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Jerry Goodisman
Syracuse University

J. Chaiken
Syracuse University

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Scaling and the Smoluchowski equations

J. Goodisman and J. Chaikena

Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100

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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 Kjk. The Kjk are said to be scale if Kj/k=λ^a γ^b Kjk for 1≤k. It can then be shown that, for large k, the number density or population of k-mers is given by Ak^e^−bk, where A is a normalization constant (a function of a, b, and time), a=−(μ+n), and b=μ+n 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/√mk (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 μ+n=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 μ+n.


INTRODUCTION

Smoluchowski’s equations for coalescence growth in condensed phases, proposed1 in 1917, continue to have applications2,3 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 demonstrated4–8 for the case of kernels which scale. (Exact solutions are also possible when the kernels have special forms2,4,8 and power series solutions have been attempted.9) The kernel Kij, which specifies the rate of combination of i-mers and j-mers, is sometimes5 said to scale if Ksiaj =α^ω^j Kij, 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 Ksiaj=α^2ω^β^Kij for i=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=A(k^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 workers4–8 using different mathematical methods.

For the simple scaling kernels (Ksiaj=α^2ω), we were able to show10 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 super-particle 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 (Ksiaj=α^2β^Kij), assumed to hold for i=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

4Electronic mail: jchaiken@syr.edu

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

\[ \frac{dn_k}{dt} = \sum_{i=1}^{k'} K_{i,k-n_k n_{i-k}} - \sum_{i=1}^{\infty} K_{k,i-n_k n_{i-k}}. \]  

(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, \(K_{ij} = K_{ji}\).

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

\[ \frac{dn_k}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} K_{i,k-n_k n_{i-k}} - \sum_{i=1}^{\infty} K_{k,i-n_k n_{i-k}}. \]  

(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 \(n_1(0) = N\delta_{11}\), conservation of particles requires

\[ \sum_{k=1}^{\infty} n_k = N \]  

(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

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

(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.,

\[ K_{ki,ij} = \lambda^{2a_i} K_{ij}, \]

where \(\omega\) 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 \(\omega\). 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

\[ K_{ai,bi} = \alpha^i \beta^i K_{ij}, \]

for \(i \leq j\). Physically, neither \(\mu\) nor \(\nu\) can be greater than 1, \(5\) 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.,

\[ \sum_{k=1}^{\infty} n_k = \sum_{k=1}^{\infty} k^{a+1} e^{-bk} = N. \]  

(5)

The average value of a cluster size is given by

\[ \langle k \rangle = \frac{\sum_{k=1}^{\infty} k^a e^{-bk}}{\sum_{k=1}^{\infty} k^{a+1} e^{-bk}}. \]  

(6)

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

\[ -\frac{d\langle k \rangle}{dt} = \frac{\sum_{j=1}^{k} e^{-b(j+k)} j^a k^a(j^2 - 2jk + k^2)}{2 \left[ \sum_{j=1}^{\infty} j^a e^{-bj} \right]^2}. \]

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

\[ A = \frac{N}{\sum_{k=0}^{\infty} k^{a+1} e^{-bk}} \int_0^{\infty} dx x^{a+1} e^{-bx} \Gamma(a + 2). \]  

(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 \(A^k e^{-bk}\) 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 \(K_{ij} = c i^{\mu} j^{\nu}\) for \(i \leq j\) and \(K_{ji} = K_{ij}\). Then substituting and dividing by \(n_k\) gives

\[ \frac{1}{A} \frac{dA}{dt} + (\ln k) \frac{da}{dt} - \frac{db}{dt} = cA \sum_{i=1}^{k} i^{\mu+a}(k-i)^{\nu+1} k^{-a} - cA \sum_{i=1}^{k} k^{i^{\mu+a} e^{-bi}} - cA \sum_{i=k+1}^{\infty} i^{\nu+a} e^{-bi} - cA K_{ai,bi} e^{-bk}. \]  

(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

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

\[
\sum_{j=m}^{n} f(j) \approx \int_{m}^{n} dx f(x) + \frac{1}{2} f(a) + \frac{1}{2} f(b),
\]

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

\[
- \frac{k}{cA} \frac{db}{dt} = \int_{1}^{1/2} x^{\mu+\nu} (k-x)^{\nu-a} k^{-a} dx + \frac{1}{2} (k-1)^{\nu-a} k^{-a} + \frac{1}{2} \int_{1}^{k} k^{\mu+\nu} e^{-bx} dx - \frac{1}{2} k^{\mu+\nu} e^{-b}
- \frac{1}{2} k^{\mu+\nu} e^{-bk} - \int_{k}^{\infty} x^{\mu+\nu} k^{a} e^{-bx} dx
- \frac{1}{2} (k+1)^{\mu+\nu} k^{a} e^{-bk+1}.
\]  
(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 \( k^{a} \); 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 \( k^{\mu+\nu+a} e^{-bk} \), are also negligible (\( b \) is positive for all \( t \)). This leaves

\[
- (cA)^{-1} \frac{d b}{d t} = k^{\mu+\nu+a+1} \int_{1/2}^{1} y^{\mu+\nu} (1-y)^{\nu-a} dy
- k^{\mu+\nu+a+1} \int_{1/2}^{1} y^{\nu} e^{-bky} dy
- k^{\mu+\nu+a+1} \int_{1/2}^{\infty} y^{\mu+\nu} e^{-bky} dy.
\]  
(11)

If \( \mu \) and \( \nu \) are less than 1, the last two integrals are less than

\[
\int_{0}^{\infty} y^{\nu} e^{-bky} dy = \Gamma(a+1) \left( \frac{b}{k} \right)^{\nu+1},
\]

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

Using (7) for \( A \), (11) becomes

\[
- \frac{k \Gamma(a+2) \frac{db}{dt}}{Nc b^{\nu+2}} = k^{\mu+\nu+a+1} \int_{0}^{1/2} y^{\mu+\nu} (1-y)^{\nu-a} dy
\]

\[
\equiv k^{\mu+\nu+a+1} K(\mu, \nu).
\]  
(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

\[
\frac{b^{-(a+1)} - b_{0}^{-(a+1)}}{a + 1} = Nc \left[ \frac{K(\mu, \nu)}{\Gamma(a+2)} \right] t,
\]  
(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

\[
K(\mu, \nu) = \int_{0}^{1/2} y^{-\nu} (1-y)^{-\mu} dy
\]

\[
= \sum_{n=0}^{\infty} \frac{\mu(\mu + 1) \cdots (\mu + n - 1)}{n!}.
\]

The series converges rapidly.

**MEANING OF SCALING PARAMETERS**

If simple scaling obtains, i.e., \( K_{i,j} = a^{\mu} b^{\nu} K_{ij} \), the scaling parameter for the kernels is given \(^2\) by

\[
2\omega = \alpha + (d - d_{c})/D.
\]  
(14)

Here, \( \alpha \) 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 \( d_{c} \) 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 \( \omega \) can be found by simple physical arguments. The kernels or rate constants \( K_{ij} \) 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, the relative velocity for a \( j \)-mer and a \( k \)-mer may be calculated\(^{13}\) from the Maxwell distribution to be

\[
v_{jk} = \sqrt{\frac{8kT(m_j + m_k)}{\pi m_j m_k}},
\]

(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 \( \sigma_{jk} \), 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 \( D_{jk} \) 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 \( D_{ij} \) 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 \( \mu \) and \( \nu \) 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

\[
\sqrt{\frac{i + j}{ij}} \left( i^{1/3} + j^{1/3} \right)^2,
\]

where the first factor comes from the relative velocity of the colliding particles and the second from the cross section. For \( i < j \), 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

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

(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 \( v_j \), 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 \( v_j \) and \( v_k \) respectively, which results in formation of a \((k+j)\)-mer. We derive a formula for the velocity of the resulting particle, \( v_{jk} \), and, averaging over the direction of \( v_j \) relative to \( v_k \), a formula for the average speed \( v_{avg} \). 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 \( \alpha \). 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 \( v_k \) and the \( j \)-mer is moving with a velocity \( v_j \) in the \( x-y \) plane such that \( v_j = v_x + p_j \cos \theta \). The resulting \((j+k)\)-mer has a velocity \( v_{jk} \) which makes an angle \( \psi \) 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

\[
k v_k + j v_j \cos \theta = (j+k) v_{jk} \cos \psi,
\]

\[
j v_j \sin \theta = (j+k) v_{jk} \sin \psi.
\]

Squaring both equations and adding eliminates \( \psi \) and yields
\[ (j + k)^2 v_{jk}^2 = k^2 v_j^2 + j^2 v_k^2 + 2 j k v_j v_k \cos \theta. \]

The expression for \( v_{jk} \) must be averaged over \( \theta \) according to

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

\[
= \left( \frac{(kv_k + j v_j)^3 - [kv_k - j v_j]^3}{6(j + k)kv_j v_k} \right)^{1/2}.
\]

(17)

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

\[
v_{jk} = \frac{3(kv_k)^2 + (jv_j)^2}{3(j + k)kv_k}. \tag{18}
\]

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

\[
3(j + k)^{\alpha+1}(k)^{\alpha+1} \approx 3 k^{2\alpha+2} + j^{2\alpha+2}. \tag{19}
\]

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 \( (\alpha+1)\approx \frac{1}{2} \) from the coefficient and \( 2\alpha+1=0 \) from the exponent of \( j \) or \( k \). Thus \( \alpha \) should be between \(-\frac{1}{3} \) and \(-\frac{1}{2} \) (it obviously cannot be both) for scaling. Our explicit calculations using (17) in fact give a value of \( \alpha \) between \(-\frac{1}{5} \) 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 \( v_{k,j} \), with about \( \frac{1}{2} (j+k-1) \) different results, so we take \( v_{k,j} \) as the average of the \( v_{k,j} \). However, all
The kernel \( K_{jk} \) is very accurate, and the value of \( \frac{v}{H} \) between them is not visible. The dashed line is the best fit of the results to the power function \( v^\alpha \); the parameters \( p \) and \( \alpha \) 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 \( pk^a \). The best fit is for \( \ln p = -0.004 47 \pm 0.004 63 \) (i.e., \( p = 1 \) within standard error) and \( a = -0.5765 \pm 0.0013 \), with \( R^2 = 0.9997 \). Thus scaling is very accurate, and the value of \( \alpha \) indeed lies between \(-\frac{1}{3}\) and \(-\frac{2}{3}\).

We now calculate the relative velocity of colliding clusters. Consider a \( j \)-mer, moving at velocity \( v_j \), colliding with an \( i \)-mer, with velocity \( v_i \), so the relative velocity is \( v_i - v_j \). Averaging over the angle between \( v_i \) and \( v_j \), we obtain

\[
\langle v_{\text{rel}} \rangle = \frac{(v_i + v_j)^3 - (v_j - v_i)^3}{6v_ip_i}.
\]

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

\[
\langle v_{\text{rel}} \rangle = \frac{1}{6} \frac{c^3}{p^a} \left[ 1 + 3(j^a/i^a) \cdots - (1 - 3(j^a/i^a) \cdots) \right] = ct^a.
\]

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

\[
m_{j+k}v_{\text{rel}}^2 - \frac{1}{2}m_jv_i^2 - \frac{1}{2}m_jv_k^2 = \frac{1}{2}m_{j+k}c^2[(j+k)^{1-2(0.5765)} - j^{1-2(0.5765)} - k^{1-2(0.5765)}],
\]

where \( m_j \) 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 \( K_{aj,bk} = a^bb^xK_{jk} \) for \( j < k \), one can show that the population of \( k \)-mers for large \( k \) is given by \( n_k = A_k e^{-bk} \), where \( A \), \( a \), and \( b \) are constants whose values depend on \( \mu \) and \( \nu \) and, in the case of \( b \), on time.

We show that \( n_k = A_k e^{-bk} \) solves Eq. (1) for large \( k \) by direct substitution, assuming \( K_{jk} = c j^b k^a \) 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 \( n_k = A_k e^{-bk} \) 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 \( b^a + b^{-1} \) is a linear function of \( t \). In the proof, we required \( 2 + \mu + \nu \geq 2a > 0 \) 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 \( k \geq 1 \) 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 \( \mu + \nu = 2 \cdot 0.577^{0.909} \).

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.

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. 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 $n_k=Ak^ke^{-bk}$ is monotonically decreasing for $\alpha=0$; i.e., $\mu+\nu\geq 0$. To yield a distribution peaked at some value of $k$, $\mu+\nu$ would have to be negative. For the ballistic model $\alpha=-(\mu+\nu)$, 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 dissipation.

**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 $K_{jk}=a^{j+b}K_j$ for $j\leq k$, the number densities for large $k$ approach $n_k=Ak^ke^{-bk}$, where $\alpha=-(\mu+\nu)$, and $b$ decreases with time according to (13).