Electronic degrees of freedom and unimolecular rate constants in metal clusters

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We calculate the modifications of the unimolecular rate constants for free metallic clusters due to thermally exited electronic degrees of freedom. The effect is essentially taken into account by substituting Helmholtz's free energy of the electronic system for the ground state energy. The activation energy pertaining to the electronic ground states of the mother and daughter cluster is then replaced by the first difference in Helmholtz's free energy. © *1994 American Institute of Physics.*

I. INTRODUCTION

The purpose of this letter is to show how electronic excitations will modify the unimolecular rate constant of evaporation of metal clusters. The problem is particularly strong in the context of the observed shell structure of metal clusters produced in a hot source.[1-3] The reason is that for metal clusters the smallest electronic excitation energy can become comparable to, or even smaller, than the experimentally relevant temperatures. In experiments where evaporation is actually observed, the temperature will be around 5% of the activation energy for evaporation.[4,5] The average level spacing in the case of nonspherical clusters can be estimated simply by the Fermi energy divided by the number of valence electrons (or better as[6] $4E_F/3N$). The Fermi energy and the activation energy are comparable in magnitude. Consequently, thermal electronic excitations will be important already in clusters with less than hundred valence electrons. If we alternatively consider excitations across the shell gap, the relevant excitation energy is of the order of the Fermi energy divided by the shell number. Then, only for clusters with more than 10 000 electrons, the shell gap will be comparable to T. However, even for temperatures smaller than the shell spacing, excitations will be important.[7] This is indeed confirmed by detailed calculations where the electrons are treated in the local density approximation and the ionic core is approximated by a smooth jellium.[8] These calculations indicate significant thermal corrections already for size below 1000 electrons.

The possibility of electronic excitations will open up a part of phase space that hitherto has not been included in the statistical description of decay processes. It may seem surprising that these new dimensions in phase space should be important since the electronic subsystem in a metal cluster only absorbs a small fraction of the total excitation energy. However, the characteristic energy associated with, e.g., odd-even staggering and shell structure are also small[9,10] in spite of their strong experimental signature.[1] In fact, they are of the order of magnitude of the level spacing (depending on the precise experimental conditions). Hence, when we focus our attention on the size dependence of these electronic properties of metal clusters, we must expect strong modifications due to finite temperatures.

II. RATE CONSTANTS AND GENERALIZED DISSOCIATION ENERGIES

In order to be able to formulate the problem in a way that is susceptible to solution, we will briefly review the considerations that were used by Weisskopf[11] to predict the evaporation rate of neutrons from hot atomic nuclei. The idea was later applied to clusters by Engelking.[12]

We will only consider evaporation, i.e., processes that occur with a typical time which is long compared to the relevant molecular time scale. As an estimate for this molecular time, one can take the phonon vibrational period although the precise value is not important for this work. Hence, violent fragmentation is excluded from the treatment. In other words, we will assume that the evaporation is a statistical process with an associated activation energy. By the statistical assumption we mean that all, or at least a representative subset of states of the system within a (small) energy interval are accessible during a time period of the order of the decay time. All states with the proper values of the conserved quantities will then be populated equally according to the principle of detailed balance. This principle, in turn, is based on the assumption of the validity of microscopic time reversal.

The trick employed by Weisskopf is to divide the states into two classes: One class consisting of the states describing the cluster (molecule, nucleus) as evaporated, i.e., as the systems $A_{N-1}+A_1$, and one describing the condensed or non-evaporated, A_N. The relative statistical weight of these two classes is given by the number of states pertaining to each class, $n(A_{N-1}+A_1)$ and $n(A_N)$. Using level densities, these numbers are expressed as $n(A_{N-1}+A_1)=\rho(A_{N-1}+A_1)dE$ and $n(A_N)=\rho(A_N)dE$. Since the number of conversions per time interval from $A_{N-1}+A_1$ to A_N is equal to the corresponding turnover for the inverse process, the rate constants R are related as

$$R_{N-1,1\to N}\rho(A_{N-1}+A_1)=R_{N\to N-1,1}\rho(A_N). \tag{1}$$

(All conserved quantities except the energy are suppressed in the notation here.)

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The constant $R_{N-1,1\to N}$ is simply the time constant for formation of cluster A_N starting with clusters A_{N-1} and A_1. Enclosing the system in a box of volume V, the result for this production rate is

$$R_{N-1,1\to N}=\frac{p\sigma}{VM}, \tag{2}$$

where σ is the capture cross section, p is the relative momentum, and M is the reduced mass. The decay constant can then be written as

$$k_N\equiv R_{N\to N-1,1}=\frac{p\sigma}{MV}\frac{\rho(A_{N-1}+A_1)}{\rho(A_N)}. \tag{3}$$

To evaluate this expression one needs to know the capture cross section and the level densities; the latter with due respect paid to energy conservation. Furthermore, one should either specify the kinetic energy of the evaporated atom or alternatively integrate over this quantity. For the purpose of the present discussion, we can take any approximation for treating the kinetic energy of the evaporated atom.[13] The only important point is that its density of state can be convoluted out from Eq. (3) and rate constant can then be written in the simple form given by Engelking;[12]

$$k_N=a\sigma\frac{\rho_{N-1}(E-D_N)}{\rho_N(E)}, \tag{4}$$

where ρ_N and ρ_{N-1} are the densities of states of the mother and daughter clusters, respectively, and E is the excitation energy of the mother cluster. The detailed expression for the coefficient a depends on the treatment of the kinetic energy of the evaporated atom,[12] but it is of little interest in this context. The separation energy, D_N, for cluster N is defined as

$$D_N\equiv -E_N+E_{N-1}, \tag{5}$$

where E_N is the ground state energy of cluster N. It should be noted that the separation energy refers to the electronic as well as the ionic ground states of both parent and daughter. It may seem surprising that the ionic ground states should determine the evaporation rate since the clusters are manifestly not in the ground state. The result becomes clear when it is remembered that the ground states are singled out as the zero point for excitation energy when the level densities are evaluated.

For the sake of argument, we will equate the separation energy to the activation energy. The more general case of an activation barrier in the capture cross section can be incorporated by specifying σ as a function of the energy of the approaching fragment.

The total level density of cluster N is composed of two contributions, one for the ionic degrees of freedom and one for the electronic. Assuming that the ionic motion does not change markedly the electronic density of states, we can approximate the total level density with a convolution;

$$\rho_{\mathrm{tot},N}(E)=\int_0^E d\epsilon\ \rho_{i,N}(E-\epsilon)\rho_{\mathrm{el},N}(\epsilon), \tag{6}$$

where $\rho_{i,N}$ is the ionic and $\rho_{\mathrm{el},N}$ the electronic level density for size N, respectively. In order to proceed, we use the fact that the electronic heat capacity is small compared to the ionic one.[14] Thus, the energy carried by the electronic excitations is small compared to the total excitation energy, i.e., $\epsilon\ll E$. The integral can then be approximated by a cumulant expansion to first order;

$$\rho_{\mathrm{tot},N}(E)=\int_0^E d\epsilon\ \rho_{i,N}(E-\epsilon)\rho_{\mathrm{el},N}(\epsilon)$$

$$\approx\int_0^E d\epsilon\ \rho_{i,N}(E)\exp\left(-\epsilon\frac{d\ \log(\rho_{i,N})}{dE}\right)\rho_{\mathrm{el},N}(\epsilon) \tag{7}$$

or

$$\rho_{\mathrm{tot},N}(E)\approx\rho_{i,N}(E)\int_0^\infty d\epsilon\ \rho_{\mathrm{el},N}(\epsilon)e^{-\epsilon/T_{i,N}}, \tag{8}$$

where we have defined the temperature of the ionic system in the usual way as[15]

$$T_{i,N}^{-1}=\frac{d\ \log(\rho_{i,N}(E))}{dE}. \tag{9}$$

Since the integral is nothing but the canonical partition function for the electronic subsystem at temperature $T_{i,N}$, the level densities can be written in terms of Helmholtz' free energy or equivalently with the help of the electronic partition function as

$$\rho_{\mathrm{tot},N}(E)=\rho_{i,N}e^{-F_{\mathrm{el},N}(T_{i,N})/T_{i,N}}=\rho_{i,N}(E)Z_{\mathrm{el},N}(T_{i,N}). \tag{10}$$

The density of state of the daughter cluster can be treated in a similar fashion, and hence, the effect of the electronic degrees of freedom is to modify the rate constant by the ration of the partition functions

$$k_N=k_{N,\mathrm{ion}}\exp\left(-\frac{F_{\mathrm{el},N-1}(T_{i,N-1})}{T_{i,N-1}}+\frac{F_{\mathrm{el},N}(T_{i,N})}{T_{i,N}}\right), \tag{11}$$

where $k_{N,\mathrm{ion}}$ is the conventional rate constant where the electronic excitations are neglected. Note that in the above equations the electronic free energy is measured from the ground state ($F_{\mathrm{el},N}(T=0)=0$).

III. DISCUSSION

The above result can be cast into a more transparent form when it is applied to large clusters. For these, the total excitation energy is large compared to the separation energy, $D/E\ll 1$. Then, the ionic part of the rate constant can be approximated, using the cumulant expansion, by an Arhenius-type formula,

$$k_{N,\mathrm{ion}}=\omega e^{-D/T}, \tag{12}$$

where ω can depend only weakly on temperature. By approximating the temperatures of the parent and the daughter to be the same we can then express the total rate constant as

$$k_N=\omega\ \exp(\Delta_1F_N/T), \tag{13}$$

where

$$\Delta_1F_N\equiv(E_N+F_{\mathrm{el},N})-(E_{N-1}+F_{\mathrm{el},N-1}). \tag{14}$$

The electronic free energies are measured from the electronic ground state of the respective clusters. On the other hand, the binding energies E_N are precisely these ground state energies. Hence, the expression tells us, that we simply have to substitute separation energies by the corresponding differences in electronic free energies. At zero temperature, the expression reduces properly to the usual, purely ionic form.

The above derivation was based on the assumption that there is no activation barrier to the evaporation. This is a reasonable assumption and supported by what is known from evaporation (and sticking) from plane metal surfaces. However, there still remains a question concerning the transition state. While the total potential energy of the system is likely to increase monotonically when the evaporating atom moves out from the cluster, there is a possibility that the electronic shell structure of the cluster is disturbed when the atom is in close contact to the surface. This would mean that the electronic free energy in this region would be strongly coupled to the ionic motion and the above assumption of the independence of the electron density of states of the ionic motion would not be valid.

In order to examine this question, we have studied the electronic level structure in this transition region in a model calculation for an interaction of a monomer with a 92 electron jellium cluster ($r_s=4.0$). Since we are only interested in qualitative effects, we approximate the self-consistent potentials of the clusters with square wells with the depth and radii chosen so that the level structures are similar to those of the self-consistent jellium model (for $N=92$, we take $V_0=0.22$ a.u., $R=18.06$ and for $N=1$, $V_0=0.22$ a.u., $R=4.7$). The electronic level structure of the system of these two potential wells was solved using a plane wave basis. Figure 1 shows the density of states for two different distances between the clusters. In the upper figure the monomer is so far away that the density of state is a superposition of the density of states of the individual clusters. The lower figure shows that even when the potentials are in contact (the distance from the center of the monomer potential to the surface of the 92 atom cluster is 4 a.u.), the shell structure is essentially intact. Only a slight lowering of the monomer level is seen in the figure.

We can use a perturbation theory to see what happens in larger clusters. By assuming that the monomer potential is a δ function perturbation at the surface of the larger cluster, we can approximate the matrix element of the perturbation potential as

$$\Delta V_{\ell mm'} \approx \frac{4\pi r_s^3 V_0}{3} R_\ell(r_N)^2 \int d\Omega\ Y^*_{\ell m}(\Omega) Y_{\ell m'}(\Omega)\delta(\Omega), \tag{15}$$

where $R_\ell(r_N)$ is the radial part of the wave function evaluated at the cluster surface. Since $R_\ell(r_N) \propto N^{-1}$ (or for the highest ℓ value $R_\ell(r_N) \propto N^{-2/3}$) and the distance between the energy shells goes down as $N^{-1/3}$ or slower,[16] the effect of the perturbation goes down with the cluster size.

On the basis of these estimates we can conclude that when the atom moves out from the surface the energy spectrum of the cluster is not strongly disturbed and we do not have to take separately into account this transition region.

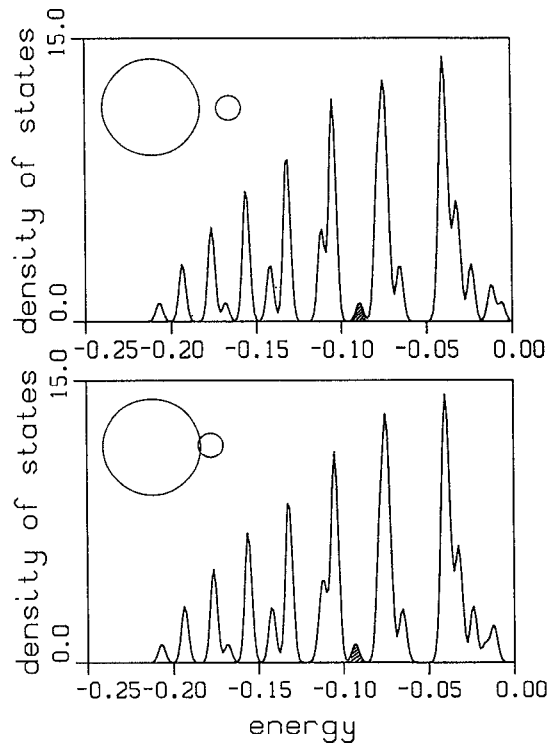

FIG. 1. Density of states (in arbitrary units) of a system consisting of a 92 atom jellium cluster and a jellium monomer. The discrete levels (in atomic units) are convoluted with a Gaussian with a width of 0.002 a.u. The insets show the distance between the clusters. The monomer level is shaded.

Note however, that the exact degeneracies will be lifted and this requires special consideration for low temperatures.

Equations (13) and (14) show explicitly that the rate constant for evaporation depends on the electronic shell structure through the electronic free energy F_N, which have been evaluated for the spherical jellium model by Brack *et al.*[8] However, the capture cross section σ, in Eq. (5), hidden in the frequency ω in Eq. (13), also depends on the shell structure. Classically this cross section would be simply πR^2, but the polarization interaction between the atom and the cluster increases this cross section. The long range polarization potential between the atom and a neutral cluster is proportional to $-\alpha_N/r^6$, where the polarizability α_N depends on the electronic structure. It is slightly smaller for magic clusters with a closed electronic shell than for open shell clusters.[1] Nevertheless, in the case of large clusters (with $N>100$) the variation caused by the shell structure becomes very small. Thus, we do not believe that shell oscillations in the capture cross section σ has any marked effect on the rate constant of evaporation.

We have not considered the effect of the ionic degrees of freedom, i.e., $k_{\text{ion},N}$ in Eq. (11). Bertsch *et al.*[17] have shown, using the Weisskopf formulation, that the phonon degrees of freedom will reduce the desorption rate of finite clusters compared to the desorption from an infinite surface. For large clusters, the result approaches to the classical result. In this model, the reduction of the evaporation rate is a monotonous function of the cluster size and does not have any effects on the electronic shell structure.

The weak coupling between the electronic and ionic degrees of freedom reduces the shell structure effects in two ways: The electronic structure is affected by the surface roughness and by the shape fluctuations. The magnitude of these effects is difficult to estimate. While these effects will slightly change the average electronic free energy entering Eq. (14), we do not expect them to change the basic formulation derived above.

Undoubtedly, the above formula equation (13) could also be derived from macroscopic equilibrium considerations. We feel, however, that a microscopic derivation is more valuable. In particular, it is possible to treat the experimentally important case of isolated systems which by definition are microcanonical.

The main result of this work indicates that it is necessary to abandon the timehonored practice of describing unimolecular decays by a single parameter. To obtain the correct rates, one has to incorporate the exited electronic states and as we have seen, this can be done approximately by translating activation energies into activation free energies. For this purpose, it is necessary to know the spectrum of electronic excitations. Finally, we want to remark that similar modifications to the rate constant can occur for other reasons than electronic excitations. This is most easily seen from Eq. (9). If the logarithmic derivative of the level density depends significantly on one or more parameters with dimension energy, the rate constant will depend on these parameters as well as on the separation energy.

On the other hand, we see that an experimental measurement of separation energies will yield the *free* separation energies and not the *ground state* separation energies. For small clusters, however, it is necessary to keep in mind the corrections to this simple picture due to both the modifications of the level densities in the transition state and the different ionic temperature of mother and daughter.

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