1 - \exp[K_1\Theta - K_2\Theta 2^{2/3} - (\tau-1)\ln 2]\frac{p}{p_s} \right.$$
$$\left. + O\left[\left(\frac{p}{p_s}\right)^2 \right] \right\}. \tag{3}$$

Writing $p/\rho = kT + Bp + O(p^2)$, where B is the second virial coefficient, leads to the identification of K_1 and K_2:

$$K_1 = -\frac{1}{\Theta} \ln \left(\frac{p_s}{q_0 kT} \right) \tag{4}$$

and

$$K_2 = -\frac{1}{\Theta 2^{2/3}} \ln \left(\frac{-Bp_s}{kT} \exp\left(-K_1\Theta\right) 2^{\tau-1} \right). \tag{5}$$

Equations (4) and (5) are then used to calibrate a truncated expansion of the K_i in powers of $1/r$ with r the cluster radius, or equivalently, in $i^{-1/3}$

$$K_i = 1 + \alpha_1 i^{-1/3} + \alpha_2 i^{-2/3}, \tag{6}$$

with $\alpha_{1,2}$ a pair of unknown coefficients. The expansion represents a size dependent surface tension.

However, observe the development based on evaluating the ratio p/ρ directly:

$$\frac{p}{\rho} = \frac{kT \Sigma_{i=1}^{\infty} n_i/V}{\Sigma_{i=1}^{\infty} i n_i/V}$$
$$= kT \left(1 - \exp(K_1\Theta - K_2\Theta 2^{2/3} - \tau \ln 2)\frac{p}{p_s} \right.$$
$$\left. + O[(p/p_s)^2] \right). \tag{7}$$

In comparison with Eq. (3) we see that q_0 has cancelled and the $O(p)$ term is different. Comparing with the virial expansion, it leads to

$$K_2 = -\frac{1}{\Theta 2^{2/3}} \ln \left(\frac{-Bp_s}{kT} \exp(-K_1\Theta) 2^{\tau} \right), \tag{8}$$

which is not the same as Eq. (5). From Eq. (1) at $i = 1$, we have

$$K_1 = -\frac{1}{\Theta} \ln \left(\frac{n_1 p_s}{q_0 p V} \right). \tag{9}$$

The inconsistency arises from the representation of μ_v. If the model is to be calibrated against imperfect vapor properties, then one had better ensure that the model takes into account imperfect behavior in its formulation.[3] As we now show, the inclusion of the correction terms makes an important difference to the original DM derivation of K_2, but only slightly alters the revised development, and this restores consistency. We have

$$\frac{kT}{V}[n_1 + n_2 + O(p^3)], \tag{10}$$

$$\rho = [n_1 + 2n_2 + O(p^3)]/V, \tag{11}$$

which on eliminating n_2 leads to

$$n_1 = \frac{pV}{kT}\left(1 + \frac{Bp}{kT} + O(p^2)\right). \tag{12}$$

Hence,

$$n_i \simeq \exp\left(-K_i\Theta i^{2/3} - \tau \ln i + \ln(q_0 V) + \frac{iB(p - p_s)}{kT}\right)$$

$$\times \left(\frac{p}{p_s}\right)^i \tag{13}$$

is a more accurate expression for the cluster populations than Eq. (2). Calculating p/ρ using Eq. (13) we find that Eq. (8) is altered to the slightly more accurate form:

$$K_2 = -\frac{1}{\Theta 2^{2/3}} \ln\left(\frac{-Bp_s}{kT}\exp(-K_1\Theta + Bp_s/kT)2^\tau\right). \tag{14}$$

However, the original DM development produces the following result:

$$\frac{p}{\rho} = \frac{p_s \exp(K_1\Theta + Bp_s/kT)}{q_0}$$

$$\times \left[1 - \frac{Bp}{kT} - \exp\left(K_1\Theta - K_2\Theta 2^{2/3} - (\tau - 1)\ln 2\right.\right.$$

$$\left.\left. - \frac{Bp_s}{kT}\right)\frac{p}{p_s} + O\left[\left(\frac{p}{p_s}\right)^2\right]\right] \tag{15}$$

which is to be compared with Eq. (3). Using the virial expansion, K_2 is given by Eq. (14) rather than Eq. (5) and so the model is consistent. There is therefore a factor of two missing from the logarithm in the expression for K_2 in Eq. (5) and in the original DM model. Equation (14) gives a smaller K_2 than DM calculated for a given value of B. This increases the resulting nucleation rate by reducing the nucleation barrier height, and alters the predictions of the model significantly.

This is illustrated in Fig. 1, where the predicted nucleation rates for n-nonane are plotted, normalized by experimentally measured values.[4] The original data have been reinterpreted using a more accurate expression for the equilibrium vapor pressure, as suggested by Hung $et~al.$[5] We follow DM and use values of τ and q_0 equal to 2.19 and 1.87×10^{26} m^{-3}, respectively. The nucleation rates J are calculated from the cluster populations n_i in the usual way.[5] Material properties measured by Viisanen and Strey[6] were used. These are the same as used by DM but with a revised surface tension: $\sigma = 24.7316 - 0.099\,236\,2$ $\theta + 8.380\,83 \times 10^{-5}\ \theta^2$ in 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. The original and corrected models both fail, however, to account for the temperature dependence of the experimental nucleation rates for n-nonane.
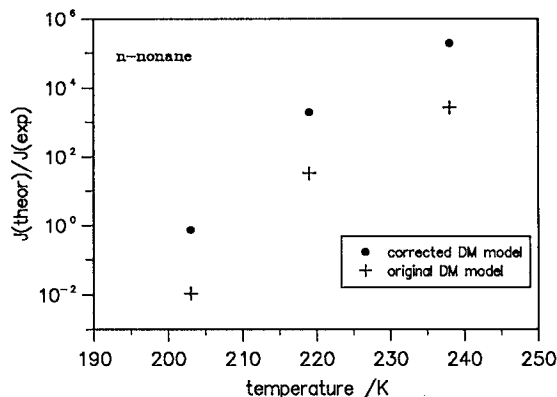

FIG. 1. Predicted nucleation rates for n-nonane for a range of temperatures, geometrically averaged over supersaturation and normalized by experimental data (Ref. 4). Comparison of original and corrected DM model.

Although the inclusion of the additional terms proportional to the second virial coefficient was crucial in resolving the inconsistency in the model, its contribution, in Eqs. (13) and (14) is numerically small, and it is possible to ignore it and use Eqs. (2) and (8) instead. Substituting for K_1 and K_2 we can write, using Eq. (9):

$$\frac{n_i}{n_1} = \exp\left[-\left(i^{2/3} + i^{1/3}\left[\frac{K_2^0 - 1 + 2^{-2/3}}{2^{-1/3} - 2^{-2/3}}\right]\right.\right.$$

$$\left.\left. + \left[\frac{K_2^0 - 1 + 2^{-1/3}}{2^{-2/3} - 2^{-1/3}}\right]\right)\Theta - \tau \ln i + (i - 1)\ln S\right], \tag{16}$$

where K_2^0 is given by

$$K_2^0(\tau) = K_2 - 2^{-2/3}K_1 = -\frac{1}{\Theta 2^{2/3}} \ln\left(\frac{-Bp_s}{kT}2^\tau\right). \tag{17}$$

We conclude that the model is independent of q_0 and that τ is therefore the only free parameter. The τ-dependence can be made explicit by collecting all the terms in Eq. (16). We have

$$n_i \propto \exp\left[\tau\left(\frac{(i^{1/3} - 1)\ln 2}{2^{1/3} - 1} - \ln i\right)\right]. \tag{18}$$

The expression in parentheses is positive for $i > 2$ and so n_i increases as τ increases. The nucleation rate is proportional to n_{i*} where $i*$ is the critical size where the free energy is at a maximum. Increasing τ will also change $i*$ to some extent, but nevertheless, it is expected that the nucleation rate will increase as τ increases.

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