

## LETTERS TO THE EDITOR

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## NOTES

### On the variation of the interfacial tension with cluster size in connection to homogeneous nucleation from the vapor phase

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A few years ago, Dillman and Meier<sup>1,2</sup> presented a theory of homogeneous nucleation from the vapor phase that is based upon an ansatz for the free energy of a spherical nucleating cluster. This free energy reads

$$f = f_{\infty} + \kappa_i \gamma s_1 i^{2/3} + \tau k_B T \ln(i) - k_B T \ln(q_0) \quad (1)$$

with  $f_{\infty}$  the free energy per molecule in the bulk liquid,  $\gamma$  the interfacial tension of a macroscopically flat liquid-vapor interface,  $s_1 i^{2/3}$  the interfacial area of a spherical *i*-mer,  $k_B$  is Boltzmann's constant,  $T$  the absolute temperature, and  $q_0$  and  $\tau$  are parameters that are scaled on critical properties of the system. They find a very good agreement with experimental nucleation rates without adjustable parameters. Equation (1) differs from an expression originally proposed by Fisher<sup>3</sup> by the quantity  $\kappa_i$  which takes into account the size dependence of the interfacial tension.

Later on, the model of Dillman and Meier was criticized<sup>4</sup> because of an inconsistent treatment of vapor properties in the scaling procedure. A consistent treatment in this respect was shown to lead to a much less satisfactory agreement between theory and experiments.<sup>4</sup>

Several papers have recently appeared that are still based upon the free energy ansatz Eq. (1), but with different choices of the parameters. These parameters now follow from a combination of physical arguments and scaling on properties of the (super)saturated vapor.<sup>5-7</sup>

The purpose of this letter is to show that a contribution to  $\tau$  follows from the interfacial free energy.  $\kappa_i$  and  $\tau$  are therefore not independent of each other and certain choices of  $\kappa_i$ , as used in Refs. 1 and 7, even imply a size dependency of  $\tau$ .

Dillman and Meier<sup>1</sup> write the curvature correction factor as

$$\kappa_i = 1 + \alpha_1 i^{-1/3} + \alpha_2 i^{-2/3}, \quad (2)$$

where  $\alpha_1$ ,  $\alpha_2$  are temperature-dependent quantities obtained from the saturated vapor pressure and the second virial coefficient. In order to find a physical interpretation of these quantities, consider a very general expression of the size dependent interfacial tension

$$\sigma(R) = \gamma + \int_0^{2/R} \left( \frac{\partial \sigma(R)}{\partial (2/R)} \right) d(2/R) \quad (3)$$

with  $R$  the equimolar droplet radius. Helfrich<sup>8</sup> introduced the following expression for the free energy associated with the bending of a surface to second order in the principal curvatures  $c_1$  and  $c_2$

$$f_c = \int_A \left[ \frac{K}{2} (c_1 + c_2 - 2c_0)^2 + K_g c_1 c_2 \right] dA, \quad (4)$$

where  $K$  is the bending elastic modulus,  $c_0$  the spontaneous curvature,  $K_g$  the modulus associated with Gaussian curvature, and  $A$  the interfacial area. Combining Eqs. (3) and (4), with  $\sigma = \text{constant} + (\partial f_c / \partial A)$ , leads to a second order expansion of the interfacial tension in the inverse droplet radius

$$\begin{aligned} \sigma(R) &= \gamma + \int_0^{2/R} \left( \frac{\partial^2 f_c}{\partial A \partial (2/R)} \right) d(2/R) \\ &= \gamma - 4Kc_0 \frac{1}{R} + (2K + K_g) \left( \frac{1}{R} \right)^2. \end{aligned} \quad (5)$$

It is interesting to note that comparing Eq. (5) with an expression obtained by Tolman in 1949<sup>9</sup>

$$\sigma(R) = \gamma \left( 1 - \frac{2\delta}{R} \right) \quad (6)$$

gives the so-called Tolman length  $\delta = 2c_0 K / \gamma$ . This relation was also obtained by Blokhuis and Bedeaux<sup>10</sup> using the (generalized) Laplace equation.

From perturbation methods and renormalization group theory it follows that  $K$  and  $K_g$  vary with the length scale  $L$  via<sup>11-16</sup>

$$K(L) = K_0 - \frac{\alpha k_B T}{4\pi} \ln(L/a), \quad (7)$$

$$K_g(L) = K_{g0} + \frac{\alpha_g k_B T}{4\pi} \ln(L/a), \quad (8)$$

where  $a$  is a molecular length and the subscript 0 indicates the bare values (i.e., the values at length  $a$ ). Values of  $\alpha=1$ ,<sup>11</sup>  $\alpha=2$ ,<sup>16</sup>  $\alpha=3$ ,<sup>13,14</sup>  $\alpha_g=10/3$ ,<sup>15</sup> and  $\alpha_g=4$ <sup>14</sup> have been proposed. This size dependence is caused by thermal undulations of the interface. Combining Eqs. (5), (7), and (8) gives, with  $i \propto L^3/a^3$

$$4\pi R^2 \sigma = \kappa_i \gamma s_1 i^{2/3}$$

$$\begin{aligned} &\equiv 4\pi R^2(\gamma - 4K_0c_0/R + (2K_0 + K_{g0})/R^2) \\ &+ \frac{1}{3}((\alpha_g - 2\alpha) + 4\alpha c_0 R)\ln(i). \end{aligned} \quad (9)$$

From this equation it follows that the value of the parameter  $\tau$  in Eq. (1) is (at least) partly determined by the interfacial free energy of the system. Comparing Eq. (2) with Eq. (9) [and Eq. (6)] gives

$$\alpha_1 = -4K_0c_0 \left(\frac{4\pi}{3\bar{v}}\right)^{1/3} \gamma^{-1} = -2\delta \left(\frac{4\pi}{3\bar{v}}\right)^{1/3} \quad (10)$$

and

$$\alpha_2 = (2K_0 + K_{g0}) \left(\frac{4\pi}{3\bar{v}}\right)^{2/3} \gamma^{-1} \quad (11)$$

with  $\bar{v}$  the volume per molecule in the cluster. For Lennard-Jones systems, molecular dynamics simulations<sup>17</sup> and analytical calculations<sup>10</sup> indicate that  $\delta = 2c_0K/\gamma = 0$ . As both  $K$  and  $\gamma$  remain finite, this implies [Eq. (9)] that, in that case,

$$\tau = \frac{1}{3}((\alpha_g - 2\alpha) + 4\alpha c_0 R) \quad (12)$$

is independent of cluster size. If this interfacial contribution was the only contribution to  $\tau$ , we would have  $-(\frac{5}{18}) \leq \tau \leq (\frac{2}{3})$ . However, one may expect other contributions to  $\tau$ , e.g., from internal degrees of freedom<sup>18</sup> ( $\tau = -\frac{3}{2}$ ), and finite size effects<sup>19</sup> ( $\tau = \frac{8}{3}$ ), leading to  $(\frac{5}{18}) \leq \tau \leq (\frac{11}{6})$ . The upper value is close to the values of  $2\frac{5}{36} \leq \tau \leq 2\frac{1}{2}$  obtained by Fisher<sup>3</sup> from Monte Carlo calculations on a 3D Ising model.

Some consequences for existing theories of vapor phase nucleation will now be discussed. First, the finite values of  $\alpha_1$  used by Dillman and Meier<sup>2</sup> and by Laaksonen *et al.*<sup>7</sup> are, in view of the analysis presented here, inconsistent with the constant value of  $\tau$  that they use. This follows from the fact that a finite  $\alpha_1$  implies a finite  $c_0$ , so that, according to Eq. (12),  $\tau$  becomes size dependent. Kalikmanov and van Dongen<sup>5,6</sup> use the argument  $\delta = 0$  to put  $\kappa_i = 1$ . However, the second order term in the expansion of the interfacial tension,

$\alpha_2$ , is expected to be significantly larger than zero as both  $K$  and  $K_g$  are expected to be of order  $k_B T$ .<sup>10</sup> At present, no analytical models of real liquid vapor interfaces exist from which the bending elastic moduli follow. This, together with the uncertainty in the contribution of the interface undulations to  $\tau$  (caused by the uncertainty in the renormalization constants  $\alpha$  and  $\alpha_g$ ) does not make the present analysis particularly useful for setting up a quantitative theory of homogeneous vapor phase nucleation. I hope to have made clear, however, that a straightforward physical interpretation of the expansion parameters of the interfacial tension leads to an additional consistency requirement for the cluster free energy.

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