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Dimers in nucleating vapors

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The dimer stage of nucleation may affect considerably the rate of the nucleation process at high supersaturation of the nucleating vapor. Assuming that the dimer formation limits the nucleation rate, the kinetics of the particle formation–growth process is studied starting with the definition of dimers as bound states of two associating molecules. The partition function of dimer states is calculated by summing the Boltzmann factor over all classical bound states, and the equilibrium population of dimers is found for two types of intermolecular forces: the Lennard-Jones (LJ) and rectangular well+hard core (RW) potentials. The principle of detailed balance is used for calculating the evaporation rate of dimers. The kinetics of the particle formation–growth process is then investigated under the assumption that the trimers are stable with respect to evaporation and that the condensation rate is a power function of the particle mass. If the power exponent $\lambda = n/(n+1)$ (n is a non-negative integer), the kinetics of the process is described by a finite set of moments of particle mass distribution. When the characteristic time of the particle formation by nucleation is much shorter than that of the condensational growth, $n+2$ universal functions of a nondimensional time define the kinetic process. These functions are calculated for $\lambda = 2/3$ (gas-to-particle conversion in the free molecular regime) and $\lambda = 1/2$ (formation of islands on surfaces). [S1063-651X(98)06309-0]

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I. INTRODUCTION

Current kinetic approaches to the problem of nucleation of supersaturated vapors assume the particle formation to go along the scheme

$$(g)+(1) \rightleftharpoons (g+1) \tag{1}$$

with the kinetic coefficients (forward $\alpha_g c_1$ and backward β_{g+1} rates) being known functions of g [the number of condensing vapor molecules (monomers) in a g-mer] and the parameters of the carrier gas. The most widespread statement of the problem expresses the steady-state nucleation rate $\mathcal{J}$ in terms of α and β [1]. This part of the problem was solved many times by numerous authors (see the recent overview [2] and references therein). The result is as follows.

The nucleation rate expressed in terms of condensation and evaporation coefficients and the monomer concentration looks as follows:

$$\frac{\mathcal{J}}{\mathcal{J}_2} = \frac{1}{1+x_2+x_2x_3+x_2x_3x_4+\cdots}. \tag{2}$$

Here $\mathcal{J}_2(c_1) = \frac{1}{2}\alpha_1 c_1^2$ is the rate of dimerization [reaction $(1)+(1)\rightarrow(2)$], c_1 is the monomer number concentration, and

$$x_g = \frac{\beta_g}{\alpha_g c_1} = \frac{c_g^*}{c_1} \tag{3}$$

with $c_g^* = \beta_g/\alpha_g$.

There exist other expressions for the nucleation rate that follow from Eq. (2) after some identity transformations.

The second part of the problem—finding the condensation and evaporation rates—has been attacked from the following two positions.

(i) *Ab initio calculations* [3–8]. Starting with the classic or quantum-mechanical equations of motion the rates of reactions $(g)+(1)\rightarrow(g+1)$ (condensation) and $(g)\rightarrow(g-1)+(1)$ (evaporation) have been calculated. This approach requires a solution of the many-body problem (or at least the evaluation of multiple integrals) and the knowledge of intermolecular potentials. Although nowadays respective numerical methods are well developed, this approach is so cumbersome that it requires some approximations, the reliability of which is still not clear. In particular, the problem of how to introduce a g-mer is far from a resolution.

(ii) *A parametrization of the rates α and β* [2,9–11]. For example, the condensation rate is simply replaced by the product of the geometrical cross section times the thermal velocity of vapor molecules. The evaporation rate is expressed in terms of equilibrium distribution of vapor clusters at saturation by using a detailed balance consideration. Next, this distribution is either calculated starting with the statistical mechanics or expressed in terms of physico-chemical constants of bulk liquids (surface tension, bulk density, etc.).

The latter approach, although the most widespread, is essentially restricted when describing the properties of the smallest clusters for which the macroscopic notions such as surface tension or liquid state density do not work. Meanwhile, the initial stages of the nucleation process can either affect appreciably the nucleation rate or even entirely define the latter as, e.g., in the case of small ‘‘magic’’ embryos whose ability to decay is suppressed by their very high binding energies [7]. There are other situations where the initial steps of new phase formation are of primary importance: at very high supersaturations the mass of the critical embryo is small and the formation process is regulated only by the dimer stage [12,13].

This paper addresses the study of the thermodynamic properties of dimers and their role in the particle formation–growth process.

The dimers give us a very good opportunity to perform an explicit analysis, i.e., to calculate exactly all values of interest. Next, assuming that the nucleation process is limited by the rate of dimer formation, it becomes possible to build up almost ''perfect nucleation theory,'' i.e., the theory allowing for a full description of the particle formation–growth process and including only microscopic characteristics of nucleating systems.

The first part of the paper starts with the definition of the dimer. The most natural way to do this is to consider as a dimer the bound states of two particles. But even in this case it is not easy to answer the following question: what does the term ''bound state'' mean? Should we consider as dimers the quasistationary states with positive energies belonging to the continuous spectrum (meaning the states below the centrifugial barrier)? The answer to the latter question is yes, because the probability of underbarrier penetration is typically small and corresponding decay rates are comparable to or lower than that of the direct processes of breaking the dimers by incident carrier gas molecules. Once the dimer has been defined as a bound state of two molecules, it cannot decay into two monomers without an intervention of a third molecule, so its lifetime should depend on the presence of the carrier gas. Neither can it form as a result of a binary collision: a third participant is needed to take the energy excess away (see Fig. 1).

The classical approach and the semiclassical quantization rule are applied for calculating the energy density of bound and quasibound states of two molecules and then the probability for a dimer to exist. After this the equilibrium concentration of dimers is found and the detailed balance consideration yields the dimer evaporation rate.

The second part of the paper analyzes the kinetics of dimer controlled nucleation. Assuming that the particles containing more than two molecules are stable against evaporation ($\beta_{g>2}=0$), the nucleation-growth equations are solved exactly for the condensation efficiencies growing as a power $\lambda=n/(n+1)$ of the particle mass (n is a non-negative integer). In this case the growth equations are reduced to a finite set of $n+2$ ordinary differential equations. When the lifetime of dimers is short as compared to the time scale of the particle formation-growth process (e.g., the characteristic time for changing the monomer concentration), the description of the growth kinetics becomes universal, i.e., it depends on $n+2$ universal functions of specially chosen nondimensional time.

In our analysis we use the following two intermolecular potentials.

(i) The rectangular well potential with hard core (RW dimers),

$$U(r)=\begin{cases}\infty, & r<a\\ -U_0, & a<r<R\\ 0, & r>R.\end{cases} \tag{4}$$

(ii) The Lennard-Jones potential (LJ dimers),

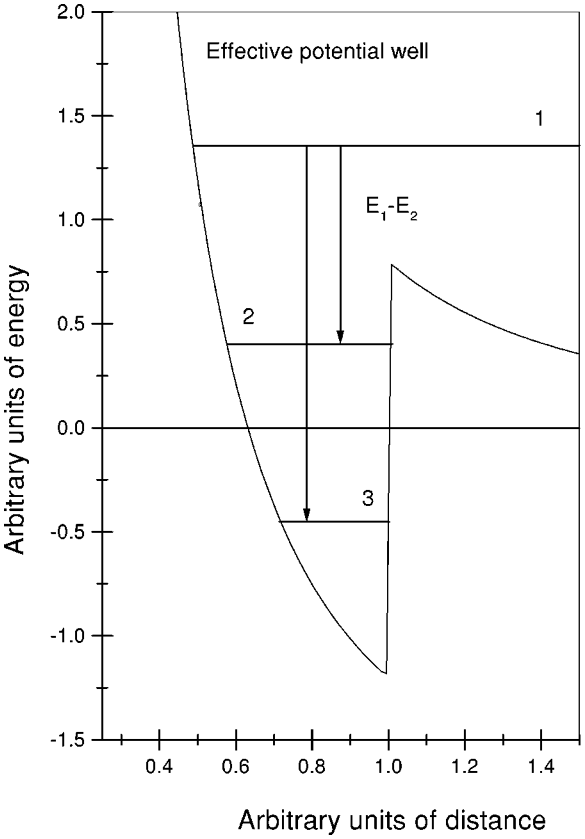

FIG. 1. Formation of a dimer. Two monomers interacting via potential $U(r)$ may form a bound state only after the transition from the state 1 to the states 2 or 3, whose energies lie below the potential barrier. A third participant is needed to take the energy excess E_1-E_2 away. Similarly, a dimer cannot decay without aquiring a portion of energy for jumping up to an unbound state 1 from the states 2 or 3. Not all bound states lie below zero energy. The state 2 is also bound and must be taken into consideration in calculating the thermodynamic properties of dimers.

$$U(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \tag{5}$$

where ϵ is the depth of the energy well and σ is the collision diameter.

II. PARTITION FUNCTION OF DIMERS

The process of spontaneous nucleation in vapors begins with the formation of dimers that, in turn, are able either to grow further or to decay back into two monomers. Even this first stage of the nucleation process is far from being simple. Neither the formation of a dimer nor its decay can happen without a third participant.

Another very important problem is how to introduce the dimer. In this paper we propose to consider as a dimer only the bound states of two molecules. We add to those the ''classical'' bound states with positive energies. Although they belong to the continuous spectrum, their widths are small because of the low penetrability of the corresponding centifugal barrier. It is important to stress that these defined dimers are not able to decay without an external intervention. Their lifetimes are thus of the order of intercollision times

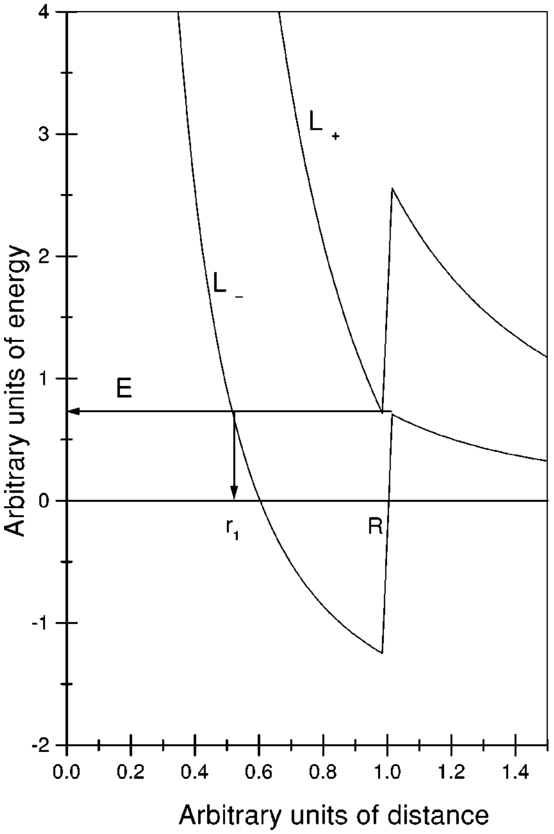

FIG. 2. The limits of integration over L in Eq. (14). The state with the positive energy E is still bound once the maximum of the effective potential $[U(r)+\hbar^2L^2/2\mu r^2]$ touches the energy level (curve $L=L_-$). When L exceeds L_+ no more bound states can exist at given energy E.

l/v, i.e., much longer than the characteristic collision time R/v (l being the mean free path of a molecule, R the dimer size, and v the thermal velocity of molecules). There are quite strong grounds for this way of introducing the dimers: all unbound states have characteristic lifetimes of the order of R/v. This time is of the order of 10^{-11} s, which is typically much shorter (at least by 10^2) than the characteristic intercollision time l/v.

In order to estimate the dimer decay rate, we first find the number of bound states in the equilibrium, which allows for evaluating the equilibrium concentrations of dimers.

Let us consider an equilibrium state of the vapor (+carrier gas) and calculate the equilibrium population of dimers. To this end we find the energy density $\omega(E)$ of bound states of the Hamiltonian describing the relative motion of two molecules in the dimer:

$$H=\frac{p^2}{2\mu}+U(r). \tag{6}$$

Here μ is the reduced mass of two molecules and E is the energy of their relative motion. The partition function of the dimer is then defined as

$$Z_b=\int \omega(E)e^{-\beta E}dE \tag{7}$$

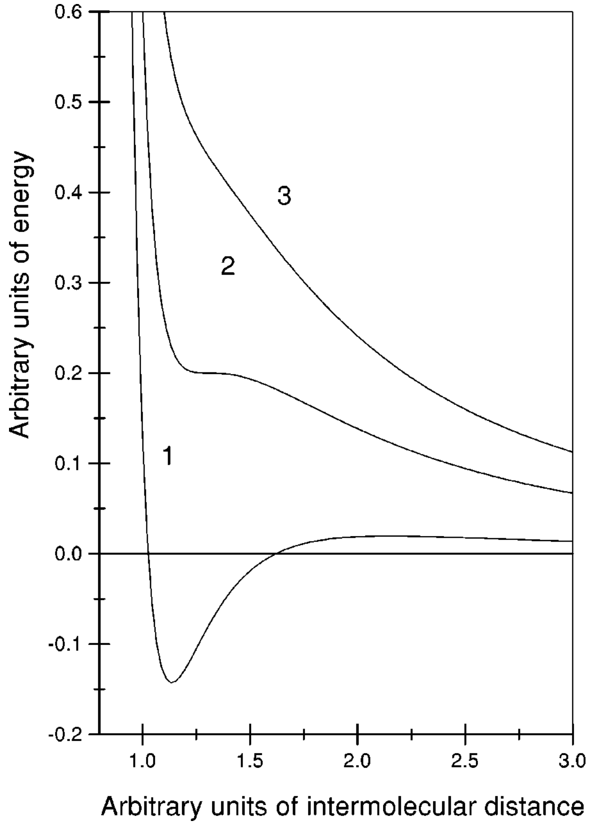

FIG. 3. Bound states in a LJ potential. Bound states with positive energies exist only at $L<L_{\max}$ (curve 1). Above $L=L_{\max}$ defined from the conditions $[U(r)+\hbar^2L^2/2\mu r^2]'=0$ and $[U(r)+\hbar^2L^2/2\mu r^2]''=0$, the effective potential well disappears. Curve 2 corresponds to the critical value $L=L_{\max}$. At $L>L_{\max}$ no bound states exist (curve 3).

($\beta=1/kT$). The probability w_2 to meet a dimer in a normalization volume V is given by the ratio $w_2=Z_b/Z_t$, where

$$Z_t=\frac{1}{(2\pi\hbar)^3}\int d^3p\int_V d^3r\, e^{-\beta H(p,r)}=\frac{V(2\pi\mu kT)^{3/2}}{(2\pi\hbar)^3}. \tag{8}$$

A. Negative energies

The contribution of the states with negative energy is readily found as

$$Z_b(E<0)=\frac{1}{(2\pi\hbar)^3}\int d^3p\, d^3r\, e^{-\beta H(p,r)}\theta(-H(p,r)). \tag{9}$$

Here $\theta(x)$ is the Heaviside step function: $\theta(x)=1$ at $x>0$ and $\theta(x)=0$ otherwise.

Integrating over p in Eq. (9) yields

$$Z_b(E<0)=\frac{2\pi(2\mu kT)^{3/2}}{(2\pi\hbar)^3}\int e^{\beta|U(r)|}q(r)d^3r. \tag{10}$$

Here we introduced

$$q(r)=\gamma(3/2,\beta|U(r)|)\theta(-U(\mathbf{r})), \tag{11}$$

where $\gamma(\alpha,x)=\int_0^x t^{\alpha-1}e^{-t}dt$ is the incomplete gamma function.

It is important to emphasize the convergence of the integral in Eq. (10) at $r\rightarrow\infty$.

The contribution from the bound states with positive energies is considered separately for RW and LJ dimers.

B. Positive energies: RW dimers

For the rectangular potential, Eq. (8) takes an especially simple form:

$$Z_b(E<0)=\frac{2\pi V_0(2\mu kT)^{3/2}}{(2\pi\hbar)^3}e^{\beta U_0}\gamma(3/2,\beta U_0), \qquad (12)$$

where $V_0=4\pi/3(R^3-a^3)$ is the volume of the interaction zone.

The centrifugial barrier in the rectangular potential well also enables the existence of an infinite set of bound states with positive energy.

In order to find $Z_b(E>0)$, we start with the semiclassical Bohr's rule for determining the position of the discrete levels in the potential well:

$$\int_{r_t}^{R}\left(\sqrt{2\mu(E+U_0)-\frac{\hbar^2L^2}{r^2}}\right)dr=\pi n\hbar. \qquad (13)$$

Here r_t is the turning point, $n,L\gg 1$.

We transform the expression for $Z_b(E>0)$ as follows:

$$Z_b(E>0)=\sum e^{-\beta E}=\sum_{n,L}(2L+1)e^{-\beta E}$$

$$=\int dE\, e^{-\beta E}\int dL^2\omega(L,E). \qquad (14)$$

Here the summation goes over all bound states with positive energies. The choice of the limits of integration in Eq. (14) is explained in Fig. 2.

The density of bound states $\omega(L,E)=dn/dE$ with given angular momentum L is defined as

$$\omega(L,E)=\frac{dn}{dE}=\frac{\mu}{\pi\hbar}\int_{r_t}^{R}\frac{dr}{\sqrt{2\mu(E+U_0)-\frac{\hbar^2L^2}{2r^2}}}. \qquad (15)$$

This expression follows immediately after differentiating Eq. (13) with respect to E. The integration is readily performed to give

$$\omega(L,E)=\frac{R}{2\pi\hbar(E+U_0)}\begin{cases}\sqrt{2\mu(E+U_0)-\frac{\hbar^2L^2}{R^2}} & \text{at}\quad \hbar^2L^2>2\mu a^2(E+U_0),\\ \sqrt{2\mu(E+U_0)-\frac{\hbar^2L^2}{R^2}}-\frac{a}{R}\sqrt{2\mu(E+U_0)-\frac{\hbar^2L^2}{a^2}} & \text{at}\quad \hbar^2L^2<2\mu a^2(E+U_0).\end{cases} \qquad (16)$$

The next step is the integration over L^2:

$$\int\omega(L,E)dL^2=\frac{R^3(2\mu U_0)^{3/2}}{3\pi\hbar^3(E+U_0)}\left\{1+\left[1-\frac{E}{U_0}\left(\frac{R^2}{a^2}-1\right)\right]^{3/2}\theta\left[U_0-\left(\frac{R^2}{a^2}-1\right)E\right]\right\}. \qquad (17)$$

The contribution of the bound states with positive energy is thus

$$Z_b(E>0)=\frac{R^3(2\mu U_0)^{3/2}}{3\pi\hbar^3}G(\beta U_0), \qquad (18)$$

where

$$G(x)=\int_0^\infty\frac{e^{-sx}ds}{s+1}+\int_0^1 ds\,\frac{(1-s)^{3/2}\exp[-xs/(k^2-1)]}{s+k^2-1} \qquad (19)$$

and $k=R/a$. The second integral gives the core contribution.

The final result has the form

$$Z_b=\frac{R^3(2\mu U_0)^{3/2}}{3\pi\hbar^3}F_{\rm RW}(T), \qquad (20)$$

where

$$F_{\rm RW}(T)=\left(1-\frac{a^3}{R^3}\right)\left(\frac{kT}{U_0}\right)^{3/2}\gamma\left(\frac{3}{2},\frac{U_0}{kT}\right)\exp\left(\frac{U_0}{kT}\right)+G\left(\frac{U_0}{kT}\right). \qquad (21)$$

C. Positive energies: LJ dimers

In contrast to the rectangular well, there is a restriction on the maximal angular momentum at which the bound states still exist in the LJ potential (see Fig. 3). In increasing L, the minimum of the effective potential $U+\hbar^2L^2/2\mu r^2$ disappears. The conditions for this event to happen are

$$[U(r)+\hbar^2L^2/2\mu r^2]'=0 \quad \text{and} \quad [U(r)+\hbar^2L^2/2\mu r^2]''=0. \tag{22}$$

They are fulfilled at $r=5^{1/6}\sigma$ and $\hbar^2L^2/8\epsilon\mu\sigma^2=9\times 5^{-5/3}$. The maximal possible position of the last discrete level is 0.8ϵ.

In order to calculate the density of bound states with positive energy, we again start with the Bohr quantization rule, which now contains $2\pi n\hbar$ on its right-hand side instead of $\pi n\hbar$ as was in the case of the vertical wall in the rectangular potential well. The density of states is now

$$\omega(L,E)=\frac{\mu}{2\pi\hbar}\int_{r_1}^{r_2}\frac{dr}{\sqrt{2\mu(E-U)-\dfrac{\hbar^2L^2}{r^2}}}. \tag{23}$$

The total contribution of bound states at $E>0$ to Z_b is

$$Z_b(E>0)=\frac{\mu}{2\pi\hbar}\int_0^{0.8\epsilon}dE\,e^{-\beta E}\int_{r_1(E)}^{r_2(E)}dr \times\int_{L_-}^{L(r)}\frac{2L\,dL}{\sqrt{2\mu(E-U)-\dfrac{\hbar^2L^2}{r^2}}}. \tag{24}$$

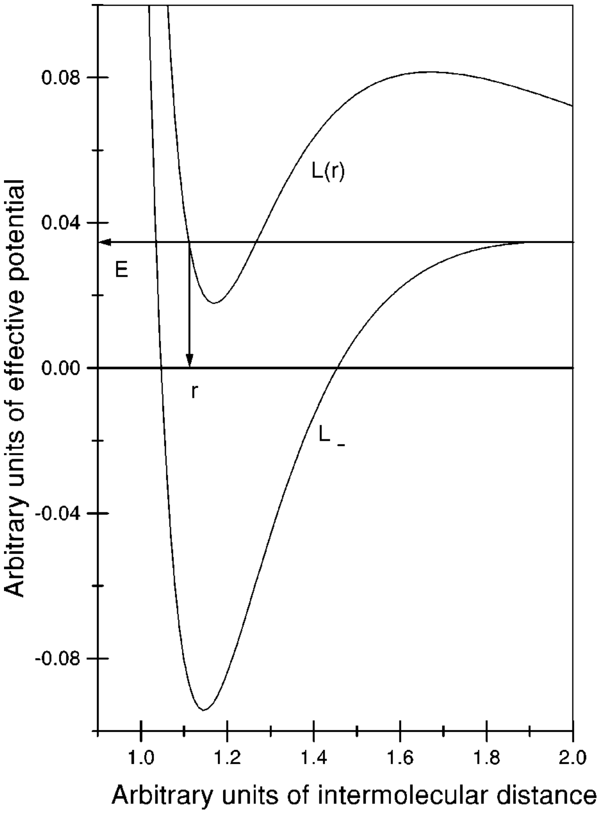

FIG. 4. The limits of integration in Eq. (24). At given energy E the integration over L begins with the minimal value L_- when the state with this energy can still be bound and finishes at $L=L(r)$. At $L>L(r)$ the point r becomes inaccessible.

The limits of integration in the (r,L^2) plane are explained in Fig. 4. The value L_- is the minimal angular momentum at which the state with energy E is still bound. The upper limit $L(r)$ is just the root of the equation $2\mu[E-U(r)]=\hbar^2L^2/r^2$.

Integrating over L^2 gives

$$\frac{\mu}{2\pi\hbar}\int_{r_1}^{r_2}dr\int_{L_-}^{L(r)}\frac{dL^2}{\sqrt{2\mu(E-U)-\dfrac{\hbar^2L^2}{r^2}}} =\frac{\mu}{\pi\hbar^3}\int_{r_1}^{r_2}r^2dr\,\sqrt{2\mu(E-U)-\frac{\hbar^2L_-^2}{r^2}}. \tag{25}$$

After a trivial nondimensionalization, one has instead of Eq. (24)

$$Z_b(E>0)=\frac{4\sigma^3(2\mu\epsilon)^{3/2}}{\pi\hbar^3}\Lambda_2(4\beta\epsilon), \tag{26}$$

where

$$\Lambda_n(x)=\int_0^{0.8}e^{-xy}dy\int s^n\sqrt{y-s^{-12}+s^{-6}-a(y)s^{-2}}\,ds. \tag{27}$$

The integration goes over all s obeying the condition $y-s^{-12}+s^{-6}-a(y)s^{-2}>0$ and $s<s_0(y)$, where

$$s_0(y)=\left(\frac{1+\sqrt{1-5y}}{y}\right)^{1/6} \tag{28}$$

is the root of the set of two equations:

$$y-s_0^{-12}+s_0^{-6}-a(y)s_0^{-2}=0, \tag{29}$$

$$a(y)=\frac{3}{s_0^4}-\frac{6}{s_0^{10}}. \tag{30}$$

Equation (30) follows from the condition $\partial_s[y-s^{-12}+s^{-6}-a(y)s^{-2}]=0$.

The expression for $Z_b(E>0)$, Eq. (26), should be added to the total number of states with negative energy:

$$Z_b(E<0)=\frac{4\sigma^3(2\mu\epsilon)^{3/2}}{3\pi\hbar^3}x^{-3/2}\Phi_{3/2}(x), \tag{31}$$

where $x=4\beta\epsilon$ and

$$\Phi_\nu(x)=\int_0^1 e^{x(u-u^2)}\gamma(3/2,x(u-u^2))\frac{du}{u^\nu}. \tag{32}$$

Equation (32) is readily derived from Eq. (10) by substituting there the LJ potential and replacing variables.

The final result has the form

$$Z_b=\frac{4\sigma^3(2\mu\epsilon)^{3/2}}{3\pi\hbar^3}F_{\rm LJ}(T), \tag{33}$$

where

$$F_{\mathrm{LJ}}(T)=[(kT/4\epsilon)^{3/2}\Phi_{3/2}(4\epsilon/kT)+3\Lambda_2(4\epsilon/kT)]. \tag{34}$$

D. Equilibrium concentration

We summarize the above calculations by writing down the expressions for $w_2=Z_b/Z_t$.

1. RW dimers

$$w_2=\frac{2V_R}{\sqrt{\pi}V}\left(\frac{U_0}{kT}\right)^{3/2}F_{\mathrm{RW}}(T), \tag{35}$$

where the function $F_{\mathrm{RW}}(T)$ is defined by Eq. (21) and $V_R=4\pi R^3/3$ is the dimer volume. Multiplying Eq. (35) by the total number of monomeric pairs $N_1^2/2$ in the volume V and dividing the result by V gives the equilibrium concentration n_2 of RW dimers:

$$n_2=\frac{n_1^2V_R}{\sqrt{\pi}}\left(\frac{U_0}{kT}\right)^{3/2}F_{\mathrm{RW}}(T). \tag{36}$$

Here n_1 is the vapor concentration at saturation.

2. LJ dimers

Similarly we have

$$w_2=\frac{V_\sigma}{V\sqrt{\pi}}\left(\frac{4\epsilon}{kT}\right)^{3/2}F_{\mathrm{LJ}}(T) \tag{37}$$

and

$$n_2=\frac{n_1^2V_\sigma}{2\sqrt{\pi}}\left(\frac{4\epsilon}{kT}\right)^{3/2}F_{\mathrm{LJ}}(T), \tag{38}$$

where $V_\sigma=4\pi\sigma^3/3$.

For LJ dimers we can introduce and find the average size of the dimer:

$$R_{\mathrm{av}}=\frac{1}{Z_b}\int r\rho(r,\beta)dr, \tag{39}$$

where $\rho(r,\beta)$ is the radial density of the bound states at a given temperature:

$$\rho(r,\beta)=4\pi r^2e^{\beta|U(r)|}q(r)+\frac{\mu r^2}{\pi\hbar^3}\int dE\,e^{-\beta E}\sqrt{2\mu(E-U)-\frac{\hbar^2L_-^2}{r^2}} \tag{40}$$

or

$$R_{\mathrm{av}}=\sigma\frac{\Phi_{5/3}(4\beta\epsilon)+3(4\beta\epsilon)^{3/2}\Lambda_3(4\beta\epsilon)}{\Phi_{3/2}(4\beta\epsilon)+3(4\beta\epsilon)^{3/2}\Lambda_2(4\beta\epsilon)}, \tag{41}$$

where the function Λ_n is defined by Eq. (27).

III. DIMER CONTROLLED NUCLEATION

An interesting application of the above results is the study of the kinetics of dimer controlled nucleation, i.e., the case when trimers and higher-mers are stable with respect to evaporation, i.e., $\beta_g=0$ at $g>2$. They, however, can grow by condensing the vapor molecules. This situation corresponds to very high supersaturation when the mass of critical embryo is close to 1. Such cases are not rarities.

A. Nucleation rate

The nucleation rate for the dimer controlled nucleation is given by Eq. (2) $(x_{g>2}=0)$:

$$\mathcal{J}=\frac{1}{2}\alpha_1c_1^2\frac{1}{1+x_2}. \tag{42}$$

The most remarkable feature of the dimer controlled nucleation is its simplicity even as compared to the nonbarrier nucleation when the dimers are already stable particles [12]. The point is that at $c_m\ll c_M$ the dimerization rate α_1 does not enter the final expression for the nucleation rate, the latter being dependent only on the equilibrium dimer concentration.

Let us begin by calculating the dimer evaporation rate. To this end we use the principle of detailed balance. In equilibrium the rate of dimer formation should be equal to the rate of dimer decay or

$$\frac{1}{2}\alpha_1n_1^2-\beta_2n_2=0. \tag{43}$$

Now Eq. (36) gives for the evaporation rate of RW dimers

$$\beta_2=\frac{(kT/U_0)^{3/2}\alpha_1\sqrt{\pi}e^{-\beta U_0}}{2V_0F_{\mathrm{RW}}(T)}. \tag{44}$$

The same value for LJ dimers is [see Eq. (38)]

$$\beta_2=\frac{3\alpha_1}{\sigma^34\sqrt{\pi}(4\epsilon/kT)^{3/2}}\frac{1}{F_{\mathrm{LJ}}(T)}. \tag{45}$$

Equation (44) and (45) contain the dimerization rate α_1. A dimer is not able to form without a third participant (a molecule of carrier gas) whose role is just to take the energy excess away (see Fig. 1), so the value of $\alpha_1\propto\sigma^2v(\sigma^3c_M)$ (c_M is the number concentration of the carrier gas). Considering all temperature-dependent factors to be of the order of unity yields then the following order-of-magnitude estimation of the evaporation rate:

$$\beta_2\propto\alpha_1/\sigma^3\propto v\sigma^2c_M\propto(v/l)(\sigma^2/l^2) \tag{46}$$

or the respective lifetime $\tau\propto 1/\beta_2\propto 10^{-6}$ s.

Fortunately, at small pressure of the condensing vapor $c_1\ll c_M$ the dimerization rate α_1 does not enter the final expression for the nucleation rate, the latter being dependent only on the equilibrium dimer concentration. Indeed

$$x_2=\frac{\beta_2}{\alpha_2}\propto\frac{v\sigma^2c_M}{v\sigma^2}\propto\frac{c_M}{c_1}\gg 1$$

so the unity on the right-hand side of Eq. (42) can be neglected, and the expression for the nucleation rate takes the form

$$\mathcal{J}=\frac{2\sqrt{\pi}}{3}\alpha_2 c_1^3\sigma^3(4\epsilon/kT)^{3/2}F_{\mathrm{LJ}}(T). \tag{47}$$

Assuming that $\alpha_2=\pi R_{\mathrm{av}}^2 v$ we find

$$\mathcal{J}=\frac{4\pi}{3\sqrt{3}}a^2(T)\sigma^5 c_1^3\sqrt{\epsilon/\mu}\left(\frac{4\epsilon}{kT}\right)F_{\mathrm{LJ}}(T)=A(T)c_1^3, \tag{48}$$

where we introduced $a(T)=R_{\mathrm{av}}/\sigma\approx 1.32$ (see Fig. 7 of Sec. IV), and

$$A(T)\approx 4.213\sigma^5\sqrt{\epsilon/\mu}\left(\frac{4\epsilon}{kT}\right)F_{\mathrm{LJ}}(T). \tag{49}$$

B. Nucleation kinetics

Below we consider the kinetics of particle formation assuming the following.

(i) At the initial moment of time the source of a condensable vapor is switched on. The productivity of the source I (the number of produced particles per unit volume at a time) is independent of time.

(ii) There are no particles at $t=0$.

(iii) The stable particles (g-mers) resulting from the nucleation process grow by condensing the vapor molecules. The condensation efficiency α_g is a power function of the particle mass g:

$$\alpha_g=\alpha g^{\lambda}, \tag{50}$$

where α is the rate constant.

(iv) A quasiequilibrium between dimers and monomers is onset, i.e.,

$$c_2=\frac{\alpha_1 c_1^2}{2\beta_2}. \tag{51}$$

This assumption means that the dimers are not long-livers within the global scale of the whole process whose characteristic time is much longer than $1/\beta_2$ (the estimate is given below).

Let us write down equations governing the kinetics of particle formation.

$$d_t c_1=I-3Ac_1^3-c_1\sum_{g\geqslant 3}\alpha_g c_g(t). \tag{52}$$

The physical meaning of this equation is apparent: the monomers (molecules of the condensable vapor) are produced by the source [the first term on the right-hand side of Eq. (52)] and disappear because of nucleation [the process $(1)+(1)+(1)\to(3)$, the second term] and condensation onto the surfaces that already formed g-mers (the third term). The nucleation rate constant A has been introduced by Eqs. (48) and (49).

The trimer balance is given by the following equation:

$$d_t c_3=Ac_1^3-\alpha_3 c_1 c_3. \tag{53}$$

The first term on the right-hand side of this equation contributes to the change of the trimer concentration due to the nucleation process producing stable trimers, while the second term describes the trimer loss due to the process $(3)+(1)\to(4)$. The remaining equations have the structure

$$d_t c_g=\alpha_{g-1}c_1 c_{g-1}-\alpha_g c_1 c_g. \tag{54}$$

The initial conditions to these equations (no preexisting particles) claim

$$c_g(t=0)=0. \tag{55}$$

In order to solve these equations, let us multiply Eqs. (52)–(55) by g^{λ} and sum over all g from 3 to ∞. After a tiny rearrangement we find

$$d_t\phi_{\lambda}=3^{\lambda}Ac_1^3+\alpha c_1\sum_{g\geqslant 3}[(g+1)^{\lambda}-g^{\lambda}]g^{\lambda}c_g, \tag{56}$$

where

$$\phi_{\gamma}(t)=\sum_{g\geqslant 3}g^{\gamma}c_g(t). \tag{57}$$

Approximating the difference on the right-hand side of Eq. (56) by the derivative $(g+1)^{\lambda}-g^{\lambda}\approx\lambda g^{\lambda-1}$ gives

$$d_t\phi_{\lambda}=3^{\lambda}Ac_1^3+\lambda\alpha c_1\phi_{2\lambda-1}. \tag{58}$$

This procedure being applied to $\phi_{2\lambda-1}$ expresses it in terms of $\phi_{3\lambda-2}$. Further steps produce the links $(3\lambda-2)\to(4\lambda-3)\to(5\lambda-4)\ldots$. This consideration shows that at $\lambda=n/(n+1)$ the set of equations for the moments is closed at the $n+2$ step. In what follows we restrict ourselves to the cases $\lambda=1/2$ and $\lambda=2/3$ $(n=1,2)$.

At $\lambda=1/2$ one has

$$\begin{gathered} d_t c_1=I-3Ac_1^3-\alpha c_1\phi_{1/2}, \\ d_t\phi_{1/2}=\sqrt{3}Ac_1^3+\frac{1}{2}\alpha c_1\phi_0, \\ d_t\phi_0=Ac_1^3. \end{gathered} \tag{59}$$

At $\lambda=2/3$ this set is a little longer,

$$\begin{gathered} d_t c_1=I-Ac_1^3-3\alpha c_1\phi_{2/3}, \\ d_t\phi_{2/3}=3^{2/3}Ac_1^3+\frac{2}{3}\alpha c_1\phi_{1/3}, \\ d_t\phi_{1/3}=3^{1/3}Ac_1^3+\frac{1}{3}\alpha c_1\phi_0, \\ d_t\phi_0=Ac_1^3. \end{gathered} \tag{60}$$

Before solving these equations, we introduce the following nondimensional unknown functions and the variable:

$$C=c_1\sqrt{\frac{\alpha}{I}},\quad \varphi=\sqrt{\frac{\alpha}{I}},\quad \tau=\sqrt{I\alpha}t, \tag{61}$$

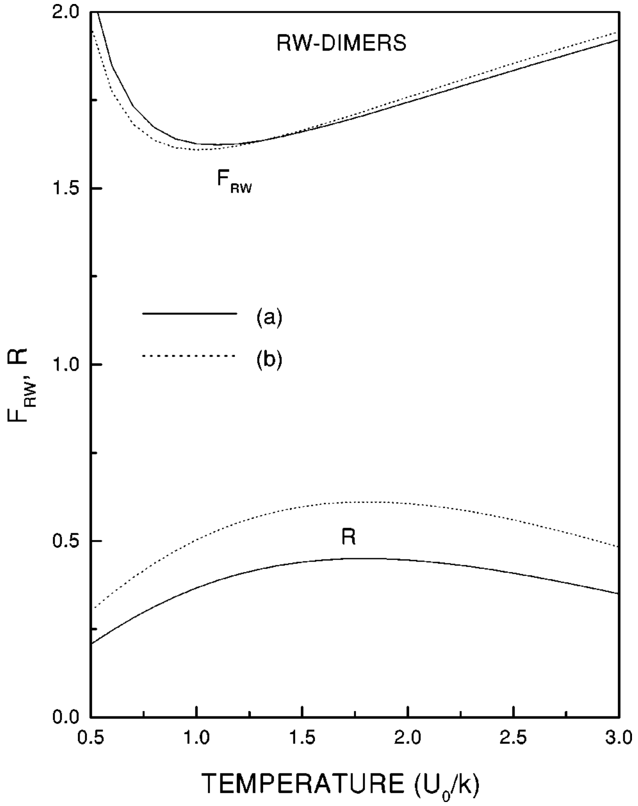

FIG. 5. RW dimers. The partition function $F_{\mathrm{RW}}\propto Z_b$ of a RW dimer as a function of temperature [Eqs. (20) and (21)]. The relative contribution R of the states with positive energies is also shown: (a) no hard core, (b) the hard core radius is one-half of the dimer size $(k=2)$.

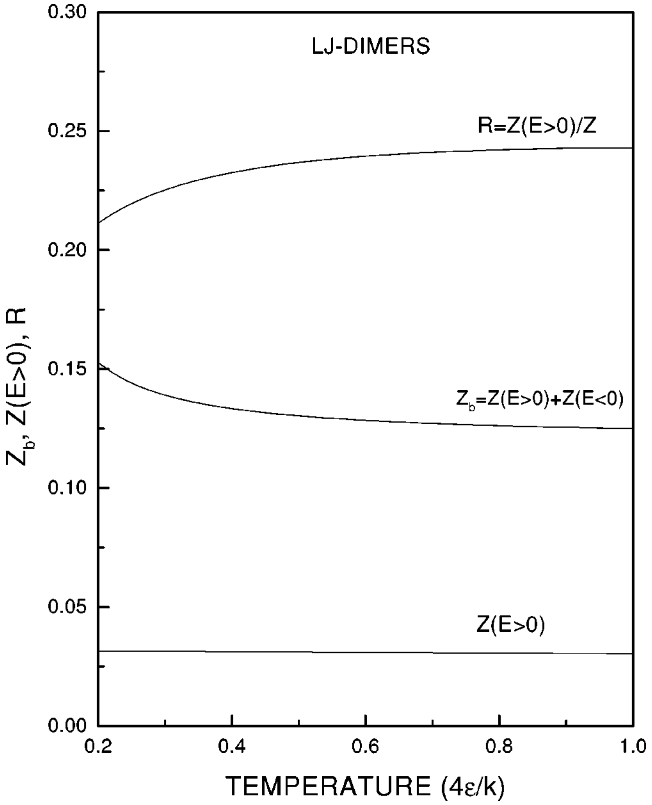

FIG. 6. LJ dimers. The partition function of LJ dimers (in units of $\pi\hbar^3/[4\sigma^3(2\mu\epsilon)^{3/2}]$, Eq. (33)). The contribution of the state with positive energies is not so essential and almost independent of temperature.

and the governing parameter,

$$\mu=\frac{A}{\alpha}\sqrt{\frac{I}{\alpha}}. \tag{62}$$

Equations (59) take the form

$$\begin{aligned} d_\tau C&=1-3\mu C^3-C\varphi_{1/2},\\ d_\tau\varphi_{1/2}&=\sqrt{3}\mu C^3+\frac{1}{2}C\varphi_0,\\ d_\tau\phi_0&=\mu C^3. \end{aligned} \tag{63}$$

The set (60) becomes

$$\begin{aligned} d_\tau C&=1-3\mu C^3-C\varphi_{2/3},\\ d_\tau\varphi_{2/3}&=3^{2/3}\mu C^3+\frac{2}{3}C\varphi_{1/3},\\ d_\tau\varphi_{1/3}&=3^{1/3}\mu C^3+\frac{1}{3}C\varphi_0,\\ d_\tau\varphi_0&=\mu C^3. \end{aligned} \tag{64}$$

The parameter μ may be evaluated by order of magnitude. As follows from Eq. (49), the constant $A\propto v\sigma^5$ while $\alpha\propto v\sigma^2$. Hence

$$\mu\propto\frac{\sigma^2 I^{1/2}}{v^{1/2}}. \tag{65}$$

Assuming $\sigma=10^{-8}$ cm and $v=10^4$ cm/s gives $\mu=10^{-14}\sqrt{I}$, so μ becomes of the order of unity only for unlikely productive sources. Normally μ is extremely small. It is clear, therefore, how important it is to investigate the asymptotic behavior of the solution to the above equations in the limit of small μ.

In order to clarify the idea of our asymptotic approach, we notice first that at $\mu=0$ no reasonable solutions to the sets (63) and (64) come up: the monomer concentration grows linearly with time while the moments ϕ remain zero. In order to avoid this difficulty let us rescale the variable τ and unknown functions as follows.

At $\lambda=1/2$,

$$\tau=\mu^{-1/7}\zeta,\quad C=\mu^{-1/7}x,\quad \varphi_{1/2}=\mu^{1/7}y,\quad \varphi_0=\mu^{7/3}z. \tag{66}$$

At $\lambda=2/3$,

$$\begin{gathered} \tau=\mu^{-1/9}\zeta,\quad C=\mu^{-1/9}x,\quad \varphi_{2/3}=\mu^{1/9}y,\\ \varphi_{1/3}=\mu^{1/3}z,\quad \varphi_0=\mu^{5/9}u. \end{gathered} \tag{67}$$

Rescaling the set (63) yields

$$d_\zeta x=1-3\mu^{4/7}x^3-xy,\quad d_\zeta y=3^{1/2}\mu^{2/7}x^3+\frac{1}{2}xz, \tag{68}$$

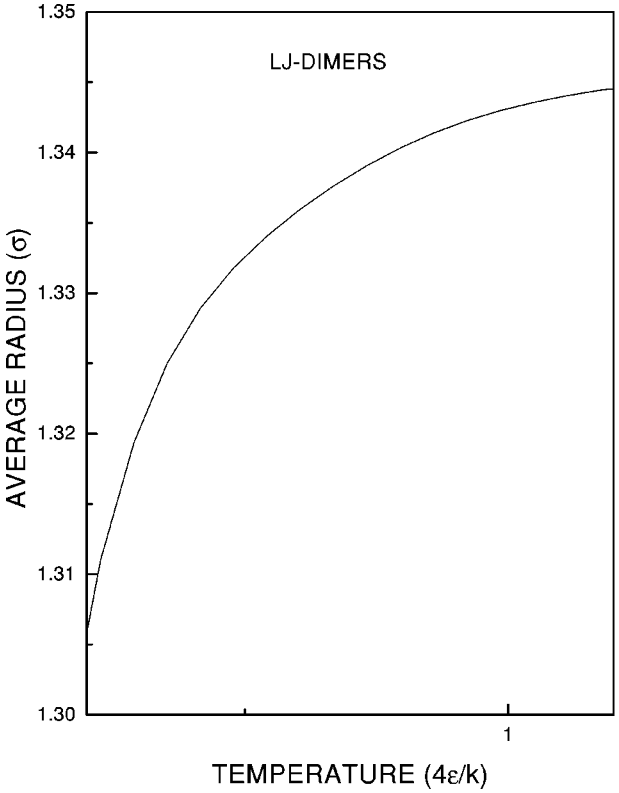

FIG. 7. The radius of a LJ dimer vs temperature. In contrast to the traditional approach defining the dimer in terms of the number of all states of two molecules confined by a cutoff radius, no artificially introduced size parameter appears for the dimer introduced as their bound states. The spatial restriction is inferred naturally from the definition of the dimer. The dimer radius of a LJ dimer [Eq. (41)] is shown as a function of temperature.

$$d_\zeta z = x^3.$$

Similar operation with Eqs. (64) gives

$$d_\zeta x = 1 - 3\mu^{2/3}x^3 - xy, \quad d_\zeta y = 3^{2/3}\mu^{4/9}x^3 + \frac{2}{3}xz, \tag{69}$$

$$d_\zeta z = 3^{1/3}\mu^{2/9}x^3 + \frac{1}{3}xu, \quad d_\zeta u = x^3.$$

Now the idea of rescaling becomes apparent: the small factor μ is removed in the last equation of the sets (63) and (64) while the positive powers of μ still accompany the term x^3 responsible for the particle formation. These terms can now be ignored at small μ. Equations defining the universal kinetics of the particle formation–growth process look as follows.

At $\lambda = 1/2$,

$$d_\zeta x = 1 - xy, \quad d_\zeta y = \frac{1}{2}xz, \quad d_\zeta z = x^3. \tag{70}$$

At $\lambda = 2/3$,

$$d_\zeta x = 1 - xy, \quad d_\zeta y = \frac{2}{3}xz, \quad d_\zeta z = \frac{1}{3}xu, \quad d_\zeta u = x^3. \tag{71}$$

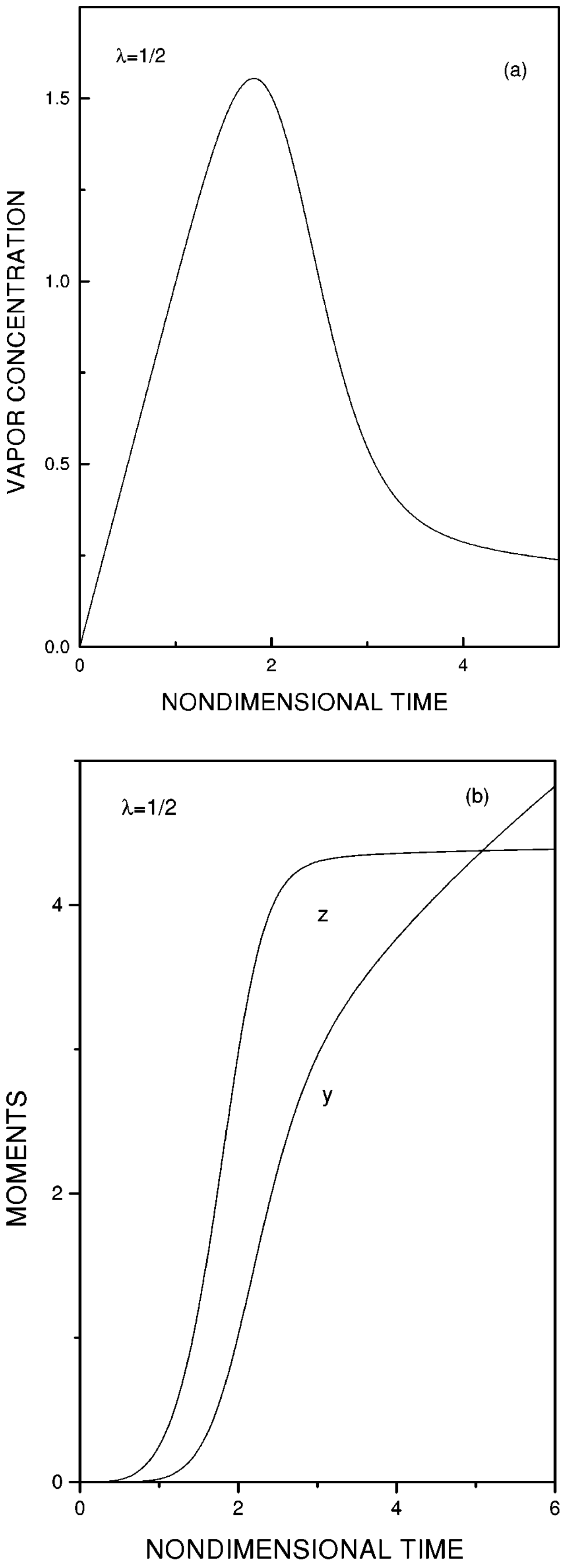

FIG. 8. Kinetics of particle formation–growth at $\lambda = 1/2$. Shown are (a) universal function x describing the time dependence of vapor concentration and (b) universal functions describing the time dependence of particle number concentration (curve z) and the moment of the order of 1/2 (curve y).

It is also possible to find the asymptotic behavior of the universal functions at large ζ. The vapor concentration is expected to drop at $\zeta\to\infty$, which means that the derivative $d_\zeta x$ can be neglected. Then $x\approx 1/y$ and the rest of the set (70) for the universal functions are solved to give the following.

At $\lambda=1/2$,

$$x\propto\zeta^{-1/2},\quad y\propto\zeta^{1/2},\quad z\propto\text{const}=z_0=4.611. \tag{72}$$

At $\lambda=2/3$,

$$x\propto\zeta^{-2/3},\quad y\propto\zeta^{2/3},\quad z\propto\zeta^{1/3},\quad u\propto\text{const}=u_0=8.601. \tag{73}$$

All the above results are readily extended to arbitrary n.

IV. RESULTS AND DISCUSSION

We introduced the dimers as the bound states of two molecules. This definition differs from that commonly accepted in the theory of nucleation where the work for embryo formation is connected with the free energy of two molecules. The partition function of two molecules obviously overestimates the total number of dimers by taking into account short-living states on an equal footing with the bound states whose lifetime depends on external intervention (e.g., collisions with the carrier gas molecules). Another disadvantage that arises in including all the states into consideration is the necessity to introduce spatial constraints that would allow for distinguishing between dimer and nondimer configurations of two molecules.

Figures 5 and 6 show the temperature dependence of the dimer partition functions for RW and LJ dimers. It is very interesting to expand on the contribution of the bound states with positive energies. It is not great (less than 25%) and almost independent of the temperature in the case of LJ dimers.

In contrast to RW dimers where dimer and nondimer spatial configurations are distinctly separated, in the case of LJ dimers such separation is not easy unless our definition is introduced. If only bound states are attributed to the dimer states, then the spatial restriction for the dimer configuration arises automatically. The average dimer radius as the function of temperature is shown in Fig. 7.

On discussing the thermodynamic properties of dimers, we investigated the nucleation formation of disperse particles assuming that the dimer stage alone limited the particle formation rate. This is an extension of our previous work [12], where the nonbarrier nucleation (stable dimers) was considered. In addition to the asymptotic analysis of Ref. [12], we found a very effective ansatz allowing for the condensation-nucleation equations to be reduced to a finite number of the first-order differential equations for the moments of the particle mass spectrum. The second and very substantial achievement was the rescaling of these equations in the limit of low nucleation rates [the parameter $\mu\ll 1$, Eq. (62), which allowed for further simplification of the kinetic problem and finally reduced it to finding four universal functions of the nondimensional time]. Equations (70) and (71) for these functions were solved numerically. Figures 8 and 9 demonstrate the results.

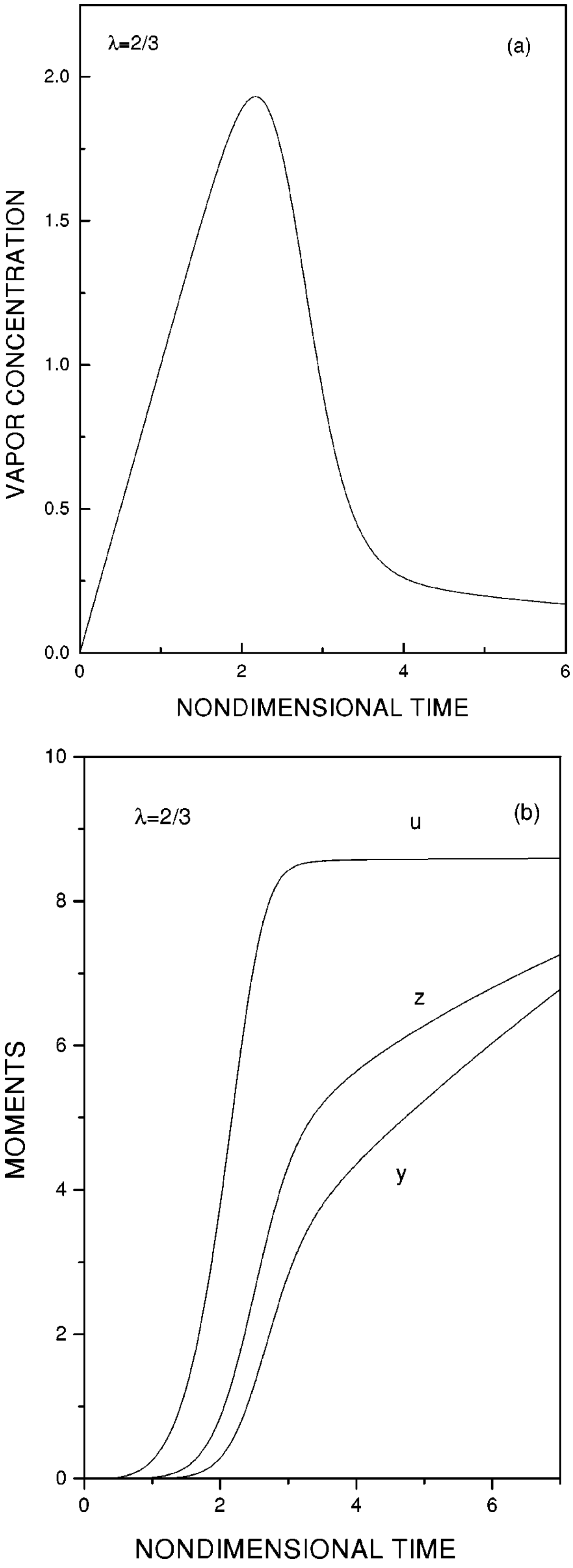

FIG. 9. Kinetics of particle formation–growth at λ = 2/3. Shown are (a) universal function x describing the time dependence of vapor concentration and (b) universal functions describing the time dependence of particle number concentration (curve u), the momemt of the order of 1/3 (curve z), and the moment of the order 2/3 (curve y).

The dimensionless concentration of the condensable vapor is seen to grow linearly until the moment when the nucleation process has produced enough particles to deplete the vapor by condensation with the rate comparable to the source productivity. These newly born particles continue to grow and consume more and more vapor so the source is unable to support a finite concentration level. The concentration drops with time [Figs. 8(a) and 9(a)]. The moments of the mass spectrum are seen to grow with time except ϕ_0 (particle number concentration), which remains a constant at $t\to\infty$ [Figs. 8(b) and 9(b)]:

$$\phi_0 = 4.611\sqrt{I\alpha}\mu^{3/7} \propto A^{3/7}\alpha^{-8/7}I^{5/7} \quad (\lambda = 1/2),$$

$$\phi_0 = 8.601\sqrt{I\alpha}\mu^{5/9} \propto A^{5/9}\alpha^{-4/3}I^{7/9} \quad (\lambda = 2/3).$$

V. CONCLUSION

We introduced the dimers as bound states of two molecules and outlined the role of the dimer stage in the particle formation process. The calculations of the thermodynamic properties of these introduced dimers were performed for van der Waals dimers, i.e., two molecules kept together by an intermolecular potential. Side by side with the states with negative relative energy we introduced into consideration quasibound states with positive energy of relative motion that arose due to the centrifugal barrier.

The next step was the use of the dimer evaporation rate in the kinetic scheme describing the formation and evolution of disperse composition of the particles resulting from the nucleation process, the limiting stage of which being the jump over the dimer state. The fact that $\beta_2/\alpha_2 c_1 \ll 1$ (the dimer evaporation time is much shorter than the condensation time) helped us to get rid of the dimerization rate [see Eqs. (49) and (50)]. The latter value is defined by three-body processes and is not yet well studied.

The time evolution of the mass spectrum forming in the nucleation-condensation process was shown to depend on a finite number of the particle spectrum moments once the homogeneity exponent λ defining the condensation rate is specified as $\lambda = n/(n+1)$. Fortunately, this specification includes two practically important cases: $\lambda = 1/2$ and $\lambda = 2/3$. The former exponent is used for describing the formation of island films (see, e.g., Refs. [15,14] and references therein), while the latter corresponds to the condensation rate proportional to the area of growing particle surface and is thus used in the Physics of Aerosols for the description of the particle growth in the free molecular regime [16].

The renormalization transformation applied above to the growth equations allowed for a derivation of rather simple equations for the set of universal functions describing the kinetics of the nucleation-condensation process. The influence of external parameters (the source productivity and temperature) on the process is reduced to rescaling the concentration-time plane.

ACKNOWLEDGMENT

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