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Scaling and the Smoluchowski equations

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The Smoluchowski equations, which describe coalescence growth, take into account combination reactions between a j-mer and a k-mer to form a $(j+k)$-mer, but not breakup of larger clusters to smaller ones. All combination reactions are assumed to be second order, with rate constants K_{jk}. The K_{jk} are said to scale if $K_{\lambda j,\gamma k}=\lambda^{\mu}\gamma^{\nu}K_{jk}$ for $j\leqslant k$. It can then be shown that, for large k, the number density or population of k-mers is given by $Ak^{a}e^{-bk}$, where A is a normalization constant (a function of a, b, and time), $a=-(\mu+\nu)$, and $b^{\mu+\nu-1}$ depends linearly on time. We prove this in a simple, transparent manner. We also discuss the origin of odd-even population oscillations for small k. A common scaling arises from the ballistic model, which assumes that the velocity of a k-mer is proportional to $1/\sqrt{m_k}$ (Maxwell distribution), i.e., thermal equilibrium. This does not hold for the nascent distribution of clusters produced from monomers by reactive collisions. By direct calculation, invoking conservation of momentum in collisions, we show that, for this distribution, velocities are proportional to $m_k^{-0.577}$. This leads to $\mu+\nu=0.090$, intermediate between the ballistic (0.167) and diffusive (0.000) results. These results are discussed in light of the existence of systems in the experimental literature which apparently correspond to very negative values of $\mu+\nu$.
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INTRODUCTION

Smoluchowski's equations for coalescence growth in condensed phases, proposed[1] in 1917, continue to have applications[2,3] to cluster formation in gas, liquid, and solid-state systems. While Smoluchowski found an elegant solution to a modified form of the equations in the case of all kernels (rate constants) being equal, it was a long time before asymptotic solutions, valid for large cluster sizes, were demonstrated[4–8] for the case of kernels which scale. (Exact solutions are also possible when the kernels have special forms[2,4,8] and power series solutions have been attempted.[9]) The kernel K_{ij}, which specifies the rate of combination of i-mers and j-mers, is sometimes[6] said to scale if $K_{\alpha i,\alpha j}=\alpha^{2\omega}K_{ij}$, with ω being the scaling parameter. A more general definition of scaling and a more refined classification of kernels were introduced by van Dongen and Ernst,[5] according to which kernels scale if $K_{\alpha i,\beta j}=\alpha^{\mu}\beta^{\nu}K_{ij}$ for $i\ll j$. For scaled kernels, the asymptotic solution to the Smoluchowski equations is that the number of particles of size k is given by $n_k=Ak^{a}e^{-bk}$, where A is a normalizing constant, a depends on the scaling parameters μ and ν (or ω), and b (but not a) is a function of time. This has been proven by several workers[4–8] using different mathematical methods.

For the simple scaling kernels ($K_{\alpha i,\alpha j}=\alpha^{2\omega}$), we were able to show[10] the validity of the asymptotic solution for n_k in a simple manner, making the approximations involved more explicit. The theory is currently being applied very successfully (see following paper) to cluster formation in supersonic expansions of rare gases, for which accurate experimental data have recently become available.[11] In the present contribution, we extend the demonstration of the asymptotic form for n_k to kernels obeying the van Dongen-Ernst scaling ($K_{\alpha i,\beta j}=\alpha^{\mu}\beta^{\nu}K_{ij}$), assumed to hold for $i\leqslant j$. We also clarify the consequences of our previous proof for odd-even alternation and discuss a more appropriate scaling of the kernels than the ballistic and diffusional models, which are the most frequently used in discussing agglomeration in the gas phase. Our model should be applicable when monomers are the most abundant species, so that nonreactive collisions do not alter the velocity distribution.

SMOLUCHOWSKI EQUATIONS

It is assumed that only monomers exist at time 0, that monomers can stick together on collision to form dimers, that monomers and dimers can stick together to form trimers, etc. Only binary collisions are considered explicitly, including collisions between all n-mers and all m-mers existing at any time. It is further assumed that all collisions between species lead to irreversible coalescence, so that evaporation or disintegration of clusters is neglected. Disintegration of larger clusters is less important than coalescence of smaller ones when the number of n-mers decreases rapidly with n. Neglect of disintegration may also be justified by considering that the equations give the net rate of cluster formation (association minus dimerization).

Thus, the Smoluchowski kinetic equations describe the collision of an n-mer with an m-mer to form an $(n+m)$-mer, which can be destroyed only by collision of the $(n+m)$-mer with another cluster to form a larger one. The processes included are all assumed to be second-order reactions, with the rate of each reaction being proportional to the product of the concentrations of the two reacting species. Thus, the rate of formation of n-mers is the sum of the rates of the reactions of j-mers and $(n-j)$-mers, where j runs from 1 to k', where

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$k'=k/2$ if k is even and $(k-1)/2$ if k is odd. The rate of destruction of n-mers is the sum of the rates of reactions of n-mers with all species. Letting n_k be the concentration of k-mers and K_{ij} the kernel or rate constant for reaction of i-mers with j-mers, we have

$$\frac{dn_k}{dt}=\sum_{i=1}^{k'}K_{i,k-i}n_i n_{k-i}-\sum_{i=1}^{\infty}K_{ki}n_k n_i-K_{kk}n_k n_k. \tag{1}$$

The last term arises because collision of two k-mers to form a $(2k)$-mer leads to the loss of two k-mers. The values of the second-order rate constants reflect the mass transfer rates and the reactive cross sections. Of course, $K_{ji}=K_{ij}$.

There are $k/2$ terms in the first sum for even k and $(k-1)/2$ for odd k. The effect of this is seen in the results of numerical integration of the equations.[10,12] Although all the n_k values are close to a smooth curve as a function of k, the values for even k are above the curve and the values for odd k are below it. However, the deviations from the smooth curve are important only for small k, so that the population alternation disappears for larger k. The reason for this will be made clear below.

Equation (1) may be simplified by dropping the last term and, in the first sum, halving the term for $i=k/2$ (which exists only for even k). Both approximations are less important for larger k. The resulting equation may be written as

$$\frac{dn_k}{dt}=\frac{1}{2}\sum_{i=1}^{k-1}K_{i,k-i}n_i n_{k-i}-\sum_{i=1}^{\infty}K_{ki}n_k n_i. \tag{2}$$

In (2) there is no distinction between even and odd k. Equation (2) is to be solved under the assumption that at $t=0$ only monomers are present. If the initial concentration of monomers is N, so that $n_k(0)=N\delta_{k1}$, conservation of particles requires

$$\sum_{k=1}^{\infty}n_k k=N \tag{3}$$

at any time. Smoluchowski was able to give an analytical solution to Eq. (2) in the case of all K_{ij} being equal, say, $K_{ij}=K$. The solution, which satisfies (3), is

$$n_k(t)=\frac{N[KNt/2]^{k-1}}{[1+KNt/2]^{k+1}}. \tag{4}$$

The population of monomers decreases with time, and the population of every other cluster first increases and then decreases.

More appropriate and more general than the assumption $K_{ij}=K$ is the assumption that the K_{ij} scale with particle size, i.e.,

$$K_{\lambda i,\lambda j}=\lambda^{2\omega}K_{ij},$$

where ω is the scaling exponent. It may be shown[4–8] that, for large values of k, n_k approaches $Ak^a e^{-bk}$, where A, a, and b depend on ω. We have given[10] a simple proof that this asymptotic solution is valid. Here, the proof is extended to the case where the K_{ij} scale according to

$$K_{\alpha i,\beta j}=\alpha^{\mu}\beta^{\nu}K_{ij}$$

for $i\leqslant j$. Physically, neither μ nor ν can be greater than 1,[2,5] if $\mu=\nu=1$, gelation occurs.

Some preliminary results are required first. Assuming that $n_k(t)=Ak^a e^{-bk}$ for all k, we determine A by normalization, i.e.,

$$\sum_{k=1}^{\infty}kn_k=A\sum_{k=1}^{\infty}k^{a+1}e^{-bk}=N. \tag{5}$$

The average value of a cluster size is given by

$$\langle k\rangle=\frac{\sum_k k^{a+1}e^{-bk}}{\sum_k k^a e^{-bk}}. \tag{6}$$

Since we consider agglomeration only, $\langle k\rangle$ must increase with time. As we will show, a is time independent, so that $d\langle k\rangle/dt=(d\langle k\rangle/db)(db/dt)>0$. Differentiating,

$$-\frac{d(k)}{dt}=\frac{\sum_{j,k}e^{-b(j+k)}j^a k^a(j^2-2jk+k^2)}{2\left[\sum_j j^a e^{-bj}\right]^2}.$$

The right member being positive, $d\langle k\rangle/db$ is negative, so b decreases with time, eventually becoming small enough so that the sums above may be approximated by integrals. The normalization condition then becomes

$$A=\frac{N}{\sum_{k=0}^{\infty}k^{a+1}e^{-bk}}\cong\frac{N}{\int_0^{\infty}dx x^{a+1}e^{-bx}}=\frac{Nb^{a+2}}{\Gamma(a+2)}. \tag{7}$$

The sum has been extended to $k=0$ (this assumes that $a+1$ is positive) and approximated as an integral.

ASYMPTOTIC SOLUTION

Our proof of the asymptotic solution involves substituting $Ak^a e^{-bk}$ for n_k in Eq. (1) and making approximations which are valid for large k. For large k the sums in (1) are dominated by terms for large i, so that $Ai^a e^{-bi}$ may be substituted for n_i in the sums. We assume that the scaling and symmetry conditions on K_{ij} hold for all i and j, i.e., that $K_{ij}=ci^{\mu}j^{\nu}$ for $i\leqslant j$ and $K_{ji}=K_{ij}$. Then substituting and dividing by n_k gives

$$\begin{aligned}\frac{1}{A}\frac{dA}{dt}+(\ln k)\frac{da}{dt}-k\frac{db}{dt}&=cA\sum_{i=1}^{k'}i^{\mu+a}(k-i)^{\nu+a}k^{-a}-cA\sum_{i=1}^{k}k^{\nu}i^{\mu+a}e^{-bi}\\&\quad-cA\sum_{i=k+1}^{\infty}i^{\nu+a}k^{\mu}e^{-bi}-cAk^{\mu+\nu}k^a e^{-bk}.\end{aligned} \tag{8}$$

Since there is only one term in $\ln k$, it must vanish, which requires that $da/dt=0$, i.e., the value of a is independent of time.

We will show below that $a=-(\mu+\nu)$, so, if k is large, the last term in (8) is much smaller than the sum which precedes it, and can be neglected. Similarly, for large k the difference between $k/2$ and $(k-1)/2$ is unimportant and the upper limit in the first sum may be taken as $k/2$. With these approximations [which are the same as those used by Smoluchowski in going from (1) to (2)], there is no distinction between odd and even k in (8). Therefore, the odd-even alternation of populations disappears for large cluster sizes.

Substituting for $(1/A)(dA/dt)$ and remembering that $da/dt=0$, Eq. (8) is reduced to

$$(a+2)\frac{d\ln b}{dt}-k\frac{db}{dt}=cA\sum_{i=1}^{k/2} i^{\mu+a}(k-i)^{\nu+a}k^{-a}-cA\sum_{i=1}^{k} k^{\nu}i^{\mu+a}e^{-bi}-cA\sum_{i=k+1}^{\infty} i^{\nu+a}k^{m}e^{-bi}. \tag{9}$$

The coefficient of db/dt is $(a+2)/b-k$; for large k, $(a+2)/b$ can be neglected, reducing the left side of Eq. (9) to just $-k(db/dt)$. The sums in (9) are now approximated by integrals using the first terms of the Euler-MacLaurin expansion:

$$\sum_{j=m}^{j=n} f(j)\cong\int_m^n dx f(x)+\tfrac{1}{2}f(a)+\tfrac{1}{2}f(b),$$

which is equivalent to evaluating the integral by the trapezoid rule. Then (9) becomes

$$-\frac{k}{cA}\frac{db}{dt}=\int_1^{k/2} x^{\mu+a}(k-x)^{\nu+a}k^{-a}dx+\frac{1}{2}(k-1)^{\nu+a}k^{-a}+\frac{1}{2}\left(\frac{k}{2}\right)^{\mu+\nu+2a}k^{-a}-\int_1^k k^{\nu}x^{\mu+a}e^{-bx}dx-\frac{1}{2}k^{\nu}e^{-b}-\frac{1}{2}k^{\nu}\left(\frac{k}{2}\right)^{\mu+a}e^{-bk}-\int_{k+1}^{\infty} x^{\nu+a}k^{\mu}e^{-bx}dx-\frac{1}{2}(k+1)^{\nu+a}k^{\mu}e^{-b(k+1)}. \tag{10}$$

We substitute $x=ky$ in the three integrals to determine how they depend on k. The first is proportional to $k^{\mu+\nu+a+1}$, and we will show below that $\mu+\nu+a+1=1$. The second and fifth terms are proportional to k^{ν}; if $\nu<1$, they may be neglected for large k. The third term, proportional to $k^{\mu+\nu+a}$, may likewise be dropped since $\mu+\nu+a=0$. The sixth and eighth terms, proportional to $k^{\mu+\nu+\alpha}\,e^{-bk}$, are also negligible ($b$ is positive for all t). This leaves

$$-(cA)^{-1}k\frac{db}{dt}=k^{\mu+\nu+a+1}\int_{1/k}^{1/2} y^{\mu+a}(1-y)^{\nu+a}dy-k^{\mu+\nu+a+1}\int_{1/k}^{1} y^{\nu+a}e^{-bky}dy-k^{\mu+\nu+a+1}\int_{1+1/k}^{\infty} y^{\nu+a}e^{-bky}dy. \tag{11}$$

If μ and ν are less than 1, the last two integrals are less than

$$\int_0^{\infty} y^{a+1}e^{-bky}dy=\frac{\Gamma(a+1)}{(bk)^{a+2}},$$

so they may be neglected, leaving only one term on the right-side of (11).

Using (7) for A, (11) becomes

$$\frac{-k}{Nc}\frac{\Gamma(a+2)}{b^{a+2}}\frac{db}{dt}=k^{\mu+\nu+a+1}\int_0^{1/2} y^{\mu+a}(1-y)^{\nu+a}dy\equiv k^{\mu+\nu+a+1}K(\mu,\nu). \tag{12}$$

For (12) to hold for all large k, we must have $\mu+\nu+a+1=1$, or $a=-(\mu+\nu)$, as was to be shown. Furthermore Eq. (12) gives the time variation of b. It integrates to

$$\frac{b^{-(a+1)}-b_0^{-(a+1)}}{a+1}=Nc\left[\frac{K(\mu,\nu)}{\Gamma(a+2)}\right]t, \tag{13}$$

where $a=-(\mu+\nu)$ and b_0 is the value of b at $t=0$. Since $a+1$ is positive, (13) shows that b decreases with time. It is convenient to evaluate $K(\mu,\nu)$ by writing $(1-y)^{-\mu}$ as a power series in y, giving

$$K(\mu,\nu)=\int_0^{1/2} y^{-\nu}(1-y)^{-\mu}dy=\sum_{n=0}^{\infty}\frac{\left(\frac{1}{2}\right)^{n+1-\nu}}{n+1-\nu}\frac{\mu(\mu+1)\cdots(\mu+n-1)}{n!}.$$

The series converges rapidly.

MEANING OF SCALING PARAMETERS

If simple scaling obtains, i.e., $K_{ai,bj}=a^{\omega}b^{\omega}K_{ij}$, the scaling parameter for the kernels is given[2,6] by

$$2\omega=\alpha+(d-d_w)/D. \tag{14}$$

Here, α specifies how the velocity with which reacting partners approach each other scales with their mass or number of monomers, i.e., the velocity with which j-mers and k-mers approach is proportional to $(kj)^{\alpha}$. The parameter d is the dimensionality of the space in which the clustering or coalescence takes place. The parameter d_w is the fractal dimension of the cluster trajectory, equal to 1 for clusters moving in straight lines without collision (ballistic model) and equal to 2 for clusters diffusing like Brownian particles (Brownian model). Finally, D is the fractal dimension of the clusters, which specifies how the mass of the cluster scales with its

size or characteristic length. For ordinary clusters formed by close-packing monomers, $D=3$.

In two cases of particular interest to us, the ballistic model and the Brownian model, the value of the scaling parameter ω can be found by simple physical arguments. The kernels or rate constants K_{jk} are products of the relative velocities of the particles and their reactive cross sections. We assume that the reactive cross sections are proportional to the geometric cross sections. If there are "magic numbers" for coalescence collisions (as when particular cluster sizes allow satisfaction of valence constraints), some kernels will not scale and the populations of the clusters will deviate from the asymptotic form we have derived, as we have shown.[10,12] In the ballistic model, appropriate to particles at thermal equilibrium in the gas phase, the relative velocity for a j-mer and a k-mer may be calculated[13] from the Maxwell distribution to be

$$v_{jk} = \sqrt{\frac{8kT(m_j + m_k)}{\pi m_j m_k}}, \tag{15}$$

where m_j is the mass of a j-mer. It thus scales as $(jk)^{-1/2}$, i.e., $\alpha=-\frac{1}{2}$. The geometric cross sections, assuming spherical particles, are

$$\sigma_{jk} = \pi(R_j + R_k)^2,$$

where the volume of a j-mer, $4\pi R_j^3/3$, is proportional to j. If the reactive cross section is proportional to σ_{jk}, it scales as $(jk)^{2/3}$. Since the velocity factor scales as $(jk)^{-1/2}$, K_{jk} scales as $(jk)^{1/6}$, i.e., $2\omega=1/6$.

In the Brownian model, reacting particles do not travel in straight lines because they collide with other, nonreacting, particles between reactive collisions. The rate of reaction of a single cluster of size j with clusters of size k is proportional to the radial diffusion current of k-mers to the single j-mer. This current, according to Fick's law, is $J_k=D_{jk}(\partial c_k/\partial r)$, where $c_k(r)$ is the concentration of k-mers at a distance r from the center of the j-mer and D_{kj} is the mutual diffusion coefficient. This equation is solved with the continuity equation and the boundary conditions: $c_k(r)=0$ at $r=R_j+R_k$ (k-mers disappear by reaction on contact with the j-mer) and $c_k(\infty)=$bulk concentration of k-mers. The resulting radial diffusion current is proportional to D_{kj} and R_j+R_k, so the rate of reaction is proportional to these parameters and to the bulk concentrations of j-mers and k-mers. The mutual diffusion coefficient $D_{jk}=D_j+D_k$, where D_j is the tracer diffusion coefficient for j-mers. If the nonreactive species, which cause the motion of reactive species to be diffusive rather than ballistic, are much smaller than the reactive species, D_j is inversely proportional to R_j. Then K_{jk} is proportional to $(R_j^{-1}+R_k^{-1})$ and to (R_j+R_k), where R_j is proportional to $j^{1/3}$. Thus the scaling exponents μ and ν are $-1/3$ and $+1/3$, respectively, in this case.

In fact, the simple scaling theory does not apply in either the ballistic or the diffusional case. In the former, K_{ij} is proportional to

$$\sqrt{\frac{i+j}{ij}}(i^{1/3}+j^{1/3})^2,$$

where the first factor comes from the relative velocity of the colliding particles and the second from the cross section. For $i \ll j$, this expression is proportional to $i^{-1/2}j^{2/3}$, so that $\mu=-\frac{1}{2}$, $\nu=\frac{2}{3}$, and $a=-\frac{1}{6}$. In this case, (13) becomes

$$b^{-5/6} - b_0^{-5/6} = Nc\left[\frac{5K\left(-\frac{1}{2},\frac{2}{3}\right)}{6\Gamma\left(\frac{1}{6}\right)}\right]t. \tag{16}$$

Numerical evaluation of K makes the square bracket equal to 2.2192. With $\mu=\nu=1/12$ (so a is still $-1/6$), the square bracket equals 0.5247.

We will apply the scaling theory to cluster formation in a helium-atom nozzle beam, for which the ballistic model is inappropriate. The scaling exponent for the ballistic case was calculated using (15), which assumes that the particles are at thermal equilibrium. In the situation of interest, all k-mers with $k>1$ are created by collisions, starting with a gas of monomers, whereas establishing thermal equilibrium requires many nonreactive collisions. Since one can hardly expect the particles to be at thermal equilibrium, we calculate the j dependence of ν_j, assuming that the velocity distribution is established by the reactive collisions between particles.

NASCENT VELOCITY DISTRIBUTION FROM COLLISIONS

We consider a collision between a k-mer and a j-mer, with velocities $\mathbf{v}_j$ and $\mathbf{v}_k$ respectively, which results in formation of a $(k+j)$-mer. We derive a formula for the velocity of the resulting particle, $\mathbf{v}_{jk}$, and, averaging over the direction of $\mathbf{v}_j$ relative to $\mathbf{v}_k$, a formula for the average speed $\mathbf{v}_{k+j}$. Conservation of linear momentum is the only condition used in deriving this formula (a previous treatment[10] considered conservation of angular momentum and total energy), which gives the average speeds of clusters of all sizes in terms of the velocities of monomers. We then obtain the relative velocities of colliding clusters and thus the scaling parameter α. Although nonreactive collisions also take place, they do not change the nascent velocity distribution as long as most of the particles are monomers.

Without loss of generality, we assume that the collision occurs in the x-y plane, and that the k-mer is moving in the x direction with velocity $\mathbf{v}_k$ and the j-mer is moving with a velocity $\mathbf{v}_j$ in the x-y plane such that $\mathbf{v}_j\cdot\mathbf{v}_k=v_jv_k\cos\theta$. The resulting $(j+k)$-mer has a velocity $\mathbf{v}_{jk}$ which makes an angle ψ with the x axis. The masses of the particles are proportional to the numbers of monomers they contain. Then conservation of x and y momenta requires that

$$kv_k + jv_j\cos\theta = (j+k)v_{jk}\cos\psi,$$

$$jv_j\sin\theta = (j+k)v_{jk}\sin\psi.$$

Squaring both equations and adding eliminates ψ and yields

TABLE I. Velocities of $(j+k)$-mers, calculated from velocities of j-mers and k-mers using conservation of linear momentum.

j	k	$v(j)$	$v(k)$	$j+k$	$v(j+k)$
				1	1.000 00
1	1	1.000 00	1.000 00	2	0.666 67
1	2	1.000 00	0.666 67	3	0.527 78
1	3	1.000 00	0.527 78	4	0.448 46
2	2	0.666 67	0.666 67	4	0.444 44
2	3	0.666 67	0.527 78	5	0.391 52
1	4	1.000 00	0.447 12	5	0.394 98
1	5	1.000 00	0.393 25	6	0.355 96
2	4	0.666 67	0.447 12	6	0.353 31
3	3	0.527 78	0.527 78	6	0.351 35
1	6	1.000 00	0.354 08	7	0.325 91
2	5	0.666 67	0.393 25	7	0.323 95
3	4	0.527 78	0.447 12	7	0.322 25
1	7	1.000 00	0.324 03	8	0.301 90
2	6	0.666 67	0.354 08	8	0.300 43
3	5	0.527 78	0.393 25	8	0.298 90
4	4	0.447 12	0.447 12	8	0.298 08
1	8	1.000 00	0.300 08	9	0.282 16
2	7	0.666 67	0.324 03	9	0.281 06
3	6	0.527 78	0.354 08	9	0.279 76
4	5	0.447 12	0.393 25	9	0.278 72
1	9	1.000 00	0.280 42	10	0.265 59
2	8	0.666 67	0.300 08	10	0.264 75
3	7	0.527 78	0.324 03	10	0.263 67
4	6	0.447 12	0.354 08	10	0.262 64
5	5	0.393 25	0.393 25	10	0.262 17
1	10	1.000 00	0.263 94	11	0.251 42
2	9	0.666 67	0.280 42	11	0.250 78
3	8	0.527 78	0.300 08	11	0.249 88
4	7	0.447 12	0.324 03	11	0.248 94
5	6	0.393 25	0.354 08	11	0.248 28
1	11	1.000 00	0.249 86	12	0.239 15
2	10	0.666 67	0.263 94	12	0.238 66
3	9	0.527 78	0.280 42	12	0.237 91
4	8	0.447 12	0.300 08	12	0.237 06
5	7	0.393 25	0.324 03	12	0.236 37
6	6	0.354 08	0.354 08	12	0.236 05

$$(j+k)^2 v_{jk}^2 = k^2 v_k^2 + j^2 v_j^2 + 2jkv_j v_k \cos\theta.$$

The expression for v_{jk} must be averaged over θ according to

$$\langle v_{jk}\rangle = \frac{\int_0^\pi \sin\theta d\theta [k^2 v_k^2 + j^2 v_j^2 + 2jkv_j v_k \cos\theta]^{1/2}}{(j+k)\int_0^\pi \sin\theta d\theta}$$

$$= \frac{(kv_k + jv_j)^3 - |kv_k - jv_j|^3}{6(j+k)jkv_j v_k}. \quad (17)$$

Let us assume $k \geqslant j$. Then, if the velocities scale as j^α with $-1 < \alpha < 0$, $kv_k \geqslant jv_j$ and (17) becomes

$$v_{jk} = \frac{3(kv_k)^2 + (jv_j)^2}{3(j+k)kv_k}. \quad (18)$$

Before using (18) to calculate velocities explicitly, we verify whether scaling is consistent with (18).

Rewriting (18) and inserting $v_j = c_j^\alpha$, we have

$$3(j+k)^{\alpha+1}(k)^{\alpha+1} \approx 3k^{2\alpha+2} + j^{2\alpha+2}. \quad (19)$$

Since $j<k$, the left side is $3k^{2\alpha+2}[1+(\alpha+1)(j/k)+\cdots]$. The first term is equal to the first term on the right of (19), and the second term is $3(\alpha+1)k^{2\alpha+1}j$. If this is to equal $j^{2\alpha+2}$ from (19), we require $(\alpha+1)=\frac{1}{3}$ from the coefficient and $2\alpha+1=0$ from the exponent of j or of k. Thus α should be between $-\frac{2}{3}$ and $-\frac{1}{2}$ (it obviously cannot be both) for scaling. Our explicit calculations using (17) in fact give a value of α between $-\frac{2}{3}$ and $-\frac{1}{2}$.

We begin the calculation by taking $v_1=1=c$. Then, using (17) with $j=k=1$, $v_2=2c/3$ and v_3 (calculated from v_1 and v_2) $=19c/36$. Further results are listed in Table I and graphed in Fig. 1. Note that for a given value of $j+k$, there are $j+k-1$ ways to calculate v_{kj}, with about $\frac{1}{2}(j+k-1)$ different results, so we take v_{k+j} as the average of the v_{kj}. However, all

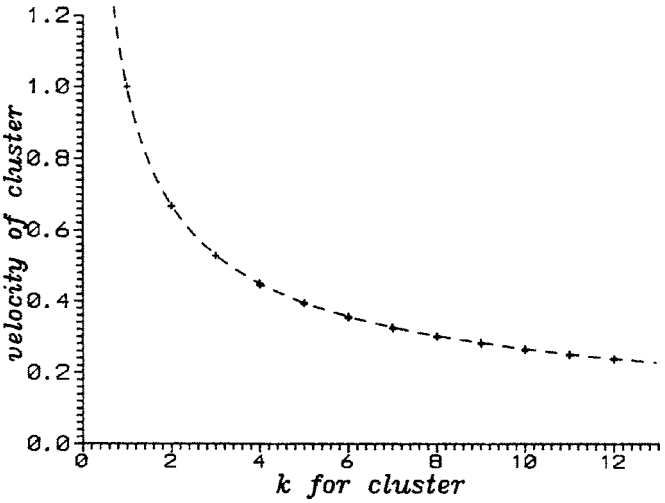

FIG. 1. Velocities of clusters of sizes k from 1 to 12 formed by coalescence, divided by the monomer velocity. For a given k, there are $k-1$ choices for the sizes of the clusters, i and j, which coalesce to form k. The results for all are shown in the graph, but they are so close together that the difference between them is not visible. The dashed line is the best fit of the results to pk^{α}; the parameters p and α are 0.9952 and −0.5765, respectively.

the results for a given $j+k$ (product cluster size) are so close together that the difference between them can hardly be seen in Fig. 1.

Also shown in Fig. 1 is a least-squares fit of v_k to the power function pk^{α}. The best fit is for $\ln p=-0.004\,47\pm.004\,63$ (i.e., $p=1$ within standard error) and $\alpha=-0.5765\pm0.0013$, with $R^2=0.9997$. Thus scaling is very accurate, and the value of α indeed lies between $-\frac{2}{3}$ and $-\frac{1}{2}$.

We now calculate the relative velocity of colliding clusters. Consider a j-mer, moving at velocity $\mathbf{v}_j$, colliding with an i-mer, with velocity $\mathbf{v}_i$, so the relative velocity is $\mathbf{v}_i-\mathbf{v}_j$. Averaging over the angle between $\mathbf{v}_i$ and $\mathbf{v}_j$, we obtain

$$\langle v_{\mathrm{rel}}\rangle=\frac{(v_j+v_i)^3-|v_j-v_i|^3}{6v_jv_i}.$$

Suppose $v_k=ck^a$ and that $j\ll i$. Then

$$\langle v_{\mathrm{rel}}\rangle\approx c\frac{i^{3a}[1+3(j^a/i^a)\cdots-(1-3(j^a/i^a)\cdots)]}{6j^ai^a}=ci^a.$$

The kernel K_{jk} is assumed proportional to the relative velocity and to the geometric cross section, $\pi(R_i+R_j)^2=\pi(i^{1/3}+j^{1/3})^2$, so the scaling parameters are $\mu=-(0.5765)$ and $\nu=2/3$. The numerical value of the integral $K(-0.5765,0.6667)$ is 2.1968, and the slope in (16) is 2.0711.

Translational kinetic energy is not conserved in a sticking collision. The change in kinetic energy is

$$m_{j+k}v_{j+k}^2-\tfrac{1}{2}m_jv_j^2-\tfrac{1}{2}m_kv_k^2=\tfrac{1}{2}m_1c^2[(j+k)^{1-2(0.5765)}-j^{1-2(0.5765)}-k^{1-2(0.5765)}],$$

where m_1 is the mass of a monomer and c its average velocity. This is negative, which means that some translational kinetic energy is converted into internal energy and/or rotational kinetic energy.

DISCUSSION

The Smoluchowski equations, Eq. (1), describe the growth of clusters by second-order reactions, in which a j-mer and a k-mer react to form a $(j+k)$-mer. We assume that only monomers are present at $t=0$. Equation (2) results if certain terms in Eq. (1), relatively small for large clusters, are neglected. Then, if all the second-order rate constants or kernels K_{jk} are equal, an exact solution is available. In the more interesting case of kernels which scale according to $K_{aj,bk}=a^{\mu}b^{\nu}K_{jk}$ for $j<k$, one can show that the population of k-mers for large k is given by $n_k=Ak^ae^{-bk}$, where A, a, and b are constants whose values depend on μ and ν, and, in the case of b, on time.

We show that $n_k=Ak^ae^{-bk}$ solves Eq. (1) for large k by direct substitution, assuming $K_{jk}=cj^{\mu}k^{\nu}$ for $j<k$. After showing that the parameter b decreases with time, we make some approximations in (1) which are valid for large k, and arrive at Eq. (8). At this point, there is no longer a distinction between odd and even k, which shows that any odd-even alternation in populations disappears in the asymptotic limit. In order for (8) to hold for all k, the parameter a must be independent of time.

This produces Eq. (12), which is satisfied provided that $a=-(\mu+\nu)$. Note that if a is negative, n_k is a monotonically decreasing function of k, so there is no most probable k. The normalization parameter A is defined in terms of a, b, and N (initial number of monomers) by Eq. (7), which assumes $n_k=Ak^ae^{-bk}$ for all k and approximates the sum over k by an integral. The time-dependent parameter b is always positive and obeys the differential equation (12), which shows that $b^{\mu+\nu-1}$ is a linear function of t. In the proof, we required $2+\mu+\nu+2a>0$ and $a+1>0$. This means $\mu+\nu<1$, which is guaranteed for physically consistent models.

Two cases of interest are the ballistic and diffusive models. In the diffusive model, the reacting particles diffuse together in the presence of other nonreactive, particles, and the kernel K_{jk} is the product of an average diffusion constant and an average particle radius. Then, assuming that the particles consist of closely packed monomers, $\mu+\nu=0$. In the ballistic model, K_{jk} is written as the product of a cross section and an interparticle velocity. At thermal equilibrium, the latter is inversely proportional to the square root of the reduced mass of the two particles, and the cross section, assumed to be proportional to the geometric cross section, scales as $j^{2/3}$, so that $\mu=-\frac{1}{2}$ and $\nu=\frac{2}{3}$.

We apply the Smoluchowski equations to clusters of He atoms formed in a nozzle-beam expansion. In this case, the particles with $k>1$ are created and destroyed by collisions, so they do not reach thermal equilibrium. Rather, their velocities are determined by the collisions which create them. Assuming only conservation of momentum, we calculated the velocity of a $(j+k)$-mer formed by collision of a j-mer with velocity v_j and a k-mer with velocity v_k. Averaging over the angle between the latter two velocities, we obtained Eq.(17) for v_{jk} and the results shown in Fig. 1 and Table I. To high accuracy, the velocity v_j scales as $j^{-0.577}$, so $\mu+\nu=\frac{2}{3}-0.577=0.090$.

In a reactive collision, some translational kinetic energy

is converted into internal energy and/or rotational kinetic energy. Thus, the nascent cluster is unstable, unless a subsequent event can remove the excess internal energy. This event is most likely a close encounter with another cluster.[14] The cross section for such an encounter is likely to be much bigger than the cross section for a reactive collision, so many such encounters can occur for each reactive collision.

Such near collisions would occur with the background gas in the diffusive case, rapidly establishing equilibrium between interparticle and internal degrees of freedom. Then the final temperature would reflect exothermicity of cluster formation in addition to the initial translational energy. Mukherjee *et al.*[15] have found from Monte Carlo calculations that, under certain conditions, the exothermicity of coalescence events can lead to a large increase in the temperature of the background gas and hence *larger* interparticle velocities, raising the values of the kernels for subsequent collisions. Our model, of course, does not involve background gas.

However, it is likely that many nonreactive collisions occur, but, if most of the clusters are monomers, most collisions would be between monomers and heavier particles. Then, because of the mass mismatch, these nonreactive collisions would not change the nascent velocity distribution.

The distribution $n_k = Ak^a e^{-bk}$ is monotonically decreasing for $a \leqslant 0$; i.e., $\mu + \nu \geqslant 0$. To yield a distribution peaked at some value of k, $\mu + \nu$ would have to be negative. For the simple scaling case ($\mu = \nu = \omega$) Botet and Jullien[6] showed that 2ω is equal to a positive term plus α, where α is the scaling factor of particle velocity with particle mass. Thus a peaked distribution requires that α be substantially less than $-\frac{1}{2}$ (its value for the ballistic model). Having looked at the requirements of conservation of energy, angular momentum and, now, linear momentum, we are forced to conclude that α will never be low enough in a gas-phase coalescing system to produce a peaked distribution.

Nevertheless, the experimental literature contains many apparent examples of peaked cluster distributions. We suggest that cluster evaporation/dissociation, neglected in the Smoluchowski model, is responsible for their existence. Dissociation is an endothermic process. If dissociation occurs after intramolecular vibrational relaxation in a cluster leaves a vibrational mode with sufficient internal energy to dissociate, we should expect the fragments produced to have less translational energy than the fragments which coalesced to form the cluster in the first place. Extensions of nucleation theory which include evaporation as well as condensation processes are possible.[2,16] The asymptotic solution has been generalized to describe kernels of all sizes.[17]

The Smoluchowski equations have been applied to a variety[2] of different systems, for some of which Monte Carlo and other simulations are appearing.[17,18] Applied to formation of clusters in He and H_2 nozzle-beam expansions (following paper), it leads to very useful results. Of course, the fact that an experimental particle-size distribution is of the form $Ak^a e^{-bk}$ does not prove that the Smoluchowski equations describe the system.[19]

CONCLUSIONS

The Smoluchowski equations, a set of differential equations for the number densities of clusters of all sizes, describe coalescence growth, ignoring cluster dissociation. The reaction between clusters of sizes j and k to form a cluster of size $j+k$ is assumed to be second order, with rate constant K_{jk}. If K_{jk} scales, so that $K_{aj,bk} = a^\mu b^\nu K_{ij}$ for $j \leqslant k$, the number densities for large k approach $n_k = Ak^a e^{-bk}$, where $a = -(\mu + \nu)$, and b decreases with time according to (13). There is thus no odd-even alternation in the population. We have given a transparent proof of this asymptotic form of n_k. By invoking conservation of linear momentum in the reactive collisions, we have shown that the velocities in the nascent cluster distribution scale as $k^{-0.577}$, which is somewhat different from the scaling in the ballistic model. It is concluded that the Smoluchowski equations will never lead to peaked population distributions because of the neglect of dissociation.

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