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Application of the Smoluchowski equation to the formation kinetics of cluster ions

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Abstract. Cluster ions with various sizes and compositions have been generated from direct laser vaporization. The Smoluchowski rate equation is extended to describe the formation kinetics of the cluster ions, which have been assumed to be produced from ion–molecule reactions with same-rate constants. By solving the kinetic equation analytically, we obtained the distribution function of the cluster ions. Analysis of the distribution function showed that the function can characterize the statistical size distribution of the cluster ions and can be reduced to the asymptotic solution suggested by Jullien [1].

PACS. 36.40.-c Atomic and molecular clusters

1 Introduction

The study of isolated cluster molecules and their ions has been a rapid expanding field and has consumed a considerable amount of recent interest in chemistry and physics. Since the introduction of the laser-vaporization techniques in experiments [2], both neutral and charged cluster species can be created with different sizes and with almost any composition. As shown in the various mass spectra appearing in the literature [3–6], the size distribution of the clusters can often be well simulated by a distribution function. Since the function describes the formation kinetics of the clusters, it should be able to be obtained from the relevant kinetic equations.

Chaiken applied an asymptotic solution [7,8], $n_k = Ak^{\alpha}e^{-\beta k}$, to simulate the experimental distribution and got satisfying results. In the formula, k represents the size of particles and α, β are the parameters to be determined. The function was first proposed by Jullien to describe the size distribution of observed clusters in irreversible homogeneous aggregation kinetics [1]. However, if the observed statistical distribution in mass spectra is to be explained, it should be further noticed that what mass spectrometers detect and record are ions. In this paper, the Smoluchowski equation was extended to describe the formation kinetics of the cluster ions. The distribution function solved from the equation is compared with the size distribution of the cluster ions observed in the experiments.

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2 Kinetic equations

The Smoluchowski rate equation was put forward to describe the irreversible aggregation process of small particles, such as clusters [9,10]:

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \frac{1}{2}\sum_{i+j=k} K_{i,j}n_i n_j - \sum_{i=1}^{\infty} K_{k,i}n_k n_i \,. \qquad (1)$$

In (1), n_k is the number of clusters of size k. $K_{i,j}$ is the aggregation rate constant for the reaction between clusters with size of i and j, whose value depends on the nature of relative motion between the reaction particles as well as the details of the reaction cross section. $K_{i,j}$ was also called "kernel" by some authors [11–13].

Equation (1) was analytically solved by Smoluchowski and Flory *et al.* [9,14,15] by the assumption that the values of the kernels are unvaried with the particle sizes. The distribution is generally called Flory distribution [16,17] and has been employed to describe the aggregation kinetics of the polymers. If the distribution of the cluster ions follows the function, their abundance should always be reduced with the increase of cluster sizes. However, this is not what is generally observed in the mass spectra of the cluster ions, which often show maximum values in the distribution.

The size distribution, which often exhibits a most probable value, can be simulated by evaluating the kernel value of $K_{i,j}$ in (1) [18–21]. For instance, by assuming the kernel as a function of the cluster size, distribution of carbon clusters was simulated [21]. However, Smoluchowski equation characterizes the formation kinetics of the neutral clusters.

In the experimental condition of direct laser vaporization, the ion–molecule reactions are involved in the formation process of the cluster ions. The formation mechanism has been suggested by Conover *et al.* [22]. In order to describe the formation kinetics of the cluster ions, we extended the Smoluchowski rate equation to take into account the ion–molecule reactions.

Formation of a neutral cluster A_k can be expressed by the following reaction:

$$A_i + A_{k-i} \rightarrow A_k$$

Formation of the cluster ion A_{k+} may involve the following ion–molecule reaction:

$$A_i^+ + A_{k-i} \rightarrow A_k^+$$

To describe the above reactions, we extended the Smoluchowski equations to the following equations:

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \frac{1}{2}K \sum_{i+j=k} n_i n_j - K \sum_{i=1}^{\infty} n_k n_i - K' \sum_{i=1}^{\infty} n_k m_i \,, \tag{2}$$

$$\frac{\mathrm{d}m_k}{\mathrm{d}t} = K' \sum_{i=1}^{k} m_i n_{k-i} - K' m_k \sum_{i=1}^{\infty} n_i \,. \tag{3}$$

Here, m_k is the number of the cluster ions with size of k, and K and K' are the kernels in the above formation reactions.

3 Solution of the kinetic equations

Using the induction method, we obtained an analytical solution of (3):

$$\begin{aligned} m_1 &= m_0 \frac{1}{(1+u)^a} \\ m_k &= m_0 \frac{\prod_{i=2}^{k}(a+i-2)}{(k-1)!} \frac{u^{k-1}}{(1+u)^{a+k-1}} \,, \end{aligned} \tag{4}$$

where $a = 2K'/K$ and $u = \frac{1}{2}Kn_0t$.

The distribution functions (4) with different values of u and a are displayed in Figs. 1a–1c. The initial species of the formation reactions are assumed to be neutral and charged monomers. As shown in the displayed function curves, the distribution function can exhibit a most probable value without adjustment of the kernel values. For comparison, several mass spectra [23] of transition metal cluster ions are shown in Fig. 2, and their size distributions are simulated by (4) as smooth curves. As shown in the figure, if the proper parameters are chosen, the function can describe the statistical distribution of the cluster ions observed in the laser-vaporization experiments. By further evaluation of the kernel values, the relative abundance of each size can be simulated.

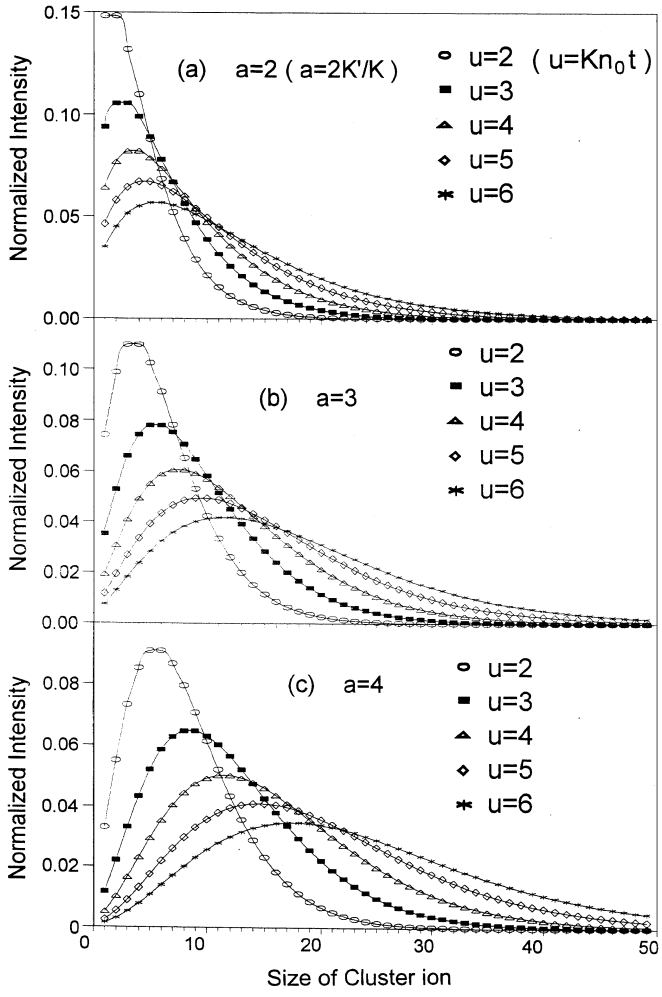

Fig. 1. Population of the cluster ions calculated according to the distribution function analytically solved from the extended Smoluchowski equation. Only the aggregation process is considered, and the initial specials are assumed to be neutral and charged monomers with the concentration ratio of 50:1. The distribution curves correspond to different values of the parameters, a and u, which are illustrated in the figures.

The normalized property of the distribution function, $\sum_{i=1}^{\infty} m_i/m_0 = 1$, can also be testified. We expand the function, $(1+u-u)^{-a}$, with the Taylor series:

$$\begin{aligned} (1+u-u)^{-a} = \frac{1}{(1+u)^a} + \frac{a}{(1+u)^{a+1}}u + \ldots \\ + \frac{a(a+1)\ldots(a+i-1)}{i!(1+u)^{a+i}}u^i + \ldots \,. \end{aligned} \tag{5}$$

Each item in the formula corresponds to the distribution function with cluster size of k. Since the left side of (5) is equal to one, the validity of normalization is thus proved.

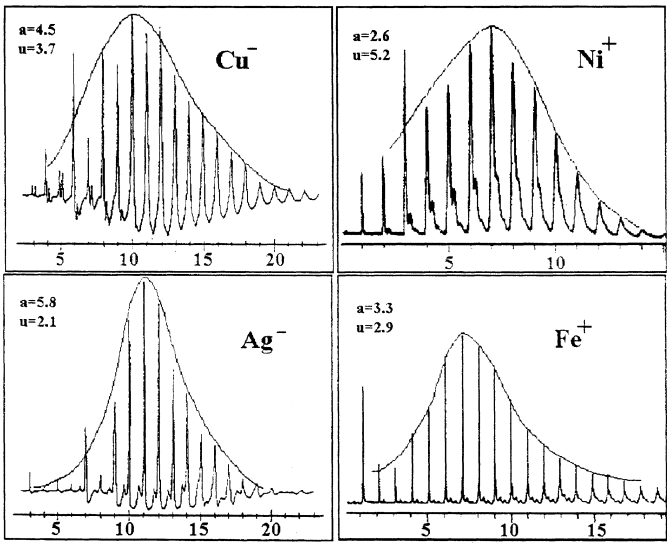

Fig. 2. Mass spectra of several transition metal cluster ions produced from laser vaporization. Most mass peaks of the cluster ions can be fit by the distribution function curve with the parameters marked in the figure.

In some special cases, the distribution function can have different representations. If $a = 1$, i.e., $K = 2K'$, the function can be simplified as:

$$m_k = m_0 \frac{u^{k-1}}{(1+u)^k} \,. \tag{6}$$

Equation (6) is similar to the solution of the Smoluchowski equation [10], the distribution function of the neutral clusters, which decreases monotonically with the cluster size.

4 Characterization of the distribution function

Equation (4) can be rewritten as

$$p(k) = \frac{\Gamma(a+k-1)}{\Gamma(a)\Gamma(k)} \frac{u^{k-1}}{(1+u)^{a+k-1}} \,, \tag{7}$$

where $p(k)$ represents the percentage of cluster ions with size k among the total cluster ions and $\Gamma(x)$ is the gamma function. Through this transformation, k becomes a continuous variable; then the distribution can be differentiated with respect to k.

4.1 The most probable cluster size

The most probable value of the cluster size, k_m, can be calculated from $\mathrm{d}p(k)/\mathrm{d}k = 0$. However, the expression of the most probable value can be obtained with the following simplification. When k is much larger than a, (7) can be approximated as:

$$p_k = \frac{k^{a-1}}{\Gamma(a)} \frac{u^{k-1}}{(1+u)^{a+k-1}} \,. \tag{8}$$

Differentiating p_x with respect to k and setting it equal to zero, we have

$$k_m = u(a-1) \,. \tag{9}$$

The representation of (9) is simple and can be easily verified by examining the distribution curves shown in Fig. 1. From (9), we can further learn that, only for $a > 1$, size distribution of the cluster ions can have a most probable value, i.e., the most abundant cluster ion is not the monomer. If $a \leq 1$ ($2K' \leq K$), i.e., the kernel between cluster ions and neutral cluster molecules is less than half of that between the neutral clusters, relative abundance of the cluster ions will decrease with the cluster size. Since the ion–molecule reaction is usually more reactive, the monotonic distribution has seldom been observed in practice except when the reaction time is very short, i.e., the value of u is quite small.

4.2 Mean size of the cluster ions

The mean size of the cluster ions can also be calculated. According to (7),

$$p(k) = \frac{1}{(1+u)^a} \frac{\Gamma(a+k-1)}{\Gamma(a)\Gamma(k)} \left(\frac{u}{1+u}\right)^{k-1} \,. \tag{10}$$

Let $\frac{u}{1+u} = \omega$, and notice the following relationship:

$$\sum_{x=1}^{\infty} x^n \omega^{x-1} = \left(\frac{\mathrm{d}}{\mathrm{d}\omega}\omega\right)^n \sum_{x=1}^{\infty} \omega^{x-1} \,. \tag{11}$$

While $n = 1$, the left side of the equation represents the mean weight of the cluster ions. Then we have

$$\bar{S} = \sum_{x=1}^{\infty} x p_x = 1 + au \,. \tag{12}$$

Both k_m and $\bar{S}$ can be measured from the recorded mass spectra of the cluster ions. Therefore, from (9) and (12), the parameters of the distribution function, a and u, can be obtained as follows:

$$a = \frac{\bar{S}-1}{\bar{S}-1-k_m} \,, \tag{13}$$

$$u = \bar{S}-1-k_m \,. \tag{14}$$

4.3 Different expressions of the distribution function

For large u, (7) can further be modified as:

$$p_k = \frac{1}{(1+u)^a \Gamma(a)} k^{a-1} e^{-(k-1)/u} \,. \tag{15}$$

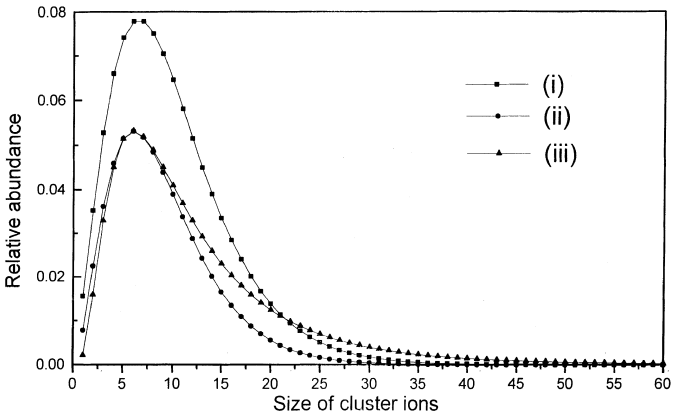

Fig. 3. Illustration and comparison of the three expressions of the distribution functions: (i) (7), (ii) (15), and (iii) (17). Parameters for the function are $a = 3$ and $u = 3$.

This expression is in accordance with the distribution function, $n_k = Ak^{\alpha}e^{-\beta k}$, proposed by Jullien [1]. Such a function was later applied by Chaiken to simulate the experimental distribution recorded in mass spectra and gave satisfying results [7, 8]. Comparing with (15), it can be found that the parameter α, given by Jullien, is equal to $a-1$ and the parameter β, is equal to $1/u$. This accordance suggests that the extended Smoluchowski equation based on the mechanism of ion–molecule reaction can specify the formation kinetics of the cluster ions.

Equation (15) can also be converted to the log-normal distribution, as was done by Chaiken [8]:

$$\ln p_k = \ln p_{k_m} + \left[(a-1) - \frac{k_m}{u}\right](\ln k - \ln k_m) \qquad (16)$$
$$- \frac{\frac{k_m}{u}}{2}(\ln k - \ln k_m)^2 - \frac{\frac{k_m}{u}}{3!}(\ln k - \ln k_m)^3 - \ldots .$$

Omitting the items after the second order, we have

$$\ln p_k = \ln p_{k_m} - \frac{(a-1)}{2}(\ln k - \ln k_m)^2 .$$

Thus,

$$p_k = p_{k_m} \exp\left[-\frac{(a-1)}{2}(\ln k - \ln k_m)^2\right] . \qquad (17)$$

Equation (17) was regarded as the log-normal function by Chaiken [7].

$$p_k = \frac{1}{\sqrt{2\pi}\sigma k} \exp\left[-\frac{1}{2\sigma^2}(\ln k - \mu)^2\right] .$$

After examining (15) and (17), one can find that both distribution functions are not normalized as (7) is. Figure 3 illustrates the differences among the three distribution functions.

5 Summary

The Smoluchowski equation was extended to describe the ion–molecule reactions for the formation of the cluster ions. An analytical solution of the rate equation was obtained. The solved distribution function exhibits a most probable value, which was generally observed in the size distribution of cluster ions produced by direct laser vaporization. The function is normalized and can describe the statistical distribution of cluster sizes without evaluation of the kernel value. Analysis of the function reveals the most probable value and mean size of the cluster ions. Other distribution functions, which have been applied to describe the cluster size distribution, were compared with this function and can be reduced from the function with approximations.

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