Chemistry - Faculty Scholarship

College of Arts and Sciences

8-18-2006

Application of Scaling and Kinetic Equations to Helium Cluster Size Distributions: Homogeneous Nucleation of a Nearly Ideal Gas

J. Chaiken
Syracuse University

Jerry Goodisman
Syracuse University

Oleg Komilov
Max-Planck-Institut für Dynamik und Selbst-Organisation

J. Peter Toennies
Max-Planck-Institut für Dynamik und Selbst-Organisation

Follow this and additional works at: https://surface.syr.edu/che

Part of the Chemistry Commons

Recommended Citation

Application of scaling and kinetic equations to helium cluster size distributions: Homogeneous nucleation of a nearly ideal gas

J. Chaiken, J. Goodisman, Oleg Kornilov, and J. Peter Toennies

---

Additional information on J. Chem. Phys.

Application of scaling and kinetic equations to helium cluster size distributions: Homogeneous nucleation of a nearly ideal gas

J. Chaiken[a)] and J. Goodisman
Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100

Oleg Kornilov and J. Peter Toennies
Max-Planck-Institut für Dynamik und Selbst-Organisation, Bunsenstrasse 10, 37037 Göttingen, Germany

A previously published model of homogeneous nucleation [Villarica *et al.*, J. Chem. Phys. **98**, 4610 (1993)] based on the Smoluchowski [Phys. Z. **17**, 557 (1916)] equations is used to simulate the experimentally measured size distributions of ^{4}He clusters produced in free jet expansions. The model includes only binary collisions and does not consider evaporative effects, so that binary reactive collisions are rate limiting for formation of all cluster sizes despite the need for stabilization of nascent clusters. The model represents these data very well, accounting in some cases for nearly four orders of magnitude in variation in abundance over cluster sizes ranging up to nearly 100 atoms. The success of the model may be due to particularities of ^{4}He clusters, i.e., their very low coalescence exothermicity, and to the low temperature of 6.7 K at which the data were collected. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2218837]

INTRODUCTION

Coalescence growth is ubiquitous in nature[1,2] and technology, being manifested in processes as disparate as homogeneous nucleation[3] and electromigration-induced production of hillocks[4] and voids[5] in metal patterns in integrated circuits. For nearly a century and a half the log-normal size distribution[6] has been employed empirically to represent distribution functions obtained from many such sources, including not only objects and particles produced by building-up processes but also objects and particles produced by breaking-down processes. In practice, however, it has been found problematic to relate the properties of a specific log-normal distribution to the microscopic conditions that produced it, so as to allow selection of reaction conditions to create a specific distribution.[7]

In the past there have been two fundamentally different approaches: the classical statistical thermodynamic theory, which dates back to Gibbs,[8] Volmer and Weber,[9] and Becker and Döring,[10] and a kinetic theory that goes back to Smoluchowski.[11] The statistical thermodynamic theory is best suited for dealing with slow nucleation processes such as occurrence in cloud chambers, certain supersonic nozzles, and shock tube flows.[12] In these situations a steady state can be assumed so that the system remains close to thermodynamic equilibrium. On the other hand, for free jet expansions dealt with here the characteristic flow time is much shorter than the time needed to reach steady state conditions. Thus a kinetic theory involving the solution of a set of reaction equations is more appropriate. The successful implementation of such a theory, however, requires knowledge of many different two- and three-body cross sections which today is not available even for such an apparently simple system as

helium.[12] The simple but elegant theory originally created by Smoluchowski and extended by others[13–17] assumes that the cross sections obey scaling relations and that only two-body interactions need to be considered.[18] In exploring this model two of the present authors discovered[18] that the log-normal distribution was closely related to the asymptotic solutions to the Smoluchowski equations appropriate to large cluster sizes. Since the early work we have continued to search for systems that could provide a revealing glimpse into the applicability of this model and the physical picture of coalescence growth it entails. This paper reports the results of applying the model to recently obtained data[19] of size distributions of small ^{4}He clusters in a free jet expansion.

Probably the main obstacle to applying the model is the difficulty in obtaining experimental distributions unambiguously produced by a coalescence growth process, uncontaminated with artifacts of either the cluster/object sizing or cluster/object detection procedures. For example, in the study of clusters produced in free jet or nozzle beam expansions,[20] the use of mass spectrometry requires discussion of fragmentation accompanying ionization. If not properly accounted for, fragmentation can lead to the overcounting of small cluster sizes and undercounting of larger sizes. Alternatively, in the study of clusters produced by laser chemistry of organometallics[21] and trapped as condensed phase(s), it is unknown whether experimentally obtained distributions incorporate the effects of agglomeration during the particle collection process as well as the effects of the coalescence growth process. Granqvist *et al.*[22] states that coalescence growth systems produce log-normal size distributions skewed towards larger sizes. Such distributions are easily distinguished from those of other systems, like those resulting from Ostwald ripening,[22] whose properties are dominated by evaporation of monomers from larger clusters. Such distributions are skewed towards smaller sizes. In all these

---
[a)]Electronic mail: jchaiken@syr.edu

125, 074305-1

cases, peaked distributions, that is, distributions with a most probable size, are commonly observed. In the helium droplet distributions analyzed in this paper, as in all the neutral noble gas clusters we have previously analyzed,[18] there is no peak or most probable size.

The Smoluchowski model attempts to exploit the apparent scaling of clustering rate constants with cluster size, deduced from the size distribution, to express all rate constants in terms of the dimerization rate constant. Despite being touted in elementary chemistry and physics texts as a nearly "ideal gas," helium turns out to be an extremely complex system when it comes to connecting cluster abundance data to a kinetic model. The helium atom-helium atom cross section has been thoroughly investigated for collision energies including the energies of interest here, i.e., $4.2\ K < T < 12\ K$.[23–25] The helium dimer has only one extremely weakly bound state at 1.3 mK and an average bond length of about 50 Å.[26] The trimer is predicted to have, in addition to its ground state, a long range Efimov state,[27] with a binding energy of only about 2 mK,[28] but so far its existence has not been confirmed experimentally.[29] Recent experiments reveal that in collisions between the helium dimer and helium or other atoms, it is possible for an atom to pass *in between* the two atoms of the dimer and to some extent between atoms of the trimer without necessarily causing dissociation of the cluster.[30] On the other hand, this no longer holds for larger clusters, and the cross sections are expected to increase relatively smoothly with size.

In this study we deduce effective rate constants which we relate to effective cross sections. These effective parameters implicitly include angular and energetic averaging and other effects. We shall use abundance data for larger clusters, ninemers, and larger. The idea here is that a scaling-type model is most appropriate for larger clusters. For example, based on the previous observations on small clusters, it is reasonable to expect that scaling more accurately represents the properties of n-mers through $n+5$-mers when n is relatively large than it represents the variation in the properties of monomers through five-mers. Also, the observed variation of the populations of larger clusters can be a statistically unbiased basis for predicting what the populations of smaller clusters would be in the absence of size-specific interactions. Such interactions, leading to magic-number-sized clusters, are expected to be most pronounced for the smallest cluster sizes.

How helium clusters accommodate or dissipate the exothermicity of cluster formation is also complicated. First we note that the dimer binding energy, 1.3 mK, is very small compared with the temperature in the early stages of the expansion, so that a considerable amount of translational energy must be dissipated during the formation of a stable dimer. The dissipation of energy by a small nascent cluster must occur either by collision of the nascent cluster with another body or, in the case of larger clusters, by evaporation of one or more monomers. In other systems,[31] the bound state potential well is very deep compared to the translational temperature of the monomers, making stabilization by evaporation competitive with and perhaps even less important than radiative cooling. This is certainly not the case for helium clusters.

We shall first briefly explain how the new helium data[32] were obtained. The theoretical model is described in the preceding paper of this journal so we shall introduce only sufficient detail to allow a description of the application of the model to these data. The analysis produces a value of the effective dimerization cross section and an equation which can be used to predict the distribution for varying source pressure P_o, nozzle temperature T_o, and nozzle diameter d_o. We shall compare the cross section with other cross sections in the literature. We shall also discuss the consequences of the observed success of this model with regard to our conceptual framework for understanding and predicting coalescence growth phenomena.

EXPERIMENT

The experimental apparatus is similar to one described in detail elsewhere[33] and so will only be briefly discussed here. The clusters are formed in a free expansion of helium gas through a 5 μm orifice with comparable length. The beam formed during the expansion is skimmed after 1 cm of propagation and subsequently collimated twice with 5 μm slits at locations 13 and 83 cm further downstream. The extremely well collimated beam impinges on a 100 nm period SiN transmission diffraction grating located 93 cm from the orifice. After the expansion, all clusters, independent of mass, have velocities within ±2% of the hydrodynamic flow rate that defines the center-of-mass beam velocity. The clusters' de Broglie wavelengths are inversely proportional to their masses so the angular dispersion by the grating depends only on their masses. All mass-selected clusters are detected as He_2^+ dimer ions produced during the 80 eV electron impact ionization of the clusters in the mass spectrometer detector located 255 cm from the orifice. Using the dimer signal guarantees unequivocal rejection of monomer background as a source of artifacts. Based on theoretical simulations for large clusters[3] and experimental data for small clusters, $N \leq 6$, the He^{2+} ion yield is nearly independent of cluster size. Considerable effort has been expended to assure that this separation and detection scheme reveals the true abundance of the various clusters.[32] In addition, the distribution is corrected for the variation in grating throughput due to the weak van der Waals attraction between the rare gas atoms and clusters and the grating surface.[34]

MODEL

We analyze the process of cluster formation using Smoluchowski's equations for coalescence growth. We assume that, at time $t=0$, i.e., the time origin, only monomers exist, and that monomers can stick together on collision to form dimers, monomers and dimers can stick together to form trimers, etc.,

$$He + He \rightarrow He_2,$$

$$He + He_2 \rightarrow He_3,$$
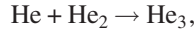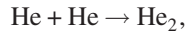
etc.

Only binary collisions are considered, including collisions between all clusters existing at any time. We further assume that all coalescence events are irreversible. It should be pointed out that, in the actual experiment, a few percent of the total helium atoms in the orifice already exist as dimers and trimers before expansion begins. One could take account of this by defining the time origin as sufficiently upstream that there are essentially only monomers present. On the other hand we note that simulations in which some dimers or trimers are present at $t=0$ eventually lead to the same distribution functions in the limit of long time.

The kinetic equations are then the equations for 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 n-1. 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 or number density of k-mers and K_{ij} the kernel or rate constant for reaction of i-mers with j-mers, we have

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

where $k'=k/2$ if k is even and $(k-1)/2$ if k is odd. The last term arises because the 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, i.e., kernels, reflect the mass transfer rates and the reactive cross sections. It is assumed that they scale such that $K_{\alpha i, \beta j} = \alpha^{\mu} \beta^{\nu} K_{ij}$ for $i \leqslant j$ where μ and ν are the scaling parameters. If $i \ll j$, the parameter μ, generally negative, describes the scaling of velocity or mass transfer rate with particle size, whereas ν, generally positive, describes the scaling of cross section with particle size. If $i > j$, the parameters μ and ν exchange places. The scaling and symmetry conditions on K_{ij} imply that

$$K_{ij} = K_{11} i^{\mu} j^{\nu} \quad \text{for } i < j \quad \text{and} \quad K_{ij} = K_{11} i^{\nu} j^{\mu} \quad \text{for } i > j, \quad (2)$$

where K_{11} is the dimer formation rate constant. Of course, $K_{ji}=K_{ij}$. Thus the predicted distributions depend only on the two scaling parameters μ and ν and the single rate constant K_{11}.

As we have shown directly in the preceding paper[35] and others[13–17] have elegantly demonstrated, there is an asymptotic solution to Eq. (1), valid for large cluster sizes, in the case of scaled kernels. The number density of k-mers n_k approaches $Ak^a e^{-bk}$ for large k, where A and a depend on μ and ν, and b also depends on μ and ν and also on the time. The parameter A is a normalization constant, assuring that at any time

$$N = \sum_{j=1}^{\infty} j n_j, \quad (3)$$

where N is the initial number density of monomers. Our demonstration[18,35] involves substituting $Ak^a e^{-bk}$ for n_k in Eq. (1) and making approximations valid for large k, i.e., $k \rightarrow \infty$.

$$Ak^a e^{-bk} \rightarrow n_k.$$

It is shown that, for (1) to be satisfied by $Ak^a e^{-bk}$, the parameter a must equal $-(\mu+\nu)$ independent of time, and the parameter b must vary with time according to

$$\frac{b^{-(a+1)} - b_0^{-(a+1)}}{a+1} = NK_{11}t \left[\frac{C(\mu,\nu)}{\Gamma(a+2)} \right], \quad (4)$$

where b_0 is the apparent value of b at $t=0$ and

$$C(\mu,\nu) \equiv \int_0^{1/2} y^{\mu+a}(1-y)^{\nu+a} dy.$$

Equation (4) shows that b decreases with time when $a+1$ is positive. Furthermore, a plot of $b^{-(a+1)}$ vs t is linear, with the slope proportional to $K_{11}N$, and a plot of $b^{-(a+1)}$ vs N is also linear, with the slope proportional to $K_{11}t$. In principle, this allows one to derive a value of K_{11} from the oligomer populations n_k for large k.

In general, the scaling parameters μ and ν contain the physical information describing the conditions of the coalescence growth process described by the kernels.[13,14] Two cases of interest are the ballistic model and the Brownian model. In the ballistic model, the particles interact directly without intervening collisions, i.e., each collision is a potential coalescence event. The kernels or rate constants K_{jk} are products of the relative velocities of the particles and their reactive cross sections. For particles at thermal equilibrium in a gas phase, the relative velocity for a j-mer and a k-mer may be calculated from the Maxwell distribution to be

$$v_{jk} = \sqrt{\frac{8kT(m_j + m_k)}{\pi m_j m_k}}, \quad (5)$$

where m_j is the mass of a j-mer, so v_{jk} is proportional to $\sqrt{(i^{-1}+j^{-1})}$. The reactive cross sections are assumed proportional to the classical geometrical cross sections, which are

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

where R_j is the effective radius of a j-mer. For spherical particles, the volume of a j-mer, $4\pi R_j^3/3$, is proportional to j and R_j is proportional to $j^{1/3}$. Thus K_{ij} is proportional to

$$(i^{-1} + j^{-1})^{1/2}(i^{1/3} + j^{1/3})^2. \quad (5a)$$

For $i \ll j$, this becomes proportional to $i^{-1/2} j^{2/3}$, so that $\mu = -1/2$, $\nu = 2/3$, and $a = -1/6$. Then (4) becomes

$$b^{-5/6} - b_0^{-5/6} = Nct \left[\frac{5C\left(-\frac{1}{2}, \frac{2}{3}\right)}{6\Gamma\left(\frac{11}{6}\right)} \right].$$

Numerical evaluation of C shows that the square bracket is equal to 2.2192.

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. The radial diffusion current is proportional to R_j+R_k, to the bulk concentration of k-mers, and to the mutual diffusion coefficient $D_{jk}=D_j+D_k$, with D_j 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 $(R_j^{-1}+R_k^{-1})\times(R_j+R_k)$. Since R_j is proportional to $j^{-1/3}$, the scaling exponents μ and ν [see Eq. (2)] are $-1/3$ and $+1/3$ in this case.

In applying the scaling theory to cluster formation in a helium-atom free jet expansion, the Brownian model is inappropriate because in the neat expansion all collisions are potential coalescence events, i.e., there are no nonreactive particles. The ballistic model is problematic for small clusters because it is unlikely that every collision leads irreversibly to coalescence. For large k, on the other hand, it may be that all collisions do result in coalescence but that sometimes monomers or other clusters evaporate off nascent clusters. A more serious problem is that clusters that are produced by coalescence/evaporation should have a translational energy distribution reflecting the energy transfer in the coalescence/evaporation collisions. The translational energy distribution for clusters that have not been involved in a coalescence event will reflect the temperature of the gas reservoir; the thermodynamic equations describing the expansion with equilibrium established and no coalescence is well known. However, establishing thermal equilibrium and the velocity distribution described by Eq. (5) requires many nonreactive collisions. Since most of the collisions in our model are reactive, we need to know the velocity distribution established by the reactive collisions.

As we have shown in detail in the preceding paper,[35] for a collision between a j-mer with velocity v_j and a k-mer with velocity v_k, which results in formation of a $(k+j)$-mer, it is straightforward to calculate the velocity of the resulting particle, v_{k+j}, using conservation of translational momentum. Then, averaging over the direction of v_j relative to v_k, we obtain a formula for the nascent speed v_{k+j} in terms of v_k and v_j. By repeated use of this formula, we calculate the nascent distribution of velocities of clusters of all sizes in terms of the velocities of monomers (see Table III in Ref. 35). A linear fit of the logarithm of calculated v_k/v_1 for $k=1,\dots,12$ to $\ln(p)+\alpha\ln(k)$ gives $\ln p=-0.004\,47\pm0.00463$ (i.e., $p=1$ within standard error) and $\alpha=-0.5767\pm0.0013$, with correlation coefficient $r^2=0.9997$. Thus $v_k/v_1=k^\alpha$ and, judging by r^2, the scaling is very accurate. 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 $\mu=-(0.5767)$ and $\nu=2/3$. Thus $\mu+\nu=0.090$, which is smaller than the value of 0.167 found for the equilibrium ballistic model. With $a=-(\mu+\nu)=-0.090$ we have

$$b^{-0.910}-b_0^{-0.910}=NK_{11}t\left[\frac{0.910C\left(-0.5765,\dfrac{2}{3}\right)}{\Gamma(1.910)}\right]. \quad (6)$$

The numerical value of the integral $C(-0.5765,0.6667)$ is 2.1968 and the square bracket in (6) equals 2.0711.

ANALYSIS OF DATA

We begin with a set of n_k, measured populations of clusters of sizes k, such as those shown by the experimental points in Fig. 1. To extract values of the parameters, we seek the best fit of all the n_k to the asymptotic form, Ak^ae^{-bk}. Because the values of n_k vary over several orders of magnitude, we define "best fit" as minimization of the sum of the *relative* squared deviations between measured and calculated values, rather than the sum of the squared deviations, which would be dominated by the first few points. Thus, we minimize

$$S=\sum_k\left(\frac{n_k-Ak^ae^{-bk}}{n_k}\right)^2. \quad (7)$$

In fitting the experimental points the value of $a=-(\mu+\nu)$ is fixed by the microscopic mass transport condition of the expansion (see above), whereas A and b can be allowed to vary as they depend on the macroscopic conditions. Then S is to be minimized with respect to the two parameters A and b. We first choose $a=-1/6$ (i.e., 0.167 of the ballistic model) and find the best values of A and b, and then repeat the process with $a=-0.090$ (coalescence model). Only these two choices are potentially appropriate for all the experimental conditions used in this study.

Numerical results are shown in Table I, including the number of data points for each pressure, the sum of the squared relative deviations S, and the best-fit values of the parameters A and b. The root-mean-square relative deviation $\sqrt{(S/n)}$, where n is the number of data points, is between 0.16 and 0.30. The fit is slightly worse (S slightly larger) for $a=-0.167$ than for $a=-0.090$, but the difference is not important because most of the deviation is due to the effect of magic numbers on the distribution. The fits for the latter choice are shown in Fig. 1 because this choice of a is most appropriate to the coalescence conditions. It properly includes the scaling of the clusters' nascent velocity distribution in the ballistic limit, i.e., each collision results in coalescence and the clusters do not equilibrate their velocities between coalescence events. We find that S increases as the source pressure decreases for both values of a. For lower pressure, the distribution is dominated by smaller clusters and the effects of magic numbers are more pronounced at smaller sizes, increasing S. We do not estimate the uncertainties for the parameters for reasons to be described below.

According to Eq. (4), $b^{-(a+1)}$ should be linear in Nt, where N is the initial monomer density, which is equal to P_o/kT_o according to the ideal gas law. Since T_o and P_o are used to calculate the value of the *initial* number density of monomers, T_o is the temperature of the gas in the source,
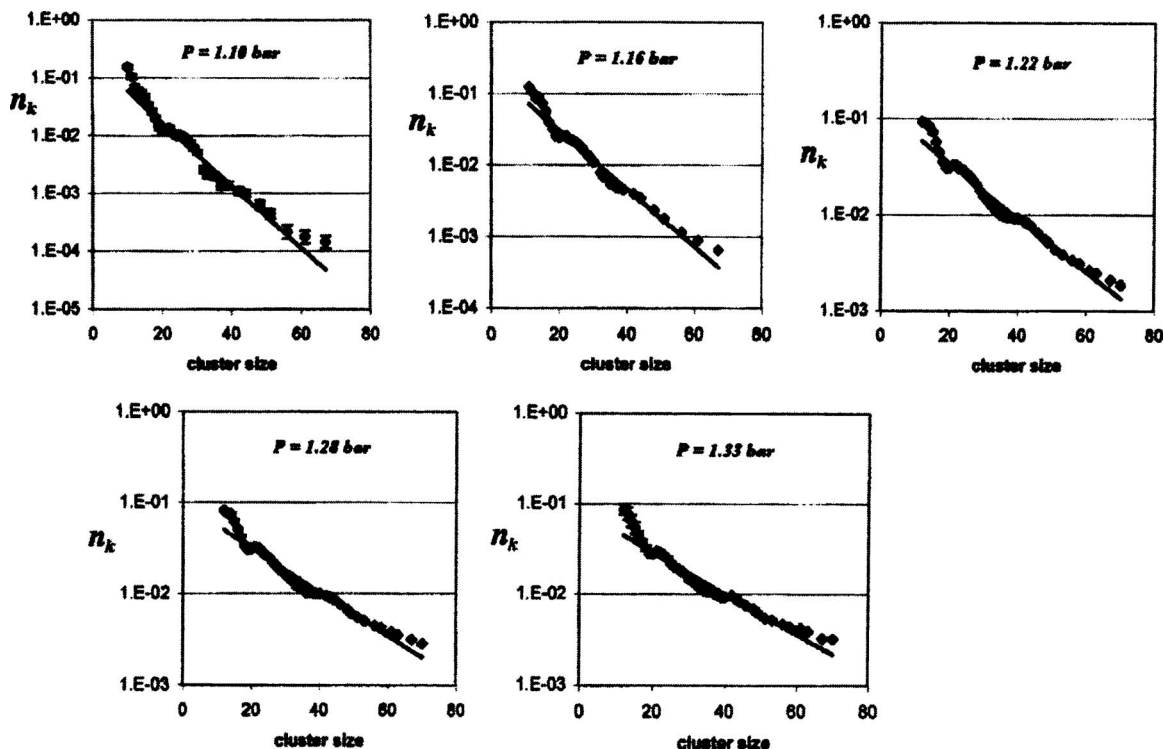
FIG. 1. Data set analyzed (n_k vs k for five different source pressures P_o), with best fits of n_k to the function $Ak^{-0.090}e^{-bk}$, which corresponds to the nascent cluster model. The diamonds are experimental values of n_k, with error bars; the lines are best-fit values. See Table I for numerical values of parameters A and b.

6.7 K, and P_o is the measured backing pressure. In doing experiments, it is convenient to collect data for the case where the temperature T_o is the same for all initial pressures. For reasons to be discussed below we shall define a reaction time τ that is also the same for all initial pressures. It should be clear, however, that what is required for the following analysis to be reasonable is for the product Nt to be constant. Thus $b^{-(a+1)}$ should be a linear function of the source pressure P_o. The plots of Fig. 2 show that this is indeed the case ($R^2=0.974$ for both models). According to Eq. (4), the slope of a plot of $b^{-(a+1)}$ vs P_o should be

$$\left(\frac{\partial b^{-(a+1)}}{\partial P_o}\right)_{t,T} = \frac{(1+a)K_{11}\tau}{kT_o}\left[\frac{C(\mu,\nu)}{\Gamma(2+a)}\right]. \tag{8}$$

The slopes are 31.45 ± 2.97 and 39.78 ± 3.76 bar^{-1} for $a=-0.167$ and -0.090, respectively. Since the coefficient of $K_{11}\tau/kT_o$ on the right side of Eq. (8) is equal to 2.2192 or 2.0711 for $a=-0.167$ or $a=-0.090$, respectively, $K_{11}\tau/kT_o$

$=14.17\pm1.34$ or 19.21 ± 1.82 bar^{-1}, respectively. The two values are not very different, but since we believe the nascent cluster velocity distribution is more appropriate, we use the latter value.

To estimate the reaction time τ corresponding to the method of producing and sampling the distribution we note first that clusters are formed in the early stages of an expansion, when the pressures are still high. Typically, it is thought[36] that several hundreds of two-body collisions occur within a distance of about two nozzle diameters in the expansion and relatively few collisions occur further downstream. The number of three-body collisions is about two orders of magnitude smaller. Thus we simply estimate τ as the nozzle diameter $d(d=5\mu)$, divided by the average speed of a He atom, v_{av} (this is discussed more thoroughly below). We note in passing that the well-known equations relating the scaling of the average velocity and temperature of free jet expansions to source pressure are valid only in the limit of

TABLE I. Details of fitting of experimental data to Ak^ae^{-bk} using protocol described in text.

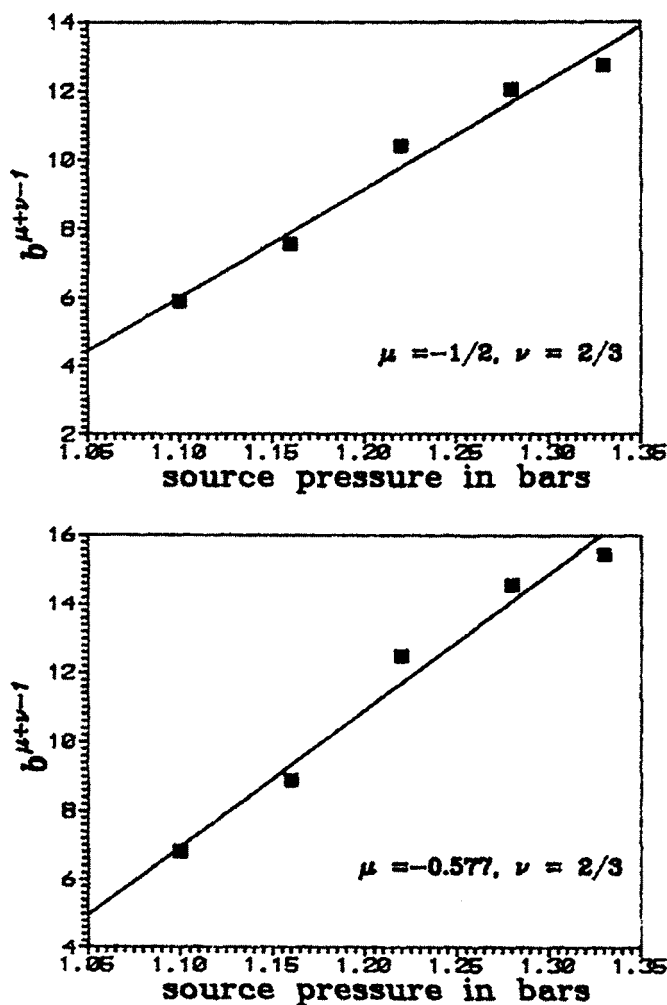| Pressure (bar)	Number of points	Assuming $a=-1/6$			Assuming $a=-0.090$		
		A	b	Sum of sq. rel. devs.	A	b	Sum of sq. rel. devs.
1.10	33	0.2925	0.1190	2.918	0.2451	0.1217	3.012
1.16	32	0.2877	0.0883	1.476	0.2399	0.0907	1.548
1.22	43	0.1869	0.0602	1.210	0.1544	0.0624	1.286
1.28	43	0.722	0.0505	1.153	0.1175	0.0527	1.238
1.33	43	0.1223	0.0472	1.279	0.1009	0.0494	1.367

FIG. 2. Plots of $b^{\mu+\nu-1}$ vs source pressure P_o with best-fit straight lines. Upper plot, $\mu+\nu=1/6$; lower plot, $\mu+\nu=0.090$. The slopes of lines are 31 and 40 bar^{-1} for upper and lower fits, respectively. $R^2=0.974$ for both fits.

no condensation and thermal equilibrium having been established,[37] conditions that are not appropriate to the current experiments.

With the above value for $K_{11}\tau=19.21$ bar^{-1}, the reactive cross section for dimerization, σ_{11}, can be estimated. Writing K_{11} as σ_{11} multiplied by the average *relative* speed of colliding atoms $v_{\rm rel}$,

$$\frac{K_{11}\tau}{kT_o} = \frac{d\sigma_{11}v_{\rm rel}}{kT_o v_{\rm av}} = 19.21 \text{ bar}^{-1}. \qquad (9)$$

The ratio of $v_{\rm rel}$ to $v_{\rm av}$ is $\sqrt{2}$ in an isotropic gas system,[38] but decreases rapidly during a free jet expansion, since $v_{\rm rel}$ decreases rapidly with expansion and $v_{\rm av}$ increases in the course of the expansion. Inside the nozzle, before any expansion occurs, we have $v_{\rm rel}/v_{\rm av}=\sqrt{2}$, $\sigma_{11}=3.55\times10^{-21}$ m$^2/\sqrt{2}$ $=2.51\times10^{-21}$ m^2, which corresponds to a collision radius of $r=0.28$ Å. For the fully expanded free jet, the ratio $v_{\rm rel}/v_{\rm av}$ was measured to be about $1/120$.[3] With $v_{\rm rel}/v_{\rm av}=1/120$, $\sigma_{11}=4.26\times10^{-19}$ m^2 (=42.5 Å) and $r=3.68$ Å. This is an upper limit since the correct effective temperature is at this point less than T_o.

DISCUSSION

We have shown (see Fig. 1) that the abundances of clusters of sizes k formed in a He free jet expansion can be well represented by $Ak^a e^{-bk}$ where $a=-0.090$ and the parameters A and b are chosen to give the best fit to the experimental data. The functional form and the value of a come from the asymptotic (large-k) solution to the Smoluchowski equations for kernels which scale according to Eq. (2); a is thus fixed and cannot be treated as a fitting parameter. This solution also predicts that $b^{-(a+1)}$ should be a linear function of the original monomer density, and hence of the pressure, and this is likewise borne out (see Fig. 2). Furthermore, the theory predicts [see Eq. (8)] that the slope should be proportional to $K_{11}\tau/T_o$, where K_{11} is the rate constant for dimerization collisions between two monomers, τ is the time of reaction, and T_o is the source temperature.

The upper limit for the reactive cross section radius of 3.68 Å corresponds to a cross section of 42.5 Å^2 and is of the same order of magnitude as the van der Waals radius for He, 2.556 Å, calculated using the molar volume of the solid[39] at 0 K. The average distance between the atoms in the bulk liquid and solid is between 3.16 and 4.0 Å, depending on the definition used.[40] Interestingly, these values bracket the radius corresponding to the measured cross section for monomer-monomer collisions. The agreement is also interesting since our analysis of the data is essentially an extrapolation from the cross sections for coalescence reactions for cluster sizes from 7-mers through 70-mers. However, the results are consistent with our expectation that the cross section should be large for small clusters and, in view of Eq. (2), approach the van der Waals radius for clusters approaching macroscopic droplets in size. This value for the cross section radius is also very reasonable when compared to a realistic scattering cross section[23–25,37] as a function of collision energy. Generally, above 1 K the cross section oscillates between 100 and 20 Å^2 which brackets our upper limit of 42.5 Å^2.

Our choice of τ in Eq. (9) may be justified further as follows. For many systems, it is known that the entire coalescence process occurs within a distance on the order of nozzle diameters from the orifice. Still, the choice of *one* nozzle diameter for τ in Eq. (9) is arbitrary. For any experimental apparatus and expansion conditions, τ will vary with the gas used. However, the solution of Eq. (1) is the same and Eq. (4) is valid in any units of time we choose. The choice of time units will affect the numerical value for the best fit normalization factor A. Calculating the time τ in units of a nozzle diameter transit time, i.e., taking $\tau=d/v_{\rm av}$ as in Eq. (9), reflects the scaling[12,36] of expansion properties with the independent parameters P_o T_o, and d_o. These macroscopic parameters, with the nature of the expanding material, define the molecular/atomic beam source.

Equation (9), which connects these parameters to the microscopic processes that produce the cluster size distribution, allows us to provide rigorous and intuitively pleasing connections with other known properties of such expansions. For example, the total number of collisions[36] in an expansion scales with $P_o d_o/T_o$. Our choice of τ will allow comparison

of distributions produced by different materials in different apparatuses and their interpretation in terms of the interparticle potentials of *effective* monomer-monomer coalescence cross sections. It should be noted, however, that these effective cross sections may or may not have a direct counterpart in what is measured in molecular beam experiments. For now we note that the limiting choices of relative velocity ratio bracket a reasonable order of magnitude estimate of the monomer-monomer reactive cross section and that presently, the scaling is not a route to a rigorous cross section measurement. It is for this reason that we did not estimate uncertainties of the parameters.

Much has been neglected in our model. Notably, there is no explicit accounting for multibody, e.g., termolecular, collisions.[12,36] Collisional stabilization of a coalescing particle which has sufficient energy to dissociate is necessary for coalescence growth of gas phase systems since radiation is generally much too slow to effectively stabilize such complexes. The good fit of the data to our distribution function may imply that the kernels we have employed include stabilizing three-body collisions implicitly. In addition, the Smoluchowski-based model does not consider evaporation explicitly, but the agreement with the observed distributions suggests that it incorporates evaporation in some way. Possibly, applying this model to other coalescence growth systems, as mentioned below, will more explicitly reveal the effects of neglecting evaporation.

In any case, collisional stabilization must be important at the earliest stage of coalescence growth because, although it is possible to produce small clusters and dimers in addition to monomers by evaporation from larger clusters, it is not possible to produce clusters larger than dimers without at some earlier point producing dimers. For this system, every collision is either a mass transport-impeding collision, a reactive collision, or a stabilization collision. For collisions between dimers and larger clusters, it is possible for a collision to be both reactive, i.e., capable of producing a third cluster larger than the collision partners, and stabilizing. So while such stabilization collisions are important for the specific case of helium *at larger cluster sizes*, they are essential for the initial production of dimers. In going forward we will need to clearly define the idea of stabilization with respect to a certain set of products. A nascent cluster may have an infinite lifetime, i.e., it has been stabilized, with respect to fragmenting, i.e., evaporating, to form one set of products, and have a finite indeed short lifetime with respect to forming a different set of products.

Collisions provide stabilization of nascent clusters by inducing a transition from the nascent state of a cluster to nearby bound or metastable states. However, helium has the lowest exothermicity of any coalescence growth system and the dimer has *only one known bound state*, with about 1.3 mK binding energy.[26] To form a stable dimer, an encounter between two monomers from a 6.7 K distribution must dispose of several Kelvin of excess kinetic energy. This process must involve a collision with a third body. This provides a very unique opportunity to connect a detailed dynamical calculation to measurements since dimers must be formed and their formation is probably rate determining for the over-

all coalescence process.[12] Furthermore a great deal of supporting information is available for guidance and consistency checking. The novelty of this particular dynamical system, in contrast to much larger sized clusters taken as a group, makes it standout in a scaling treatment of cluster size data because the interactions and potential surfaces defining it are not shared by larger clusters and thus lead to inhomogeneous kernels.

Inhomogeneous kernels, i.e., kernels that do not obey the homogeneity condition given by Eq. (2), were likewise not included in our treatment of these data. Magic numbers, as we have shown elsewhere,[18,41] are associated with kernels that are not homogeneous. The effect of such kernels on the distributions is more pronounced for small clusters. In fact, Bruhl *et al.*[32] have shown the existence of magic numbers in He based on the present data. Visual comparison of the distributions in Fig. 1 with the distribution $Ak^a e^{-bk}$ confirms this. Thus, in Fig. 1 there is a negative deviation from the fitted $Ak^a e^{-bk}$ for cluster sizes just larger than certain magic numbers. We have shown[18,41] that this is to be expected when kernels for reactions producing the magic-number cluster are larger, and/or kernels for destruction by coalescence are smaller, than what scaling would predict. This may occur when a specific cluster size satisfies all valence constraints of the monomers without strained bonds, e.g., fullerene versus cyclopropane-like structures for carbon clusters. Fullerenes are resistant to attack by other species and cyclopropane is more reactive. In the present case, the monomers and all clusters are spherically symmetric and essentially zero valent. Bruhl *et al.*[32] suggest that the magic numbers for He occur at sizes for which the cluster can just support an addition excitation level, i.e., an additional excited state to be included in calculating the partition function.

The value of $a = -(\mu + \nu)$ is important in this model and it is fixed by the choice of monomer and coalescence conditions. This leaves only two parameters, A and b, to be chosen by seeking the best fit to experiment. Conservation of linear momentum in a coalescence growth system will produce a nascent velocity distribution for which velocity decreases more rapidly with cluster size than for thermal equilibrium. For the former case, we calculate (preceding paper) $\mu + \nu = 0.090$, whereas thermal equilibrium gives $\mu + \nu = 0.167$. We have used the former value here; when there are many nonreactive collisions, so that thermal equilibrium is maintained while coalescence growth occurs, we should choose the latter.

For a diffusive regime of coalescence growth in an inert buffer gas, e.g., metal atoms entrained in a rare gas expansion or metal clusters produced by laser atoms from organometallic precursors, $a = \mu + \nu = 0$. Here, stabilization of nascent metal clusters is simpler since emission[42] from excited electronic states of dimers and possibly higher order oligomers has been observed and assigned. Because there are so many loosely bound electrons, bound state potential wells are deep and electronic state lifetimes are usually shorter than 10 ns. Thus metals will have radiative pathways available to dissipate exothermicity. For metals in inert buffer gases, one has a diffusive regime with respect to mass transport, but a coalescence-determined velocity distribution due

to the extreme mismatch between the inert gas mass (helium being most often used) and that of the metal. For this reason stabilization of nascent clusters by radiative cooling is more common.

Peaked distributions are often observed for these systems and, as mentioned earlier, there are many distributions in the literature[18,20] that have a most probable size. In the context of our model a peaked distribution corresponds to $\mu + \nu < 0$. Since conservation of linear momentum, angular momentum, or energy always gives $\mu + \nu > 0$, we conclude that a process neglected in our model must be responsible for making $\mu + \nu$ negative. We hope that application of this model to systems with different coalescence exothermicity, mass transport and energy transport will suggest the modifications that will make this model more complete.

CONCLUSIONS

The scaled Smoluchowski model, with two nonadjustable scaling parameters appropriate to a coalescence growth system and two parameters chosen to give best fit, accurately describes the cluster size distributions produced in free jet expansions of helium. The variation of the distribution with source pressure is also accurately represented and an extrapolation to small clusters leads to a reasonable value for an effective helium-helium cross section. The theory predicts a nonpeaked distribution in agreement with experiment.

[1] For an interesting review see S. Chandresekar, Rev. Mod. Phys. **15**, 1 (1943).

[2] P. Meakin, Phys. Scr. **46**, 295 (1992).

[3] S. Kotake and J. J. Glass, Prog. Aerosp. Sci. **19**, 129 (1981).

[4] J. Chaiken and J. Goodisman, Thin Solid Films **260**, 243 (1995).

[5] J. Chaiken, J. Goodisman, R. M. Villarica, J. V. Beasock, and L. H. Walsh, Mater. Res. Soc. Symp. Proc. **356**, 489 (1995).

[6] D. B. Siano, J. Chem. Educ. **49**, 755 (1972).

[7] For example, see M. J. Casey and J. Chaiken, Proc. SPIE **1626**, 217 (1992).

[8] J. W. Gibbs, Trans. Conn. Acad. Arts Sci. **3**, 108 (1876).

[9] M. Vollmer and A. Weber, Z. Phys. Chem. Abt. A **119**, 277 (1926).

[10] R. Becker and W. Doering, Ann. Phys. (Leipzig) **24**, 719 (1935).

[11] M. V. Smoluchowski, Phys. Z. **17**, 557 (1916).

[12] L. W. Bruch, W. Schöllkopf, and J. P. Toennies, J. Chem. Phys. **117**, 1544 (2002).

[13] R. Jullien, New J. Chem. **14**, 239 (1990); R. Botet and R. Jullien, J. Phys. A **17**, 2517 (1984).

[14] P. G. J. van Dongen and M. H. Ernst, *Kinetics of Aggregation and Gelation*, Proceedings of the International Topical Conference (North-Holland, Amsterdam, 1984), pp. 205–207; Phys. Rev. A **32**, 670 (1985); Phys. Rev. Lett. **54**, 1396 (1985); P. G. J. van Dongen, Physica A **145**, 15 (1987).

[15] P. G. J. van Dongen and M. H. Ernst, J. Colloid Interface Sci. **115**, 27 (1987); J. Stat. Phys. **50**, 295 (1988).

[16] T. Viscek and F. Family, Phys. Rev. Lett. **52**, 1669 (1984).

[17] F. Leyvraz and S. Redner, Phys. Rev. Lett. **57**, 163 (1986); Phys. Rev. A **36**, 4033 (1987); F. Leyvraz, J. Phys. A **32**, 7719 (1999); F. Calogero and F. Leyvraz, *ibid.* **32**, 7697 (1999).

[18] R. M. Villarica, M. J. Casey, J. Goodisman, and J. Chaiken, J. Chem. Phys. **98**, 4610 (1993).

[19] R. Bruhl, R. Guardiola, A. Kalinin, O. Kornilov, J. Navarro, T. Savas, and J. P. Toennies, Phys. Rev. Lett. **92**, 185301 (2004); R. Guardiola, O. Kornilov, J. Navarro, and J. P. Toennies, J. Chem. Phys. **124**, 084307 (2006).

[20] J. Chaiken, M. J. Casey, and R. M. Villarica, J. Phys. Chem. **96**, 3183 (1992).

[21] J. Chaiken, in *Laser Chemistry of Organometallics*, ACS Symposium Series Vol. 530, edited by J. Chaiken (American Chemical Society, Washington, DC, 1993), Chap. 1.

[22] C. G. Granqvist and R. A. Berman, Solid State Commun. **18**, 123 (1976); J. Catal. **42**, 477 (1976).

[23] H. G. Bennewitz, H. Busse, H. D. Dohmann, D. E. Oates, and W. Schrader, Phys. Rev. Lett. **29**, 533 (1972).

[24] R. Feltgen, H. Kirst, K. A. Köhler, H. Pauly, and F. Torello, J. Chem. Phys. **76**, 2360 (1982).

[25] J. C. Mester, E. S. Meyer, M. W. Reynolds, T. E. Huber, Z. Zhao, B. Freedman, J. Kim, and I. F. Silvera, Phys. Rev. Lett. **71**, 1343 (1993); J. P. Toennies and K. Winklemann, J. Chem. Phys. **66**, 3965 (1977).

[26] R. E. Grisenti, W. Schollkopf, J. P. Toennies, G. C. Hegerfeldt, T. Kohler, and M. Stoll, Phys. Rev. Lett. **85**, 2284 (2000).

[27] V. Efimov, Phys. Lett. B **33**, 563 (1970).

[28] See, for example, A. K. Motovilov, W. Saudhas, S. A. Sofianos, and E. A. Kolganova, Eur. Phys. J. D **13**, 33 (2001).

[29] R. Bruhl, A. Kalinin, O. Kornilov, J. P. Toennies, G. C. Hegerfeldt, and M. Stoll, Phys. Rev. Lett. **95**, 063002 (2005).

[30] A. Kalinin, O. Kornilov, L. Rusin, J. P. Toennies, and G. Vladimirov, Phys. Rev. Lett. **93**, 163402 (2004).

[31] Y. E. Balyaev, A. V. Demyanenko, and A. Puretzky, in *Laser Chemistry of Organometallics*, ACS Symposium Series Vol. 530, edited by J. Chaiken (American Chemical Society, Washington, DC, 1993), Chap. 17.

[32] R. Bruhl, R. Guardiola, A. Kalinin, O. Kornilov, J. Navarro, T. Savas, and J. P. Toennies, Phys. Rev. Lett. **92**, 185301 (2004).

[33] R. E. Grisenti, W. Schollkopf, J. P. Toennies, J. R. Manson, T. A. Savas, and H. J. Smith, Phys. Rev. A **61**, 033608 (2000).

[34] R. E. Grisenti, W. Schollkopf, J. P. Toennies, G. C. Hegerfeldt, and T. Kohler, Phys. Rev. Lett. **83**, 1755 (1999).

[35] J. Chaiken and J. Goodisman, J. Chem. Phys. **125**, 074304 (2006), preceding paper.

[36] D. R. Miller, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University Press, Oxford, 1988), Vol. 1, Chap. 2 and references therein.

[37] J. P. Toennies and K. Winklemann, J. Chem. Phys. **66**, 3965 (1977).

[38] E. H. Kennord, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938), pp. 112 and 113.

[39] I. J. Zucker, *Proceedings of the Physical Society*, London 77, 889 (1961).

[40] F. London, *Superfluids II: Macroscopic Theory of Superfluid Helium* (Wiley, New York, 1954), pp. 18–39.

[41] J. Chaiken and J. Goodisman, J. Cluster Sci. **6**, 319 (1995).

[42] Although a number of mechanisms were proposed it seems likely that at least some emission from nascent dimers formed by atomic recombination was observed by Y. E. Balyaev, A. V. Demyanenko, and A. A. Puretzky, in *Laser Chemistry of Organometallics*, edited by J. Chaiken (American Chemical Society, Washington, DC, 1993), Chap. 17 and references therein.