Temperature of large clusters

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Free clusters that cool by evaporation will have a defined distribution of internal energies in spite of lack of contact with a heat bath. This distribution has previously been considered for small clusters. Here we present results valid for large clusters. A simple Gaussian shape is predicted in this regime and we calculate the mean and variance of the distribution. The limit of validity of previous and present work is discussed. The analytical results are compared to numerical simulations.

INTRODUCTION

Many of the properties of materials change dramatically when the particle size is reduced to microscopic dimensions. During the past decade these ultrafine particles, clusters, have been studied from a multitude of viewpoints and with numerous experimental techniques. One of the most common methods is to heat the clusters by photoabsorption and make them evaporate neutral atoms. The specific use of the evaporation process has led to the development of some of the most powerful experimental techniques in cluster physics. Especially noteworthy is the use of evaporative ensembles to study variations in stability with size and gain information about the internal structure of clusters.[1,2] In particular, the technique has been used to study how the stability of clusters varies due to electronic shell structure.[3] Even as a probe for the plasmon absorption, evaporation techniques have been applied.[4] Hence, the interpretation of a large amounts of experimental data depend on a proper understanding of the kinetics of evaporation.

A crucial quantity in this respect is the distribution of internal energies ascribable to an ensemble of clusters of a given size. This was realized long ago by Gspann[5] and also by Klots[6] who subsequently elaborated the theory in greater detail. As a result formulas have been derived to account for both abundance spectra and internal energies for small clusters. The most striking result of that theory was the statement that if the time that has passed since the cluster first began to cool by evaporation is known, the present cluster temperature can be estimated accurately even without knowing the exact initial temperature.

The key to understand the problem of internal energies was the observation that due to the small cluster size, the heat capacity is low. Consequently, in contrast to bulk material, the evaporative cooling of clusters is not a continuous but a steplike process. One single evaporation will cool the cluster considerably. Additionally, under usual experimental conditions the experimental probe times are very long compared to the pre-exponential time in expressions for thermally activated processes. As a consequence the cluster temperature will be low compared to the activation energy for decay. Combined, these two observations lead to the prediction that two consecutive evaporations from the same cluster can have rate constants that are different by orders of magnitude.

This is demonstrated schematically in Fig. 1 which shows the evaporation process of a 50-atom sodium cluster. In each step the cluster loses one atom and cools down by the activation energy of the process which is about 1 eV. Since the evaporation rate depends exponentially on the cluster temperature, even a slight temperature change will strongly influence the rate of further evaporations. Due to the small heat capacity the temperature of a small cluster decreases dramatically with every evaporation step and the probability for further evaporations decreases from step to step by orders of magnitude.

More quantitatively, the considerations go as follows: In a decay chain with several evaporation steps the last step is always the most time consuming and will dominate the time scale. Hence the available time for the last evaporation is effectively the *total* cooling time. This well defined connection between cooling time and evaporation rate means that in an ensemble of clusters of a given size there will be a maximum decay constant for every time, t. This maximal decay rate is the inverse cooling time, t^{-1}. Converting this maximum decay constant to temperature yields a quite well defined upper limit, $T_{\max}$, for the distribution of cluster temperatures. Clusters at a temperature above $T_{\max}$ are too hot to survive in their present state during the cooling time and will not be found in the ensemble.

Furthermore, there is also a lowest temperature, $T_{\min}$, which is determined by the decay of the preceeding cluster size in the decay chain. Obviously, these clusters will also have an upper temperature limit. The ones with a temperature above this maximum will have decayed within the cooling time. Therefore, the lowest temperature of size N corresponds to the highest temperature of size $N+1$ minus the reduction in temperature due to one evaporation. Since the maximum temperature of two neighboring clusters in a decay chain is essentially the same if the activation energy is the same, the difference between the maximum and minimum temperatures is simply given by the decrease in temperature during one evaporation. This decrease is obviously determined by the separation energy and the heat capacity.[6]

Under these assumptions all features in the final energy distribution of clusters which were initially hot with a broad energy distribution can then be derived by considering only

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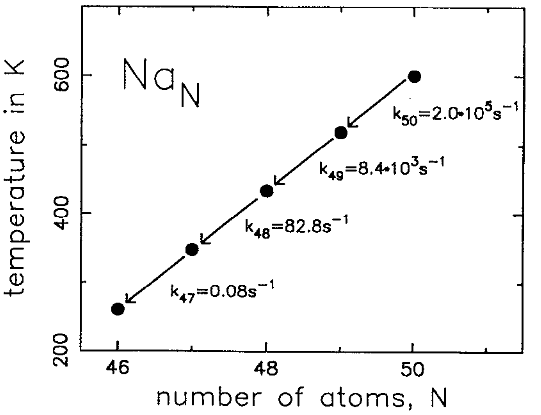

FIG. 1. A sequence of several evaporations from a Na_{50} cluster. The evaporation of only a few atoms is sufficient to cause a dramatic change in temperature. In less than 1 ms the cluster cools down from 600 to 400 K. The decay rate, k_i, decreases from step to step by orders of magnitude. The data have been calculated according to Eq. (3).

the last evaporation. The resulting energy distribution is an approximately square distribution which is limited by $T_{\max}$ and $T_{\min}$. The width in temperature is given by approximately $\Delta T \simeq D/3N$, where D is the separation energy or the activation threshold and N the number of atoms.

It should be kept in mind that the basis of the whole theory was the assumption that the last evaporation dominates the time scale. As we have argued, this assumption depends crucially on the small heat capacity of the cluster. Hence we must expect that the assumption will become progressively worse as the size and consequently the heat capacity increases. To demonstrate the difference between "small" and "large" clusters, Fig. 2 shows the evaporation of a 200-atom cluster at an initial temperature of 600 K. Compared to the 50-atom cluster of Fig. 1, the heat capacity of this cluster is larger by a factor of 4. The temperature change caused by the loss of one atom is small (only 20 K). The evaporation rate decreases from step to step by a factor of only 2 instead of about 100 as in Fig. 1.

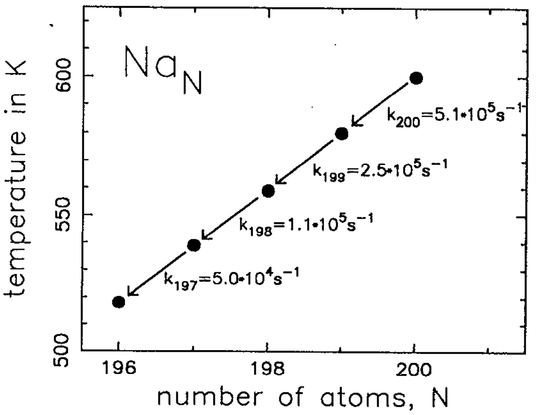

FIG. 2. The evaporation sequence of Na_{200}. In contrast to the decay of Na_{50} (Fig. 1) the evaporation rates are now of similar magnitude.

Mathematically speaking, the breakdown of the assumptions can be seen by considering the difference between the highest and the lowest temperature in the Klots' model. Since this width decreases with size, the difference between the decay constants at the lowest and highest temperatures will also decrease with size. For sufficiently large clusters these two rates will be approximately equal and, equally important, they will also be similar in magnitude to the preceding rates in the decay chain. It is then no longer possible to determine the temperature distribution by considering only the last evaporation. Rather, one should base the theory on decay chains with a number of almost equal decay rates.

It should be stressed that although Klots' theory breaks down for large clusters, predictability remains. It will still be possible to calculate temperature distributions if only the cooling time is known for clusters large compared to the crossover size. The precise distribution will be derived in the following and it will be shown that the crossover point between the validity of the Klots/Gspann theory and the one presented here is surprising low and well below the current upper limit of free clusters studied.

MODEL

To attack the problem, consider a decay chain for an initially hot cluster. The temporal development of this chain can be described by a set of coupled linear differential equations. If $I_N(t,T)$ is the probability of finding the cluster with temperature T at time t in the state with N atoms and if k_N is the rate for the loss of another atom (e.g., the decay from N to $N-1$), the time dependence of I_N can be described as

$$\frac{dI_N(t,T)}{dt}=k_{N+1}\cdot I_{N+1}(t,T+\Delta T)-k_N\cdot I_N(t,T). \qquad (1)$$

(ΔT is the temperature decrease during the decay). The population of every cluster size is coupled to the others by equations similar to Eq. (1). The population I is parameterized by N and T and for individual decay chains the evaporation process can be described as a trajectory in the (N,T)-space as demonstrated in Figs. 1 and 2. We can formulate the problem of finding the temperature as an equivalent problem of how a cluster moves along one of these trajectories in time. The trajectory generated from a single point in the diagram will be a completely deterministic curve provided we ignore the stochastic nature of the kinetic energy of the emitted fragment. However, the arrival time to a certain point will still be a stochastic variable due to the stochastic nature of the decay time. This distribution of arrival times at a certain point with a given T can be calculated. The distribution of arrival times can then be converted into a temperature distribution by simple means as will be demonstrated.

However, before doing that, we will consider the conceptually important mean value of the temporal distribution, i.e., the mean time required to reach size N from the initial size N_0. In the spirit of the large cluster approximation, we will consider cluster size a continuous or discrete variable, respectively, as most convenient.

The mean lifetime at point N is

$$t=\sum_{i=N}^{N_0} k_i^{-1}. \tag{2}$$

For large clusters, the rate constants in a decay chain can be related to the final rate provided we know the functional form of $k_i(T)$. In this work we will assume an expression of the form

$$k_N=N^{2/3}\omega e^{-D/T}, \tag{3}$$

$N^{2/3}$ is the surface term and D the activation energy. The frequency factor, ω, is for most materials between 10^{13} and $10^{15}\ \mathrm{s}^{-1}$. The precise value only slightly influences the final cluster temperature. More general expressions for k are possible and in other cases necessary[7–10] but the above captures the essential features of our problem and should be a good approximation for large clusters. We assume D constant and refer the reader to future work where the very important case of size dependent D's is presented.[11]

It should be mentioned that we use the word temperature only as a shorthand for the excitation energy per vibrational degree of freedom. Since the internal energy is conserved between evaporations, the ensemble is microcanonical during these periods and the notation is strictly speaking not justified. We expect no confusion to arise from this abuse of notation. Since the results are so insensitive to slight changes in the evaporation model, also the kinetic energy release of the fragment can be neglected.

The change in temperature for one evaporation is

$$\Delta T=-D/(3N-6)\simeq -D/3N, \tag{4}$$

where we will set the kinetic energy of the fragment to zero for convenience. If the final temperature is denoted by T, the preceding decay rates can be approximated by

$$k_{N+l}\simeq(N+l)^{2/3}\cdot\omega\cdot\exp\left(-\frac{D}{T+\dfrac{l\cdot D}{3N}}\right) \tag{5}$$

or

$$k_{N+l}\simeq k_N\cdot\left(\exp\frac{D^2}{3N\cdot T^2}\right)^{l}. \tag{6}$$

Equation (6) is valid provided $(lD/3NT)\ll 1$, or, considering the effective range of l-values $[l\simeq 3N(T/d)^2]$, for $T/D\ll 1$. With the definition

$$N_\kappa\equiv\frac{1}{3}\left(\frac{D}{T}\right)^2, \tag{7}$$

the approximation is in particular sufficient for any value of N larger than N_κ. It is easily seen from Eq. (6) that for $N<N_\kappa$ two consecutive decay rates will differ by more than e^1. In that situation the sum of decay times can be treated with acceptable accuracy by Klots' formalism. The value of N_κ is thus the characteristic size when distinguishing between large and small clusters in the context of evaporation. For time scales of μs and ms, the value of N_κ is in the range of 150–300.

A simple summation of Eq. (2) then gives

$$t\simeq k_N^{-1}\cdot\frac{1-\left[\exp\left(-\dfrac{N_\kappa}{N}\right)\right]^{N_0-N+1}}{1-\exp\left(-\dfrac{N_\kappa}{N}\right)}. \tag{8}$$

This is an implicit equation that determines the decay rate, $k(t)$, and the cluster temperature, $T(t)$, as a function of time.

The importance of the initial temperature can be estimated by considering the mass loss N_0-N. In the limit of initially very hot clusters many atoms are evaporated and N_0-N is large. In this case the initial temperature has no influence on the final cluster temperature. This can be seen more clearly if N_0-N is approximated with $[3N\cdot(T_0-T)/D]$. Equation (8) can then be rewritten as

$$t\simeq k_N^{-1}\cdot\frac{1-\exp\left(-\dfrac{N_\kappa}{N}\right)\cdot\exp\left(\dfrac{-D}{T}\cdot\dfrac{T_0-T}{T}\right)}{1-\exp\left(-\dfrac{N_\kappa}{N}\right)}. \tag{9}$$

If T_0 fulfills the condition

$$\frac{D}{T}\cdot\frac{T_0-T}{T}\gg 1, \tag{10}$$

the effect of the initial temperature can be ignored since the last term in the numerator is very small. Since on an experimental time scale the ratio D/T has a value of 20–30, a relative temperature change of just 20% is sufficient to cause a cluster temperature to be independent of its initial value. Hence, using the large N condition (7), Eq. (10) can be written as

$$t\simeq k_N^{-1}\frac{N}{N_\kappa}=k_N^{-1}\cdot\frac{3N\cdot T^2}{D^2}. \tag{11}$$

This equation is quite useful in more than one way. First of all it can of course be used to find the temperature to activation energy ratio by a simple numerical inversion. But it can also be considered an equation for the decay constant

$$k_N=3N\left(\frac{T}{D}\right)^2 t^{-1}. \tag{12}$$

Since the ratio T/D depends only weakly on both size and time, we have the remarkable result that decay constants are approximately proportional to size. Furthermore they are independent of the value of the separation energy as long as it is constant. It should be stressed that the factor of $3N$ in this expression has nothing to do with the surface term in the decay constant. It is simply the heat capacity. In other words, the large cluster condition can be formulated as the quantitative requirement that the heat capacity is larger than $(D/T)^2$. The value of (N/N_κ) has a physical interpretation, too. It simply represents the effective number of evaporations with a decay constant that is equal to the final, k_N. For $N<N_\kappa$ we clearly venture into the Klots/Gspann regime.

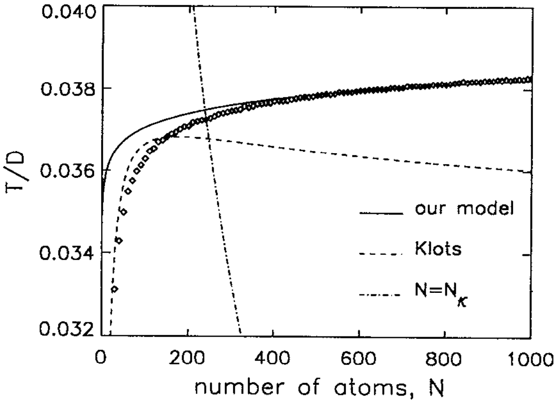

FIG. 3. The mean temperature in units of the activation energy, D, of initially hot clusters calculated for $t=1$ ms. The solid line shows the predictions of Eq. (12) in the main text. The dotted line corresponds to $[(T_{\min}+T_{\max})/2\simeq](D/\ln(N^{2/3}\omega t))-(D/6N)$, the mean value of the temperature interval predicted Klots (Ref. 6). The dots show the results of a statistical simulation. "Small" clusters ($N\leqslant N_\kappa$) are divided from "large" clusters ($N\geqslant N_\kappa$) by the dashed–dotted line.

This agrees nicely with our previous observation on the region where one crosses from the large to the small size regime.

In Fig. 3 we show the temperature, or rather T/D, of initially hot clusters after a cooling time of $t=1$ ms. The solid line shows the predictions of Eq. (13). The dashed line corresponds to $[(T_{\min}+T_{\max})/2]$, the mean value of the temperature interval predicted by the Klots/Gspann theory. The diamonds are the results of a Monte Carlo simulation of the decay process. Clusters at an average initial temperature of $D/10$ were allowed to evaporate atoms with a decay probability given by Eq. (3). The separation energy was fixed at $D=1$, and the kinetic energy carried by the evaporated atom was set equal to zero. Of course, it is possible to include an average kinetic energy of the evaporated atoms of ϵ simply by renormalizing the value of D to $D+\epsilon$ in the above formula. The results shown in Fig. 3 are mean values of approximately 8000 simulations per cluster size. For small clusters they fit to the prediction of Klots. The crossover to our model occurs at $N\simeq 200$. The dashed-dotted line corresponds to $1/\sqrt{3N}$ and divides "small" clusters ($N<N_\kappa$) from "large" clusters ($N>N_\kappa$).

In the preceding it has been tacitly assumed that the different temperatures of a given cluster size can be represented by a single value, especially with respect to the decay constant. This will now be justified. By the central limit theorem, the distribution of arrival times at size N is normally distributed if the number of evaporations is large enough. Since the parameter N/N_κ counts the number of evaporations with magnitude similar to the last one, this condition is precisely the large cluster limit. As it is well known, a normal distribution is completely determined by the mean value and the variance. The mean value is the one already used in Eq. (2). The variance is the sum of variances of the (statistically independent) individual steps,

$$\sigma_t^2=\sum_{i=N}^{N_0}\frac{1}{k_i^2}\simeq k_N^{-2}\cdot\frac{1-\left(\exp\frac{2D^2}{3N\cdot T^2}\right)^{N_0-N+1}}{1-\exp\frac{2D^2}{3N\cdot T^2}}$$

$$\simeq t^2\cdot\left(\frac{D}{T}\right)^2\cdot\frac{1}{6N} \tag{13}$$

or

$$\sigma_t\simeq t\cdot\frac{D}{T}\sqrt{\frac{1}{6N}}=t\sqrt{\frac{N_\kappa}{2N}} \tag{14}$$

(again assuming T_0 large enough). For a single decay chain the width in size can be related to the width in time

$$\sigma_N=\left|\frac{dN}{dt}\right|\sigma_t=k_N\sigma_t. \tag{15}$$

To obtain the width of the temperature distribution one can imagine the (N,T)-space covered densely with the trajectories belonging to a continuum of decay chains. Then one can transform from size to temperature,

$$\sigma_T=\frac{D}{3N}\sigma_N \tag{16}$$

which finally gives

$$\sigma_T=\frac{T}{\sqrt{6N}}. \tag{17}$$

The result of Eq. (17) is very similar to the expression of the averaged energy fluctuations of a canonical ensemble at temperature T which differs by a factor of squareroot 2 if we use $C_v=3N$ for the heat capacity. Presumably the reason for the similarity is the common statistical origin of the two distributions, the canonical and the evaporative. The relation is not trivial, however. For the canonical system the Boltzmann factor provides a high energy cutoff on the energy distribution and the level density the low energy cutoff. For the evaporative system, however, the Boltzmann factor provides both the high and the low energy cutoff. High energy clusters

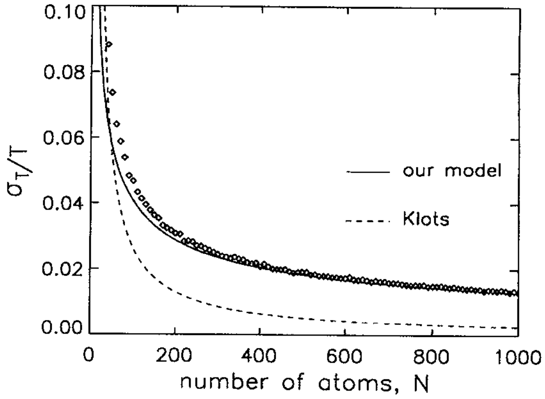

FIG. 4. σ_T/T as a function of cluster size. The dots show the results of a statistical simulation. The prediction of Klots, $(1/2\sqrt{3})\cdot(D/T\cdot 3N)$ (dashed line), fails for $N>100$. The full line corresponds to $\sigma_T/T=(1/\sqrt{6N})$.

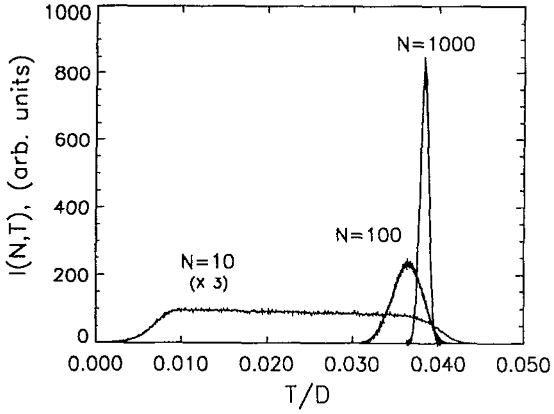

FIG. 5. The shape of the temperature distributions for sizes 10, 100, and 1000 from the Monte Carlo simulations. For $N=10$ the distribution has been multiplied by a factor 3. While for $N=10$ the distribution is nearly flat, a Gaussian shape is obtained for $N=100$, 1000.

cool faster due to the Boltzmann factor whereas it on the other hand prevents cold clusters from cooling. Hence it acts as a focussing mechanism for both the high and the low energy tail of the spectrum.

From the statistical simulations shown in Fig. 3 we calculated σ_T for different N. In Fig. 4 the results are compared to these predicted by Eq. (17). The agreement is excellent, even for $N<200$. The Klots prediction of $(1/2\sqrt{3})\cdot(D/3N)$ (a square distribution has a width of $2\sqrt{3}\cdot\sigma$) fails for $N>100$. In Fig. 5 we show the shape of the temperature distributions from simulation of the same type but with high statistics for $N=10$, 100, and 1000. For $N=10$ the distribution has, predicted by Klots,[6] nearly the shape of a square box. But already for $N=100$ the Gaussian shape seems a much better approximation than the square box.

CONCLUSIONS

The temperature of an ensemble of evaporating clusters has an average value which is determined by the cluster size and the cooling time. For clusters composed of more than a hundred atoms we find a temperature distribution which is approximately Gaussian with an almost constant mean value and a width which decreases with the square root of the cluster size. This should be compared to the approximation valid for small clusters which gives an almost square distribution with a constant upper limit and a width which is inversely proportional to size. The crossover from small to large happens around hundred atoms and is almost independent of cluster material and cooling time, provided the latter is long compared to the typical phonon time scale in the material. Furthermore we find that the average decay constant is proportional to size and inversely proportional to cooling time.

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