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The role of the attractive potential of a droplet in unary and binary steady state nucleation

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The role of the attractive potential of a droplet in steady state unary and binary nucleation under normal pressures is considered. We determined the nucleation rate by direct numerical solution of the birth and death equations. The correction due to the attractive potential is found to be unessential for three distinct systems considered (pure water, nearly ideal mixture of CCl_4 and SiCl_4 and highly nonideal mixture of H_2O and NH_3). © 1997 American Institute of Physics.
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I. INTRODUCTION

There are several analytical^{1,2} and numerical^{3–6} methods to calculate the steady state nucleation rate in unary and binary systems. All of them are based on solution of birth-death equations. To evaluate the condensation rates, which is the rate at which monomeric vapour molecules hit a cluster, clusters and vapour molecules are considered to be hard spheres without any attractive interaction. The evaporation rate at which monomers escape from a cluster is evaluated using detailed balance in chosen equilibrium.

The purpose of this paper is to check how the nucleation rate in unary and binary systems is affected if droplets' attractive potential is taken into account in calculating condensation coefficients.^{7,8} If the enhancement of nucleation rate would be significant, the considered effect should be taken into account, e.g., in formation of atmospheric aerosols.

To avoid possible effects of the the approximations used in analytical treatments, we evaluate the nucleation rate by solving numerically the birth-death equations and compare results with and without attractive correction to condensation rates.

II. THEORY

The theory is first presented for binary systems. The reduction to unary systems is given in the end of the chapter.

In steady state stage of nucleation the concentrations $c(i,j)$ of small droplets of size (i,j) (i molecules of one substance and j of another) do not depend on time. In the two-dimensional picture the net flow $I_u(i,j)$ from droplet size (i,j) "up" to size $(i,j+1)$, and the net flow $I_r(i,j)$ from size (i,j) "right" to size $(i+1,j)$, equal

$$I_u(i,j) = u(i,j)c(i,j) - d(i,j+1)c(i,j+1); \quad (1)$$

$$I_r(i,j) = r(i,j)c(i,j) - l(i+1,j)c(i+1,j), \quad (2)$$

where d and l are the evaporation coefficients ("down" and "left"), while u and r are the condensation coefficients ("up" and "right"). The standard expression for the condensation coefficients is⁹

$$u(i,j)^{(s)} = \left(\frac{2}{\pi}\right)^{1/6} 3^{2/3} (kT)^{1/2} c_u (v(i,j)^{1/3} + v_u^{1/3})^2 \times \left(\frac{1}{im_r + jm_u} + \frac{1}{m_u}\right)^{1/2}, \quad (3)$$

where c_u , v_u , and m_u are the vapour concentration, volume, and mass of the monomer u , respectively; $v(i,j)$ is the volume of the droplet (i,j) , so $v_u = v(0,1)$. Similarly,

$$r(i,j)^{(s)} = \left(\frac{2}{\pi}\right)^{1/6} 3^{2/3} (kT)^{1/2} c_r (v(i,j)^{1/3} + v_r^{1/3})^2 \times \left(\frac{1}{im_r + jm_u} + \frac{1}{m_r}\right)^{1/2}. \quad (4)$$

However, the attractive potential of the droplet leads to correction

$$u(i,j) = \eta_u(i,j)u^{(s)}(i,j); \quad (5)$$

$$r(i,j) = \eta_r(i,j)r^{(s)}(i,j), \quad (6)$$

where $\eta_u(i,j) > 1$ and $\eta_r(i,j) > 1$.⁷ The factors η_u and η_r have not been taken into account in earlier works, and the coefficients $u(i,j)$ and $r(i,j)$ have commonly considered as the most reliable part of nucleation theories. However, an estimate of the amplification factors $\eta_u(i,j)$ and $\eta_r(i,j)$ is not easy nor reliable (see Appendix), and so it is important to find out how sensitive the nucleation rate is to change of condensation coefficients.

The steady state nucleation rate J is given by the net flow through any boundary in the (i,j) space which surrounds the points $(1,0)$ and $(0,1)$ (the source of all droplets).

The boundary may be chosen to be the two lines connecting points $(i_0, 0)$, (i_0, j_0) , and $(0, j_0)$, (i_0, j_0) , which gives

$$J = \sum_{i=0}^{i_0} I_u(i, j_0) + \sum_{j=0}^{j_0} I_r(i_0, j). \quad (7)$$

To obtain the flows I_u and I_r we need to know the condensation and evaporation coefficients d and l and the concentrations c .

It is assumed, that the evaporation coefficients depend only on temperature and the size of the cluster, but not on the surrounding vapour and cluster distribution. Evaporation coefficients can be obtained from detailed balance,

$$d(i, j) = u^\chi(i, j-1) \frac{c^\chi(i, j-1)}{c^\chi(i, j)}; \quad (8)$$

$$l(i, j) = r^\chi(i-1, j) \frac{c^\chi(i-1, j)}{c^\chi(i, j)}, \quad (9)$$

where $c^\chi(i, j)$ is the concentration of clusters in the equilibrium state, where detailed balance $I_u(i, j) = 0 = I_r(i, j)$ holds for all (i, j) . χ denotes the equilibrium state used to extract the evaporation coefficients, and it may be chosen arbitrarily to be for example the saturated vapour over a bulk liquid with some mole fraction y .

For the equilibrium size distribution $c^\chi(i, j)$ we use the self-consistent form suggested by Wilemski and Wyslouzil¹⁰

$$c^\chi(i, j) = (c_u^\infty)^{1-x} (c_r^\infty)^x \left(\frac{c_r^\chi}{c_r^\infty(x)} \right)^i \left(\frac{c_u^\chi}{c_u^\infty(x)} \right)^j \cdot \exp((1-x)\Theta_u + x\Theta_r - \Theta(i, j)), \quad (10)$$

where c_u^∞ and c_r^∞ are the saturation concentrations over pure substances u and r , respectively, $c_u^\infty(x)$ and $c_r^\infty(x)$ are the saturation concentrations of substances u and r over bulk liquid with mole fraction of r substance $x = i/(i+j)$, and c_u^χ and c_r^χ are concentrations of substances u and r in the reference state χ .

Θ_u , Θ_r , and $\Theta(i, j)$ are given by

$$\Theta_u = \sigma_u s_u(1)/(kT), \quad (11)$$

$$\Theta_r = \sigma_r s_r(1)/(kT), \quad (12)$$

$$\Theta(i, j) = \sigma(i, j) s(i, j)/(kT), \quad (13)$$

where σ_u , $s_u(1)$, σ_r , and $s_r(1)$ are, respectively, the surface tension and monomer surface area of pure substances u and r , $\sigma(i, j)$ and $s(i, j)$ are the surface tension and surface area of the cluster (i, j) .

Distribution $c(i, j)$ satisfies the mass action law, and gives self-consistently c_u^χ and c_r^χ for monomer concentrations.

Using Eqs. (8) and (9) together with Eq. (10) the following expressions for evaporation coefficients are obtained:

$$d(i, j) = \frac{u(i, j-1)}{c_u} c_u^\infty(x) \times \left(\frac{c_r^\infty(x)}{c_r^\infty(x')} \right)^i \left(\frac{c_u^\infty(x)}{c_u^\infty(x')} \right)^{j-1} \left(\frac{c_r^\infty}{c_u^\infty} \right)^{x/(i+j-1)} \cdot \exp \left[\frac{x}{i+j-1} (\Theta_r - \Theta_u) + \Theta(i, j) - \Theta(i, j-1) \right], \quad (14)$$

$$l(i, j) = \frac{r(i-1, j)}{c_r} c_r^\infty(x) \times \left(\frac{c_r^\infty(x)}{c_r^\infty(x'')} \right)^{i-1} \left(\frac{c_u^\infty(x)}{c_u^\infty(x'')} \right)^j \left(\frac{c_u^\infty}{c_r^\infty} \right)^{(1-x)/(i+j-1)} \cdot \exp \left[\frac{1-x}{i+j-1} (\Theta_u - \Theta_r) + \Theta(i, j) - \Theta(i-1, j) \right], \quad (15)$$

where $x' = i/(i+j-1)$ and $x'' = (i-1)/(i+j-1)$. The evaporation coefficients are independent of the reference state χ , as they should be.

The monomer concentrations $c(0, 1) = c_u$ and $c(1, 0) = c_r$ are given; other concentrations can be found by solving the system of the conservation equations

$$0 = I_u(i, j) - I_u(i, j-1) + I_r(i, j) - I_r(i-1, j), \quad (16)$$

where $i \geq 0$, $j \geq 0$ and $i+j > 1$. The flows are given by eqs (1) and (2). To avoid double counting collision of monomers of substance r and u and mixed dimer break up into monomers in $I(1, 1)$ we replace $d(1, 1) \rightarrow \frac{1}{2}d(1, 1)$, $l(1, 1) \rightarrow \frac{1}{2}l(1, 1)$, $u(1, 0) \rightarrow \frac{1}{2}u(1, 0)$, and $r(0, 1) \rightarrow \frac{1}{2}r(0, 1)$.

We must close Eq. (16), for example by defining⁴ $c(i, j) = 0$ at $i > M$ or $j > N$, where M and N are large enough to be beyond the nucleation barrier. Then the system may be written as (see, e.g., Ref. 4)

$$\sum_{\nu=1}^{\Omega} A_{\mu, \nu} x_\nu = y_\mu; \quad \mu = 1, \dots, \Omega, \quad (17)$$

where $\Omega = (M+1)(N+1) - 1$ and

$$y_\mu = \begin{cases} 0 & : \mu \neq 1, N+1 \\ c_u & : \mu = 1 \\ c_r & : \mu = N+1, \end{cases} \quad (18)$$

$$x_\mu = c(\xi(\mu), \gamma(\mu)), \quad (19)$$

and the only nonzero elements of the matrix \mathbf{A} are the following:

$$A_{\mu, \mu} = \tilde{A}_{\xi(\mu), \gamma(\mu)} \quad : \quad \mu \neq 1, N+1, \quad (20)$$

$$\tilde{A}_{i, j} \equiv -u(i, j) - r(i, j) - d(i, j) - l(i, j); \quad (21)$$

$$A_{1, 1} = A_{N+1, N+1} = 1; \quad (22)$$

$$A_{\mu, \mu+1} = d(\xi(\mu), \gamma(\mu) + 1) \quad : \quad \mu \neq 1, N+1 \quad \text{and} \quad \gamma(\mu) < N; \quad (23)$$

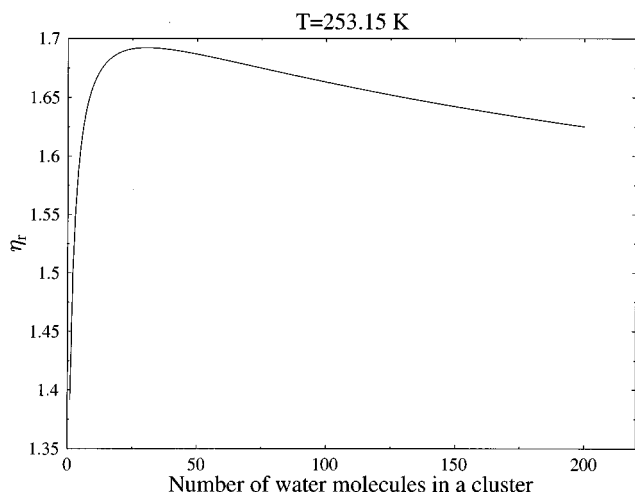


FIG. 1. The amplification factors for different size clusters $\eta_r(i, j)$ in pure water system with temperature 253.15 K.

$$A_{\mu, \mu-1} = u(\xi(\mu), \gamma(\mu) - 1) : \quad \mu \neq 1 \quad \text{and} \quad \gamma(\mu) > 0; \quad (24)$$

$$A_{\mu, \mu-N-1} = r(\xi(\mu) - 1, \gamma(\mu)); \quad (25)$$

$$A_{\mu, \mu+N+1} = l(\xi(\mu) + 1, \gamma(\mu)) : \quad \mu \neq 1, N+1. \quad (26)$$

Here

$$\xi(\mu) \equiv \text{int} \left(\frac{\mu}{N+1} \right), \quad (27)$$

$$\gamma(\mu) \equiv \mu - (N+1)\xi(\mu), \quad (28)$$

and $\text{int}(z)$ is the integer part of z . The coefficients $d(i, 0) = l(0, j) = 0$ (in $\tilde{A}_{i,0}$ and $\tilde{A}_{0,j}$).

When the system is solved and x_ν (i.e., the concentrations $c(i, j)$) are found, the nucleation rate can be calculated using Eq. (7) with $i_0 \leq M$ and $j_0 \leq N$.

The unary case is obtained from the binary one as a special case by setting $N=0$, $j \equiv 0$ and

$$I_u(i, 0) = 0, \quad (29)$$

TABLE I. The nucleation rates J and J_0 calculated with and without amplifications correspondingly. S_r is the supersaturation of water. The temperature is 253.15 K. The critical cluster size i_r^* and the amplification factor η_r^* for the critical size are also shown.

S_r	$J_0 [1/(\text{s} \cdot \text{m}^3)]$	$J [1/(\text{s} \cdot \text{m}^3)]$	J/J_0	i_r^*	η_r^*
5	2.7	4.6	1.67	79	1.67
6	0.75×10^6	0.13×10^6	1.68	57	1.68
7	0.22×10^{10}	0.38×10^{10}	1.69	45	1.69
8	0.59×10^{12}	0.1×10^{13}	1.69	37	1.69

$$u(i, 0) = 0, \quad (30)$$

$$d(i, 0) = 0, \quad (31)$$

for all i .

In solving the system (17) we used the routines *banbks* and *bandec* (with consequent iterations by *mprove*) of the “Numerical Recipes”¹¹ in one program, and the routines *F07BEF* and *F07BHF* of the NAG-library¹² in another. We chose $N=M$ and $j_0=i_0$. In all cases we increased M until the value of nucleation rate was not affected by the change of M . The rate did not change neither with variation of i_0 , unless i_0 is much smaller than M (known numerical artefact^{3,5}). The results of the two programs coincide.

III. PURE WATER

Pure water at 253.15 K is used as an example of unary systems. The liquid density, vapour pressure, and surface tension are given by Kulmala *et al.*¹³ Ideal gas approximation is used to give $c_r^\infty = p_r^\infty / (kT)$. The Lennard-Jones parameters are $D_{rr} = 2.641 \text{ \AA}$ and $\epsilon_{rr} = 809.1 \text{ K}$. The amplification factors are shown in Figure 1. The nucleation rates calculated with and without amplification factors are given in Table I for several supersaturations. Calculations are performed with $M=200$ and checked with $M=300$.

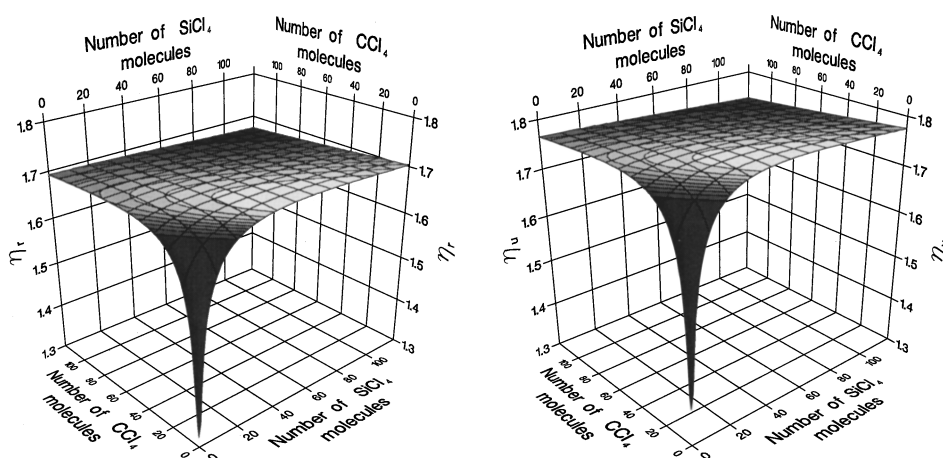


FIG. 2. The amplification factors for different size clusters $\eta_r(i, j)$ and $\eta_u(i, j)$ in $\text{CCl}_4(r)\text{--SiCl}_4(u)$ system with temperature 225 K.

TABLE II. The nucleation rates J and J_0 calculated with and without amplifications correspondingly. S_r and S_u are the supersaturations of CCl_4 and SiCl_4 correspondingly. The temperature is 225 K. The critical cluster sizes (i_r^*, j_u^*) and the amplification factors η_r^* and η_u^* for critical size are also shown.

S_r	S_u	$J_0[1/(\text{s m}^3)]$	$J[1/(\text{s m}^3)]$	J/J_0	(i_r^*, j_u^*)	η_r^*	η_u^*
6	7	0.19×10^{-11}	0.33×10^{-11}	1.74	(42,38)	1.71	1.78
6	9	0.25×10^{-7}	0.45×10^{-7}	1.80	(32,37)	1.71	1.78
7	7	0.12×10^{-8}	0.20×10^{-8}	1.67	(41,32)	1.71	1.78
8	8	0.10×10^{-4}	0.18×10^{-4}	1.80	(36,27)	1.71	1.78
9	9	0.12×10^{-1}	0.21×10^{-1}	1.75	(31,24)	1.71	1.78
10	12	0.17×10^3	0.30×10^3	1.76	(24,22)	1.71	1.78
12	12	0.14×10^5	0.25×10^5	1.79	(24,17)	1.70	1.78
10	13	0.10×10^4	0.18×10^4	1.80	(23,21)	1.70	1.78
13	14	0.13×10^7	0.23×10^7	1.77	(21,17)	1.70	1.78

IV. CARBON TETRACHLORIDE–SILICON TETRACHLORIDE

The carbon tetrachloride–silicon tetrachloride is a characteristic example of a mixture of nonpolar fluids, and is used as an example to study the effect of the droplet's attractive potential for ideal mixtures.

The saturation vapour pressures and surface tension are given by Wimpfheimer *et al.*¹⁴ For the surface tension they give the following approximation:

$$\sigma(x) = \frac{\sigma(1)x + C\sigma(0)(1-x)}{x + C(1-x)}, \quad (32)$$

where x is the molar fraction of the carbon tetrachloride (our r -substance) in the liquid; the factor $C \approx 1.47$. For the saturation vapour pressures over bulk liquid with mole fraction x , $p_r^\infty(x)$ (CCl_4) and $p_u^\infty(x)$ (SiCl_4), of this nearly ideal mixture we take $p_r^\infty(x) = p_r^\infty(1) \cdot x$ and $p_u^\infty(x) = p_u^\infty(0) \cdot (1-x)$. Ideal gas approximation is used to give $c_r^\infty = p_r^\infty/(kT)$ and $c_u^\infty = p_u^\infty/(kT)$.

The Lennard-Jones parameters for carbon tetrachloride are $D_{rr} = 5.947$ Å and $\epsilon_{rr} = 322.7$ K.¹⁵ The parameters are not available for silicon tetrachloride, but it is presumable that they do not differ much. There are data for a similar pair

CF_4 and SiF_4 ($D = 4.662$ Å and 4.88 Å; $\epsilon = 134$ K and 171.9 K, correspondingly¹⁵), and we take the ratios of ϵ_{rr} to ϵ_{uu} and of D_{rr} to D_{uu} to be the same as the ratios for this pair. The amplifications $\eta_r(i, j)$ and $\eta_u(i, j)$ are shown in Fig. 2. The nucleation rates calculated with and without the amplifications are shown in Table II for a set of several pairs of supersaturations (S_r, S_u). Calculations are performed with $M = 120$ and checked with $M = 130$.

V. WATER–AMMONIA

Opposite to the previous mixture, this one is very non-ideal. Saturation vapour pressures over a bulk liquid with mole fraction x are

$$p_r^\infty(x) = p_r^\infty(1) \cdot \Gamma_r(x) \quad (\text{H}_2\text{O})$$

and

$$p_u^\infty(x) = p_u^\infty(0) \cdot \Gamma_u(x) \quad (\text{NH}_3),$$

where $\Gamma_r(x)$ and $\Gamma_u(x)$ are the gas phase activities of components r and u , respectively. We used the activities taken from Vesala *et al.*¹⁶ The liquid densities, vapour pressures of pure substances $p_r^\infty(1)$ and $p_u^\infty(0)$ and surface tension are given by Kulmala *et al.*¹³ Ideal gas law is used also in this case.

The Lennard-Jones parameters are $D_{rr} = 2.641$ Å and $\epsilon_{rr} = 809.1$ K and $D_{uu} = 2.9$ Å and $\epsilon_{uu} = 558.3$ K. The amplification factors are shown in Fig. 3. The calculated nucleation rates are in Table III. We observe the increase in the nucleation rate similar to that in the Table II. Calculations are performed with $M = 120$ and checked with $M = 130$.

VI. CONCLUSIONS

Our calculations for pure water and two binary systems, CCl_4 – SiCl_4 representing an ideal mixture, and H_2O – NH_3 representing a highly non-ideal mixture, have shown that the dispersion forces increase, but not essentially, the nucleation rates in binary steady state nucleation at normal pressures.

In Refs. 7 and 8 the amplified condensation coefficients are estimated to be close to the conventional ones or several

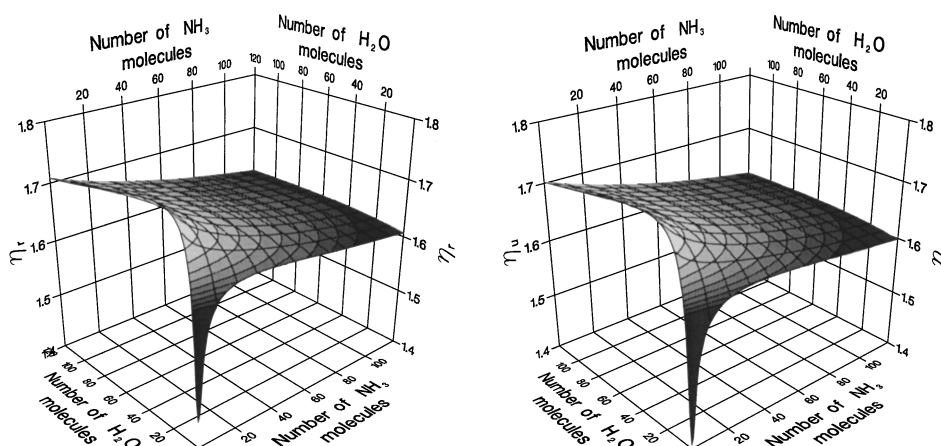


FIG. 3. The amplification factors for different size clusters $\eta_r(i, j)$ and $\eta_u(i, j)$ in $\text{H}_2\text{O}(r)$ – $\text{NH}_3(u)$ system with temperature 213.15 K.

TABLE III. The nucleation rates J and J_0 calculated with and without amplifications correspondingly. S_r and S_u are the supersaturations of water and ammonia correspondingly. The temperature is 213.15 K. The critical cluster sizes (i_r^* , j_u^*) and the amplification factors η_r^* and η_u^* for critical size are also shown.

S_r	S_u	$J_0[1/(s\text{ cm}^3)]$	$J[1/(s\text{ cm}^3)]$	J/J_0	(i_r^*, j_u^*)	η_r^*	η_u^*
2.5	0.31	0.18	0.31	1.72	(36,19)	1.70	1.69
2.5	0.45	0.18×10^3	0.30×10^3	1.67	(32,18)	1.71	1.70
3.0	0.33	0.24×10^3	0.41×10^3	1.71	(32,16)	1.71	1.70
5.0	0.11	0.10×10^4	0.18×10^4	1.80	(31,11)	1.72	1.71
6.0	0.8	0.10×10^{14}	0.18×10^{14}	1.80	(13,8)	1.71	1.69
6.0	1.8	0.11×10^{17}	0.19×10^{17}	1.72	(9,9)	1.69	1.67
7.0	0.14	0.11×10^9	0.19×10^9	1.72	(22,8)	1.73	1.71

fold larger. For the cases studied the amplification factors are in the lower bound of this estimate, having values between 1.3 and 1.8. The enhancement factor of the nucleation rate seems to be near 1.7 in all cases. Thus, although the amplification of condensation rates is applied many times during the growth to the critical size, the amplification factors cancel each other when calculating the nucleation rate, and the factor appears only once in the final result, as noted in Ref. 8. The effect of dense carrier gas, which is also studied in Refs. 7 and 8 and predicted to be remarkable, is not investigated in this paper. In unary systems the enhancement factor coincides with the amplification factor at the critical point (η_r^*), which is the analytical prediction for the enhancement factor. In binary systems it approximately coincides with the combination of amplification factors η_r^* and η_u^* calculated with the formula for average growth rate in Stauffer's analytical treatment,² which is the enhancement factor given by the analytical saddle point approximation.

The enhancement factor is not big enough to change nucleation rate considerably, and there is no need to take it into account in practical applications like formation of atmospheric aerosols.

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APPENDIX

Consider simple intermolecular potentials $-\alpha_{rr}/r^6$, $-\alpha_{uu}/r^6$ and $-\alpha_{ru}/r^6$, corresponding to the interactions between r -monomers, u -monomers and $u-r$. These potentials are replaced by a hard core (infinity) at the distances r equal to $2r_r$, $2r_u$ and r_r+r_u correspondingly, where r_r (r_u) is the radius of r -monomer (u -monomer). The potential $U_u(i,j)$ between u -monomer and the droplet (i,j) may be approximated as⁷

$$U_u(i,j;r) = - \frac{i\alpha_{ru} + j\alpha_{uu}}{\left(r^2 - \left(\frac{3}{4\pi} \right)^{2/3} (iv_r + jv_u)^{2/3} \right)^3}. \quad (\text{A1})$$

Similarly,

$$U_r(i,j;r) = - \frac{i\alpha_{rr} + j\alpha_{ru}}{\left(r^2 - \left(\frac{3}{4\pi} \right)^{2/3} (iv_r + jv_u)^{2/3} \right)^3}. \quad (\text{A2})$$

Having these potentials, we may utilize the approximation⁷

$$\eta_u(i,j) = 1 + \int_1^{+\infty} dy \left(1 - \left(1 + \frac{\mu_u(i,j)}{h(v_u(i,j)y)} \right) \times \exp \left(- \frac{\mu_u(i,j)}{h(v_u(i,j)y)} \right) \right), \quad (\text{A3})$$

where

$$\mu_u(i,j) = 48\pi^2 \frac{i\alpha_{ru} + j\alpha_{uu}}{kT(iv_r + jv_u)^2}; \quad (\text{A4})$$

$$h(z) = 2z^3 - 9z^2 + 108z + 27 + (2z^2 - 12z - 54)\sqrt{z^2 + 3z}; \quad (\text{A5})$$

$$v_u(i,j) = \left(1 + \frac{\frac{ir_r + jr_u}{i+j} + r_u}{\left(\frac{3}{4\pi} (iv_r + jv_u) \right)^{1/3}} \right)^2. \quad (\text{A6})$$

(The variables μ_u and v_u here correspond to μ/ν^3 and ν^{-1} of,⁷ and $(ir_r + jr_u)/(i+j) + r_u$ corresponds to a .) An expression for $\eta_r(i,j)$ is as Eq. (A3), with

$$\mu_r(i,j) = 48\pi^2 \frac{i\alpha_{rr} + j\alpha_{ru}}{kT(iv_r + jv_u)^2}; \quad (\text{A7})$$

$$v_r(i,j) = \left(1 + \frac{\frac{ir_r + jr_u}{i+j} + r_r}{\left(\frac{3}{4\pi} (iv_r + jv_u) \right)^{1/3}} \right)^2. \quad (\text{A8})$$

The attractive part of the Lennard-Jones potential $\Phi_{rr} = 4\epsilon_{rr}((d_{rr}/r)^{12} - (d_{rr}/r)^6)$ is approximated with $-\alpha_{rr}/r^6$, which gives $\alpha_{rr} = 4\epsilon_{rr}d_{rr}^6$, where ϵ_{rr} and d_{rr} are the Lennard-Jones parameters of the $r-r$ potential. Respective equations hold for α_{uu} and α_{ru} . The Lennard-Jones parameters for the last are taken from the Lorentz-Berthelot approximation: $\epsilon_{ru} = \sqrt{\epsilon_{uu}\epsilon_{rr}}$ and $d_{ru} = (d_{uu} + d_{rr})/2$ (see, e.g., Ref. 17). For mixtures in which remarkable surface enrichment occurs, the adsorption should be taken into account in calculating factors $\eta_r(i,j)$ and $\eta_u(i,j)$.¹⁸ For numerous reasons expressions are inaccurate for very small droplets (close to (0,1) and (1,0)).

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