

# A statistical mechanical approach to heterogeneous nucleation

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The aim of the present work is to construct a model of heterogeneous nucleation based on a statistical mechanical derivation as an alternative to the classical model based on continuum thermodynamics. The result is similar to the classical approach, but the relation to the underlying microscopic physics is clearer. In our approach, we make use of the capillarity approximation using a cluster potential energy that is independent of the position of the molecules in the cluster. The model has a qualitative agreement with the experimental results of Mahata and Alofs for the heterogeneous nucleation of water on different substrates.

## I. INTRODUCTION

Heterogeneous nucleation is a first order phase transition in which molecules nucleate onto surfaces. Heterogeneous nucleation of liquid droplets from the vapor phase has been examined experimentally by many researchers.<sup>1-4</sup> Aerosol particles form the surfaces onto which the condensation can occur.

In addition, many attempts have been made to develop a theoretical model of heterogeneous mechanism in order to explain the experimental results.<sup>5-12</sup> The problem has been approached in two ways: the first approach, which is called the classical model, is based on the work of Volmer,<sup>13</sup> Becker and Döring,<sup>14</sup> Turnbull and Vonnegut.<sup>15</sup> It was developed initially to describe the homogeneous case, where particle surfaces are not involved and nucleation relies on the clustering of vapor molecules. In the classical theory, the cluster is treated within continuum thermodynamics as a macroscopic droplet using a bulk surface tension in order to determine the energy of formation. Recent developments within the framework of this theory<sup>16-19</sup> have been quite successful in explaining the experimental data in the homogeneous case.

An alternative approach has been developed from a microscopic point of view (atomistic models). Many attempts have been made for the case of homogeneous nucleation as presented by Abraham,<sup>20</sup> Reiss, Katz, and Cohen,<sup>21</sup> and Hoare, Pal, and Wegener<sup>22</sup> and more recently with the approaches of Reiss, Tabazadeh, and Talbot,<sup>23</sup> Ellerby, Weakliem, and Reiss,<sup>24</sup> Kobraei and Anderson,<sup>25</sup> Zeng and Oxtoby,<sup>26</sup> and Suck Salk and Lutrus.<sup>27</sup> As well as these, Hale and Kiefer<sup>6</sup> and Plummer and Hale<sup>7</sup> have developed atomistic models for the heterogeneous nucleation process.

Although a microscopic approach to the problem of nucleation is preferable, the atomistic models have not, on the whole, been more successful than the classical theory. The atomistic models include many problems such as the complexity of the model and difficulties in the evaluation of

the required partition functions. Furthermore, the introduction of adjustable parameters arises in many models.

The classical theory has been criticized for its assumption that the physical properties of microscopic clusters are the same as those of the bulk liquid. Despite this criticism, it has been reasonably successful, and remains the standard theory, even though there still exist many cases of disagreement between the theoretical and experimental results in the homogeneous nucleation theory. An alternative approach based on a statistical mechanical derivation using a particular cluster model could help to explain this by giving a more solid foundation to the classical model, and may suggest improvements that could lead to a better agreement with the experimental data. This has been pursued elsewhere for the homogeneous case.<sup>28,29</sup> Here, we apply a similar approach to the case of heterogeneous nucleation.

We evaluate the Gibbs free energy for embryo formation using a statistical approach based on the law of mass action and a particular cluster potential. A description of the statistical treatment in the heterogeneous case is presented in Sec. II. In Sec. III, we compare the predictions of the model with the classical theory and experimental results.

## II. STATISTICAL MODEL FOR HETEROGENEOUS NUCLEATION

The development of our approach in the process of heterogeneous nucleation is based on the models of Hale and Kiefer<sup>6</sup> and Ford.<sup>28</sup> In the present model, we consider an ensemble consisting of  $N_p$  aerosol particles and  $N_v$  condensible vapor molecules in a volume  $V$ . Each realization consists of clusters adhering to the aerosol particles, together with monomers in the vapor phase. Clustering in the vapor phase could also occur in principle, but in negligible concentrations since binding energies are greater for clustering on the particles. The clusters on the particle can range from monomers upwards. There are  $N_i$   $i$  clusters ( $i=1,2,\dots$ ) and  $N_v$  vapor molecules in any one realization.

The partition function of the system can be expressed

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as a sum over partition functions for classifications  $\{N_i, N_v\}$ , as shown below:

$$Z = \sum_{\{N_v, N_i\}} \left[ \frac{Z_v^{N_v}}{N_v!} \prod_i \frac{Z_i^{N_i}}{N_i!} N_p^{N_i} \frac{Z_p^{N_p}}{N_p!} \right]. \quad (1)$$

The  $Z_v$  and  $Z_i$  are the partition functions for a vapor monomer and an  $i$  cluster, respectively, involving the usual integrals over momentum and position variables. However, the cluster definition limits the cluster to lie on the surface of a particle, and so  $Z_i$  is not proportional to  $V$ , but rather to the surface area of a particle. This arises from the integration over the positions available to the center of mass, as we shall see. The positions of the particles are variables in the ensemble, and are accounted for within a particle partition function  $Z_p$  which involves integrals over position and momentum of an aerosol particle.  $Z_v$ ,  $Z_i$ , and  $Z_p$  are each raised to the appropriate powers and divided by factors which make allowance for indistinguishability.  $Z_i$  involves also a contribution to the energy of a cluster because of the adhesion energy between a cluster and the particle.

The  $N_p^{N_i}$  factor in each term in  $Z$  is a numeration of the ways the  $N_i$   $i$  clusters can be disposed amongst  $N_p$  possible host particles. No blocking of one cluster by the presence of another is taken into account.

A good approximation to  $Z$  is found by identifying the maximum term in the series, corresponding to a particular distribution  $N_i, N_v$ . The normal maximization of  $\ln Z$  with respect to  $N_v, N_i$  with  $N_v + \sum_i N_i = \text{const}$  yields

$$N_i = N_p Z_i (N_v / Z_v)^i. \quad (2)$$

In the following calculations, we will evaluate the  $Z_i$ . A statistical model has been developed by Reiss, Tabazadeh, and Talbot<sup>23</sup> for the case of homogeneous nucleation. The partition function  $Z_i$  for a cluster of  $i$  molecules is given by<sup>23</sup>

$$Z_i = \frac{1}{i! h^{3i}} \int_{-\infty}^{\infty} \cdots \int_V \exp \left[ -\beta \left( \frac{p_1^2 + \cdots + p_i^2}{2m_a} \right) + U(\mathbf{r}_1, \dots, \mathbf{r}_i) \right] d\mathbf{r}_1, \dots, d\mathbf{r}_i d\mathbf{p}_1, \dots, d\mathbf{p}_i, \quad (3)$$

where  $\beta = 1/kT$ ,  $m_a$  is the mass of a monomer,  $k$  is Boltzmann's constant,  $T$  is the temperature,  $h$  is Planck's constant,  $i$  is the number of molecules in the cluster,  $V$  is the volume of the vapor-cluster system,  $U$  is the potential energy of the cluster, and  $\mathbf{r}_i$ ,  $\mathbf{p}_i$  are the coordinate position and momentum of the  $i$ th molecule. The integrals over  $i$  are constrained by a cluster definition. The potential energy  $U(\mathbf{r}_1, \dots, \mathbf{r}_i)$  of the embryo generally depends upon the coordinates of position  $\mathbf{r}_1, \dots, \mathbf{r}_i$  of molecules in the cluster.

In our approach, we separate the potential energy  $U$  into a term  $U_c$  which depends only on the cluster center of mass coordinate, and a term  $U_i$  which represents the remaining degrees of freedom. We then take  $U_i$  to be independent of monomer position within the constraining volume. This allows the integrals over position in Eq. (3) to be performed. We use a cluster that has its center at the center of mass of the molecules in the cluster. The fluctu-

ations of the center of mass in the cluster ensemble should be compensated for as noted by Reiss, Katz, and Cohen<sup>21</sup> by introducing a factor  $P(0)$ , equal to the probability density that the cluster center of mass is at the origin. This can be estimated<sup>21</sup> as follows. A single molecule moving at random in a sphere of volume  $v_i$  centered on the origin has a probability distribution for its  $x$  displacement with mean zero and variance  $1/5(3v_i/4\pi)^{2/3}$ . Using the central limit theorem, the  $x$  displacement of the center of mass of the  $i$  cluster therefore is normally distributed with variance  $(1/5i)(3v_i/4\pi)^{2/3}$ . This leads to an expression for  $P(0)$ .<sup>29</sup> Here we use the expression for  $P(0)$  for spherical clusters. The geometry of the cluster in the heterogeneous case is different but the value of  $P(0)$  is likely to be almost the same.

As a result

$$Z_i = \int dV P(0) \lambda_i \exp \left( -\frac{U_c}{kT} \right), \quad (4)$$

where  $\lambda_i$  is the partition function of  $i$  molecules free to move inside a cluster volume equal to  $\gamma v_i \exp(-U_i/kT)$  with  $\gamma = (2\pi mkT/h^2)^{3/2}$ ,  $P(0)$  ensures that the center of mass is fixed relative to the cluster geometry, and then the center of mass is allowed to move over space weighted by a Boltzmann factor involving a potential energy  $U_c$ . We assume that  $U_c$  depends only on distance  $x$  from the surface of the aerosol particle. Then the volume integral in Eq. (4) becomes  $4\pi R_p^2 \int dx \exp[-x^2 \omega^2 M / (2kT)]$ , where  $R_p$  is the aerosol particle radius,  $M$  is the cluster mass, and  $\omega$  is the frequency of oscillation of the cluster in the potential well binding it to the particle, which is supposed to be parabolic. This integral can be evaluated to give  $4\pi R_p^2 (2\pi kT / \omega^2 M)^{1/2}$ .

The equilibrium number of clusters  $N_i$  can therefore be written

$$N_i = N_p \frac{4\pi R_p^2}{V} \left( \frac{2\pi kT}{\omega^2 M} \right)^{1/2} N_v \exp \left( -\frac{\Delta G}{kT} \right), \quad (5)$$

where  $\Delta G$  is the Gibbs free energy of cluster formation, given by

$$\frac{\Delta G}{kT} = \frac{U_i}{kT} - (i-1) \left[ \ln \frac{N_v v_0}{V} \right] + \ln \left[ \frac{i!}{i^{i+1/2}} \frac{3}{5} \left( \frac{\pi}{10} \right)^{1/2} \right]. \quad (6)$$

In analogy to the homogeneous case,<sup>28</sup> the potential energy  $U_i$  in the case of heterogeneous nucleation is chosen to comprise of a surface term, a volume term, and also a term arising from the interaction of the cluster with the particle surface:

$$U_i = b f_1 g_s(i) i^{2/3} - a g_v(i) i + (\sigma_{ls} - \sigma_{vs}) A_{ls}(i), \quad (7)$$

where geometrical function  $f_1 = S_{\text{het}}/S_{\text{hom}}$  is taken from the work of Fletcher.<sup>5</sup> Here,  $S_{\text{het}}$ , and  $S_{\text{hom}}$  are the surface areas of the embryo in the heterogeneous and homogeneous case, respectively. In addition,  $\sigma_{ls}$  and  $A_{ls}(i)$  are the surface tension and surface area between the liquid embryo and the substrate. Use of the capillarity approximation would fix  $b$  using the bulk surface tension [ $b = A(1)\sigma_{lv}$ ],

where  $A(1)i^{2/3}$  is the surface area of a spherical  $i$  cluster.  $\sigma_{vs}$  is the surface tension for the vapor–substrate interface.

The functions  $g_v$  and  $g_s$  are corrections for self-consistency for the case of a single monomer. The functions  $g_v$  and  $g_s$  must equal unity in the limiting case when the number of particles in the cluster approaches infinity, and equal zero for a monomer.<sup>28,29</sup>

In the case of  $N_v = p_{ve}V/kT$ , where  $p_{ve}$  is the saturated vapor pressure, the Gibbs free energy should never reach a maximum for finite  $i$  and consequently  $p_{ve} = kT \exp(-a/kT)/v_0e$ ,<sup>28,29</sup> where  $v_0 = v_i/i$  is the cluster volume per monomer. This equation has the same form as the Clausius–Clapeyron equation, if we provisionally identify  $a$  with the molecular latent heat of condensation. We use it to introduce  $p_{ve}$  into the free energy.

The form taken by the self consistency functions is uncertain.<sup>28,29</sup> We choose the following very simple expressions to illustrate the possibilities:

$$g_s = 1 - i^{-x}, \quad g_v = 1 - i^{-y}, \quad (8)$$

with  $x \geq 2/3$  and  $y \geq 1$ . The equation for the Gibbs free energy now yields:

$$\frac{\Delta G}{kT} = \frac{bf_1}{kT} (i^{2/3} - i^{2/3-x}) - (i-1) \ln S - a(1 - i^{1-y}) + \frac{(\sigma_{ls} - \sigma_{vs})A_{ls}(i)}{kT} + \ln \left( \frac{3\pi}{5^{3/2}e} \right), \quad (9)$$

where  $S$  is the saturation ratio,  $p_v/p_{ve}$  with  $p_v$  the vapor pressure.

If we choose large values of  $x$  and  $y$  we obtain from Eq. (9),<sup>28,29</sup> for reasonably large  $i$ ,

$$\frac{\Delta G}{kT} = \frac{bf_1}{kT} i^{2/3} - (i-1) \ln S - a - \frac{m\sigma_{lv}A_{ls}(i)}{kT} + \ln \left( \frac{3\pi}{5^{3/2}e} \right). \quad (10)$$

In the previous equation, we made use of Young's equation [ $m = (\sigma_{vs} - \sigma_{ls})/\sigma_{lv}$ ], where  $m$  is the cosine of contact angle of the embryo with the substrate.<sup>5,10–12</sup> However, more possibilities exist, not considered further here, based on other values of  $x$  and  $y$ .<sup>28,29</sup>

The free energy now contains terms similar to the corresponding expression in the classical theory which is

$$\frac{\Delta G_{\text{class}}}{kT} = \frac{f_1 A(1) \sigma_{lv} i^{2/3}}{kT} - i \ln S - \frac{m \sigma_{lv} A_{ls}(i)}{kT}. \quad (11)$$

Now,  $N_v/V(2\pi kT/\omega^2 M)^{1/2} = [p_v/(2\pi m_a kT)^{1/2}](1/i^{1/2}v) = \beta(1/i^{1/2}v)$ , where  $v = \omega/2\pi$  is the oscillation frequency of the cluster on the surface and  $M = m_a i$ . Then the nucleation rate  $J$  can be written as

$$J = \beta A^* Z_f N_p A \pi R_p^2 \beta \tau_0 \frac{1}{i^{*1/2}v} \exp \left( - \frac{\Delta G^*}{kT} \right), \quad (12)$$

where  $\beta$  is the impingement rate of vapor molecules onto the surface of an aerosol particle, and  $Z_f$  is the Zeldovich factor.  $A^*$  and  $\Delta G^*$  are the surface area and free energy of

the critical cluster, that is the embryo with the maximum free energy. This expression arises from standard methods.<sup>20</sup>

Now, the cluster oscillation frequency is function of  $i$ . In simplest terms,  $\omega \propto (U_c''/M)^{1/2}$ , where  $U_c$  is the binding potential, and  $U_c \propto i^{2/3}$  is perhaps a reasonable approximation. Also,  $M \propto i$  so  $\omega \propto i^{-1/6}$ . Then

$$J = \beta A^* Z_f N_p A \pi R_p^2 \beta \tau_0 \frac{1}{i^{*2/3}} \exp \left( - \frac{\Delta G^*}{kT} \right), \quad (13)$$

where  $\tau_0$  is the period of oscillation for a monomer on the surface. The time spent by a monomer on the surface  $\tau$  is  $\tau_0 \exp(E_B/kT)$ , where  $E_B$  is the monomer adhesion energy. Finally, the number concentration of adsorbed molecules on the surface of aerosol particles can be written as  $N_{\text{ads}} \approx \beta \tau$ . Consequently, the nucleation rate can be written as

$$J = \beta A^* Z_f N_p A \pi R_p^2 N_{\text{ads}} \exp \left( - \frac{\Delta G^*}{kT} - \frac{E_B}{kT} - \frac{2}{3} \ln(i^*) \right), \quad (14)$$

with  $\Delta G^*$  given by Eq. (10) at the critical size.

The nucleation rate per unit area of aerosol particle in the classical case can be written as<sup>10–12</sup>

$$J = \beta A^* Z_f N_{\text{ads}} \exp(-\Delta G_{\text{class}}^*/kT), \quad (15)$$

with  $\Delta G_{\text{class}}^*$  obtained from Eq. (11) and where  $N_{\text{ads}}$  is the concentration of the adsorbed molecules, which in the classical case is given by  $\beta \tau_0 \exp(E_B/kT)$ , and  $E$  is the heat of adsorption<sup>10–12</sup> and  $R$  is the gas constant. The similarities between Eqs. (14) and (15) are evident. In calculations within the statistical model, however, Eq. (13) is the starting point, so that knowledge of  $E_B$  is not required.

### III. RESULTS AND CONCLUSIONS

In Fig. 1 we compared the results of our model with the experimental data of heterogeneous nucleation of water on different substrates corresponding to different contact angles.<sup>1</sup> Planar surfaces were used in the experiment, but we assume this does not alter the rate per unit surface area.<sup>10</sup>

The experimental results are those of Mahata and Alofs.<sup>1</sup> The nucleation rates lie between 1 and  $10^8 \text{ cm}^{-2} \text{ s}^{-1}$ . The supersaturations required for a nucleation rate of one droplet per  $\text{cm}^2$  of surface, per second, according to both the present model and the classical model, are shown. The two models are very close in their predictions, arising from a degree of cancellation which occurs in the expressions between  $a/kT$  appearing in Eq. (10) and  $-E_B/kT$  in Eq. (14). To this extent, the present statistical model justifies the use of the classical model even though the latter is based on questionable assumptions.

Both models show a disagreement with the experimental results of Mahata and Alofs<sup>1</sup> at large contact angles. The disagreement at large contact angles however can be explained by the mechanisms of surface diffusion and negative line tension<sup>12</sup> which are not considered here.

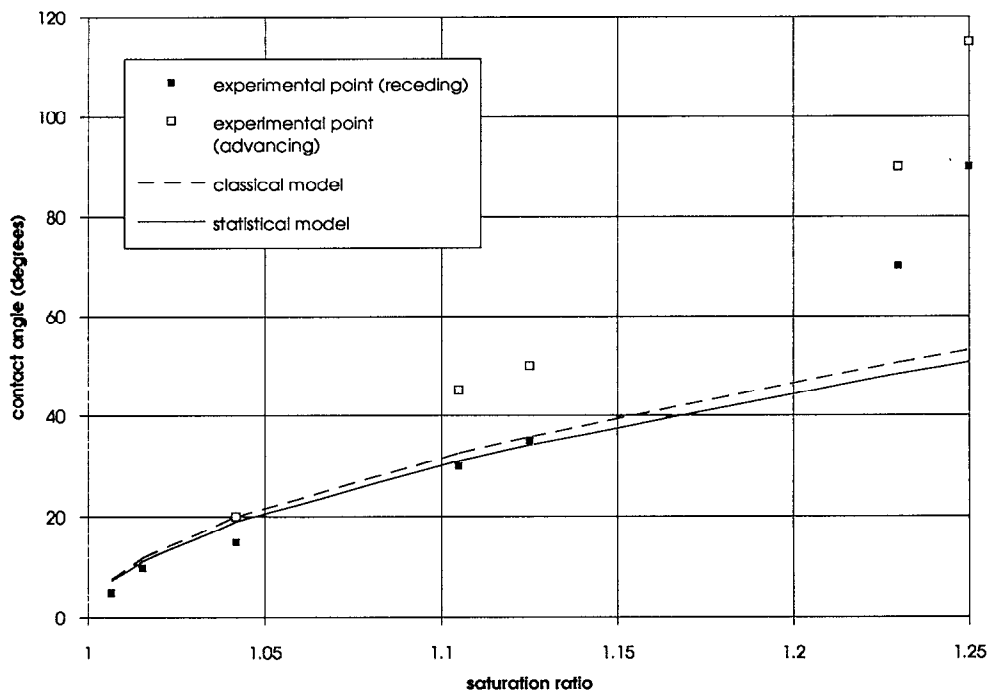


FIG. 1. Critical supersaturation for the onset of water nucleation on a plane substrate as a function of the contact angle. The experimental data were obtained by Mahata and Alofs (Ref. 1).

The main aim of this paper has been to formulate a model of heterogeneous nucleation based on a specific microscopic cluster model, to clarify the use of the usual classical theory in this area. The latter is based on continuum thermodynamic ideas which are not appropriate when dealing with small clusters. The statistical mechanical model, based on a simple cluster potential, leads to a nucleation rate expression which is similar to the classical expression. A number of different expressions might have resulted if alternative models had been used,<sup>29</sup> but the point is that the success had by classical theory can be better understood in the light of the statistical mechanical approach. Furthermore, additional effects can be treated in a realistic manner.

A further development of the theory of heterogeneous nucleation requires on the experimental side more accurate data and not just values of the critical supersaturation for the onset of nucleation, since a small uncertainty in the critical supersaturation can change the nucleation rate by many orders of magnitude. On the theoretical side, further development must take into account a size dependent surface tension,<sup>16,18,19</sup> the mechanisms of surface diffusion, the adsorption characteristics of the aerosol surfaces, and the line tension.<sup>2-4,12</sup>

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