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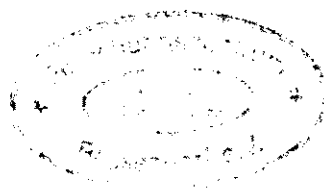
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# Evaporation Rates for Liquid Clusters

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## Abstract

An expression for the evaporation rate of neutral atoms from a hot liquid cluster is suggested. It combines Weisskopf's statistical model for the decay with a level density that is derived from the experimentally known free energy of macroscopic droplets of the cluster material. For the case of sodium clusters, a comparison with the rates based on the level density of a system of oscillators shows that this frequently used expression gives always much larger evaporation rates.

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## 1 Introduction

The electronic shell structure of simple metal clusters has been discovered in the abundance spectra after an evaporation cascade [1]. Though there are studies of the evaporative ensemble [2], the quantitative relation between binding energies and the observed abundances is not yet established. In LASER induced evaporation experiments the cascade is better understood and binding energies have been derived from the observed abundances [3, 4]. The analyses of the evaporation data are based on expressions for the rates similar or equal to the one suggested by Engelking [5]. It combines Weisskopf's rate expression [6] with Kassel's level density estimate [7] for  $3N - 6$  oscillators, among which the energy is equipartitioned. Obviously, this level density cannot be very accurate for clusters above the bulk melting temperature. The ions move through the cluster instead of oscillating around fixed positions in a molecular skeleton. This has been demonstrated by molecular dynamics simulations [8]. In the present paper an expression is suggested that is also based on Weisskopf's rate, whereas the level density is derived from the thermodynamic properties of the bulk liquid, which are experimentally well known. The assumption entering the approach is that the appropriate

scaling laws with respect to the number of atoms  $N$  ( $\propto N$  for the volume term and  $\propto N^{2/3}$  for the surface term) hold down to very small clusters of some ten atoms.

The rate constant is derived section 2, following the general scheme by Brink and Stringari [10], but making a specific model for the free energy. In section 3 the rate constant is compared with the one based on Kassel's level densities, considering Na clusters as an example. During the completion of the manuscript the work of Hervieux and Gross [12] came to our attention, who suggest a very similar approach. In section 3 the relation of their rate constant with ours is discussed.

## 2 The droplet rate constant

### 2.1 General expression

We start from the principle of detailed balance [6], used by Weisskopf to describe neutron evaporation from nuclei. It has been used in refs. [5, 10, 11] in combination with different expressions for the level densities to derive evaporation rates of atoms from clusters. The probability per unit time to evaporate an atom with the kinetic energy  $\varepsilon$  from a cluster with the energy  $E$  is [6]

$$Wd\varepsilon = g \frac{m\sigma}{\pi^2 \hbar^3} \varepsilon \frac{\omega(E - \varepsilon, N)}{\omega(E, N)} d\varepsilon \quad (1)$$

Here,  $m$  is the mass of the emitted atom,  $g$  its spin degeneracy,  $\sigma$  the cross section of the inverse reaction of absorbing one atom and  $\omega(E, N)$  is the level density of the cluster with the mass number  $N$  atoms and the energy  $E$ . It is assumed that there is no barrier for the atom leaving the cluster, e. g. we consider the evaporation of neutral atoms from neutral clusters. The absorption cross section is taken to be equal to the geometric one

$$\sigma = \pi R^2, \quad (2)$$

i. e. the atoms sticks when it hits the cluster. Here,  $R$  is the cluster radius

$$R = r_s N^{1/3}, \quad v = \frac{4\pi}{3} r_s^3 \quad (3)$$

$v$  the specific volume and  $r_s$  the Wigner - Seitz radius. The total rate is obtained by integration over all possible kinetic energies of the emitted atoms.

$$\Gamma = \frac{dN}{dt} = g \frac{mR^2}{\pi \hbar^3} \int_0^{E-E_o(N-1)} \varepsilon \frac{\omega(E-\varepsilon, N)}{\omega(E, N)} d\varepsilon \quad (4)$$

The ground state energy is denoted by  $E_o(N)$ .

In order to derive the expression for the level density we start from the Darwin - Fowler relation

$$\omega(E, N) = \frac{1}{2\pi i} \int_C d\beta' e^{\beta'(E-F(\beta, N))}, \quad (5)$$

The contour is parallel to the imaginary  $\beta'$  - axis to the right of all singularities of  $Z(\beta')$ . The free energy of the isolated cluster,  $F(\beta, N)$ , is given by the canonical partition function

$$F(\beta, N) = -\frac{1}{\beta} \ln Z(\beta, N), \quad Z(\beta, N) = \sum_i e^{-\beta E_{i,N}} \quad (6)$$

The sum runs over all quantal states  $i, N$  of the cluster. Contact with thermodynamics is made by evaluating the integral in saddle point approximation. This method has been used in nuclear physics, where a review can be found e. g. in the textbook [9], and in cluster physics [10]. The position of the saddle point  $\beta$  is determined by the equation

$$\frac{\partial}{\partial \beta} [\beta(E - F(\beta, N))], \quad (7)$$

which defines the temperature  $T(E, N) = 1/\beta$ . The standard thermodynamical potentials, as entropy

$$S(T, N) = -\frac{\partial}{\partial T} F(T, N) \quad (8)$$

and average energy

$$E(T, N) = F(T, N) + TS(T, N) \quad (9)$$

appear as quantities derived from  $F(T, N)$  and the condition (7) for the saddle point may be rewritten as the familiar implicit equation equating the cluster energy with the average energy

$$E = E(T, N), \quad (10)$$

which determines the temperature. The integral is calculated expanding the exponent of the integrand up to second order in  $\beta - \beta'$ , where the coefficient of the second order terms can be expressed in terms of the heat capacity

$$C(T, N) = \frac{\partial}{\partial T} E(T, N) \quad (11)$$

The level density becomes [10]

$$\omega(E, N) = \frac{1}{T(E, N) \sqrt{2\pi C(E, N)}} e^{S(E, N)}. \quad (12)$$

In order to evaluate the expression one has to invert the eq. (10) to find  $T(E, N)$  and inserting it into the eqs. (8 and 11) one obtains  $C(E, N)$  and  $S(E, N)$ .

It is a good approximation [10] to expand  $S(E - \varepsilon, N - 1)$  with respect to the released kinetic energy  $\varepsilon$ . Using  $\partial/\partial E S(E, N - 1) = T(E, N - 1)$

$$\omega(E - \varepsilon, N - 1) \approx \omega(E, N - 1) e^{-\varepsilon/T(E, N-1)} \quad (13)$$

one finds the familiar Maxwell distribution for the kinetic energy. Putting this into eq. (1), one obtains the average kinetic energy released,  $\bar{\varepsilon} = 2T(E, N - 1)$ . The following term in the exponent is  $\frac{\partial}{\partial E} \varepsilon^2/T(E, N - 1) = -\varepsilon^2/T^2 C$ . Compared with the leading term it is reduced by  $\varepsilon/TC \sim 1/C$  and may safely be neglected for clusters with  $N > 10$ . Carrying out the integral (4) one finds

$$\Gamma = \frac{dN}{dt} = g \frac{mR^2}{\pi \hbar^3} T(E, N) T(E, N - 1) \sqrt{\frac{C(E, N)}{C(E, N - 1)}} e^{S(E, N-1) - S(E, N)} \quad (14)$$

So far we have derived a general rate constant that is completely expressed in terms of the free energy  $F(T, N)$  of the cluster. In the following a model for the free energy is specified.

## 2.2 The droplet free energy

We make now the assumption that microstructure only shows up in the ground state energies  $E_o(N)$  of the clusters. The temperature dependence of the energy is assumed to be the same as that of a macroscopic droplet of

the liquid of the material the cluster is composed of. Then, the free energy reads

$$F_{LD}(T, N) = F_{LD}^*(T, N) + E_o(N). \quad (15)$$

The thermal part of the free energy,  $F_{LD}^*$ , which we call the liquid drop free energy for simplicity, consists of a volume and a surface part

$$F_{LD}^* = f^*N + 4\pi[r_s(T)^2\alpha(T) - r_s(0)^2\alpha(0)]N^{2/3} \quad (16)$$

The specific free energy  $f^*$ , the surface tension  $\alpha$  and the Wigner - Seitz radius  $r_s$  are assumed to be given by the experimental values at standard pressure  $p_o = 1atm$ , as quoted in the tables (e. g. in [13, 14]). It is noted that the second term, which is usually called "surface energy", is a free energy, since the experiments to measure it are carried out at fixed temperature [15]. The expression assumes a size independent surface tension  $\alpha$  and incompressibility of the liquid (then,  $f^*$  becomes pressure independent). It represents the leading terms in a leptodermic expansion into powers of  $N^{-1/3}$ . The next term of order  $N^{1/3}$  would take into account a number of effects, including the finite compressibility and the size dependence of the surface tension (curvature correction). A systematic leptodermic expansion has been worked out in the droplet model of Meyers and Swiatecki [?]. The Coulomb energy of charged clusters may be incorporated into  $E_o(N)$ .

Let us start with the volume part. Usually, the tables quote the specific heat  $c_p$  as a polynomial in  $T$ . For the liquid one may safely ignore the difference between  $c_p$  and  $c_v$ , since the volume work  $p_o v$ , where  $v$  is the specific volume of the liquid, is negligible compared with  $c$ . Using a third order polynomial, as in [14], the specific heat of the liquid is

$$c(T) = c_0 + c_1T + c_2T^2 \quad (17)$$

By integration one obtains the specific internal energy

$$e^*(T) = c_0T + \frac{1}{2}c_1T^2 + \frac{1}{3}c_2T^3 \quad (18)$$

Integrating  $c/T$  gives the specific entropy

$$s(T) = s_0 + c_0 \ln T + c_1T + \frac{1}{2}c_2T^2 \quad (19)$$

The integration constant  $s_0$  is fixed by the tables [14] that quote absolute values of  $s$ . Finally,

$$f^*(T) = e^*(T) - Ts(T) \quad (20)$$

The surface term is defined by the the surface tension and the Wigner - Seitz radius, which can be well approximated by linear expressions in  $T$ .

$$\alpha(T) = \alpha_0 - \alpha_1 T, \quad r_s(T) = r_0 + r_1 T \quad (21)$$

The entropy, energy and heat capacity are obtained by means of the standard relations (8,9,11),respectively,

$$S_{LD}(T, N) = s(T)N + 4\pi[\alpha_1 r_s^2(T) - 2r_1 \alpha(T)r_s(T)]N^{2/3}, \quad (22)$$

$$E_{LD}(T, N) = E_{LD}^*(T, N) + E_o(N) \quad (23)$$

$$E_{LD}^*(T, N) = e^*(T)N + 4\pi[\alpha_0(r_s^2(T) - r_0^2) - 2r_1 \alpha(T)r_s(T)T]N^{2/3} \quad (24)$$

$$C_{LD}(T, N) = c(t)N + 8\pi[2\alpha_1 r_1 r_s(T) - r_1^2 \alpha(T)]TN^{2/3} \quad (25)$$

Since only the internal energy is  $T$  - dependent, one may use  $E^*$  as the energy variable instead of  $E$ . The relation (24) gives  $T(E^*, N)$ . The internal energy of the cluster after emitting the atom is

$$E^*(N - 1) = E^*(N) - \varepsilon - D(N), \quad D(N) = E_o(N - 1) - E_o(N), \quad (26)$$

which must be used in eq. (24) to calculate  $T(N - 1, E^*, \varepsilon)$ . Here appear the separation energies  $D(N)$ . This form is frequently used [5, 10, 11, 12]. We will refer to the rate constant based on the expressions (15,16) for the free energy as the droplet rate.

The separation energies  $D(N)$  are still not specified. They may either be estimated by a suitable model or can be considered as free parameters to be determined from the experimental evaporation rates. A simple estimate is based on the on the liquid drop energy at zero temperature

$$D(N) = -e_0 - \frac{8\pi}{3}r_0^2\alpha_0 N^{-1/3}, \quad (27)$$

where  $e_0 = e(T = 0)$  is the bulk separation energy at zero temperature that is also accessible from the tables [14]. It does not contain the fluctuations that are due to the electronic shell structure.



The shell effects in the valence electron system also influence thermal part  $F^*$ . This effect as well as the change of the surface area by deformation of the cluster, can be studied by using the shell correction approach to  $F$ , suggested by Frauendorf and Pashkevich [16]. There the free energy has the form

$$F = F_{LD} + \delta F \quad (28)$$

where  $F_{LD}$  is the total free energy of the droplet (including the ground state energy) and the shell correction  $\delta F$  describes the influence of the valence electron shell structure on both the ground state energy and on  $F^*$ . Since the electron gas is degenerated, the latter contribution is expected to be small. On the other hand, the rate constant depends on the *difference* between the entropies of two adjacent clusters and the local changes with  $N$ , caused by shell structure, may become nonnegligible. This question will be investigated in a forthcoming paper.

### 3 Discussion

As an example, table 1 compares the droplet rate sodium with some other rate expressions. The parameters for liquid sodium are [13, 14]:  $c_0 = 4.405$ ,  $c_1 = -26.7eV^{-1}$ ,  $c_2 = 172.3eV^{-2}$ ,  $\alpha_0 = 0.0142eV\text{\AA}^{-2}$ ,  $\alpha_1 = 0.073\text{\AA}^{-2}$ ,  $r_0 = 2.065\text{\AA}$ ,  $r_1 = 2.34\text{\AA}eV^{-1}$ ,  $e_0 = -1.13eV$  and  $s_0 = 23.721$ . The table quotes the rates for different mass numbers, assuming that the parent cluster has a thermal energy corresponding to a temperature of  $50meV$ , which is typical for the evaporative ensembles. For the separation energies the liquid drop expression (27) is assumed. Shell structure is not considered.

The difference between Engelking's [5] rate, which is used in the analysis of the experimental evaporation rates [3, 4] and our droplet rate is the level density. He uses the Debye expression for a system of  $3N - 6$  oscillators with frequency  $\omega_i$ , among which the energy is equipartitioned.

$$\omega(E, N) = \frac{E^{*(3N-6)}}{(3N-6)!} \prod_{i=1}^{3N-6} \frac{1}{\hbar\omega_i} \quad (29)$$

The table quotes the rates obtained with his expression [5], assuming that the clusters have the same internal energy  $E^*$  and separation energies  $D$  as as quoted. For the small clusters the droplet rate is about four orders of

magnitude smaller than Engelking's estimate, for the largest the difference is about three orders of magnitude. The origin of the difference is the smaller heat capacity, which is  $3N - 6$  in the Kassel expression. For  $N = 20$ , the heat capacity is  $C = 54$  for the system of harmonic oscillators, whereas the droplet estimate gives 76. Most of the difference comes from the volume part. The specific heat of sodium at  $T = 50\text{meV}$  is  $c = 3.5$  to be compared with 3 for the system of harmonic oscillators. In addition, the finite size corrections to  $C$  have different sign. In the Kassel expression it is -6, whereas the surface part in  $C_{LD}$  is 6.4 for  $N = 20$ . Hence, higher temperatures are needed to give to the system of harmonic oscillators the same internal energy as to the droplet. This results in the strong enhancement of the evaporation rate. For large clusters the finite size correction become less important and the difference between the rates decreases. However, it always remains large, because of the different values of the specific heat. The larger specific heat of the liquid is a consequence of the strong anharmonicities that occur when the vibrational amplitudes become that large that the material melts.

The column  $D_E$  quotes the separation energies that have to be assumed in order to make Engelking's rate equal to the droplet rate. The separation energies obtained such are always larger than the droplet estimate. Hence, deriving separation energies from the experimental evaporation rates by means of the droplet rate expression will result in smaller values than by means of the frequently used expression by Engelking.

The droplet rate derived by Hervieux and Gross [12] differs from ours in the definition of the entropy. They use the standard relation  $S = -\partial/\partial T F(T, V)$  (fixed volume), as given for example in the textbook by Landau and Lifschitz [15], which does not contain the thermal volume expansion. It is obtained from our expression by setting the term  $r_1$ , which describes the increase of the Wigner - Seitz radius with temperature, equal to zero. Such a definition is appropriate for a surface between gas and liquid in contact with external forces and reservoirs, which is the typical macroscopic situation (grandcanonical ensemble). In addition, the preexponential factors in the expression (12) for the level density do not appear. Our definition of the entropy and the preexponential factors appear in a natural way when the *exact* level density (5) is calculated in saddlepoint approximation. In an approximative way, they may account for the fact that the *isolated* free flying cluster must be described by the microcanonical ensemble. Our entropy  $S = -\partial/\partial T F(T, N)$  (fixed  $N$ ) contains an additional contribution from the thermal expansion of

the cluster, which has the opposite sign of the standard term that originates from the  $T$ -dependence of the surface tension ( $\alpha$  decreases with  $T$  but the surface area increases with  $T$ ). At given  $T$ , the thermal energy  $E^*$  is larger since it contains a contribution from the surface energy caused by the volume expansion. For  $N = 20$  and  $T = 50meV$  one finds  $E^* = 4.04meV$  if the volume expansion is taken into account and  $3.88meV$  if not. Vice versa, if the same thermal energies  $E^*$  are considered, the temperatures without the volume expansion are slightly higher (c. f. tab.), what makes the evaporation rates larger for the latter case. However, the preexponential factor in the level density is  $T(N, E)/T(N - 1, E)\sqrt{C(N, E)/C(N_1, E)}$ , which is  $1.25 \times 1.02 = 1.28$  for  $N = 20$  and  $T = 50meV$ . It mainly compensates the decrease of the rate due to the lower temperature, such that the our droplet rate is only by a factor of 0.9 smaller than the one by Hervieux and Gross. For large  $N$  the two expressions converge to each other. This is limit of the gaskinetic rate expression, which has been discussed in refs. [10, 11, 12].

The droplet rate taking into account the surface correction is always smaller than the one by Brink and Stringari [10], who only consider the volume part of the thermal excitation (though the surface contribution to the separation energies is taken into account). The surface part of the droplet entropy (22) is positive for sodium. The second term due to the volume expansion is smaller than the first one caused by the decrease of the surface tension with temperature. Hence, there appears a negative contribution to the exponent in the rate expression (14). For  $N = 20$  and 19, the surface entropy is 22.2 and 20.2 and for 100 and 99 it is 64.9 and 63.6, respectively. The surface term decreases  $\propto N_{-1/3}$  as compared to the volume part.

The the total entropy difference is rather constant  $\approx 27$  (26.8 for the decay of  $N = 20$  and 27.0 for  $N = 500$ ), as given by the specific entropy. This has to be compared with the entropy difference of the valence electrons. Considering two spherical clusters at small temperature, where the mother has no and the daughter one hole in the electron level with angular momentum  $l$ , the electronic entropy difference is  $\ln(4l + 2)$ , which is 2.1 for  $l = 3$  being filled for  $N = 34$ . This is about the same value as the surface contribution. Deformation effects will tend to decrease this number since they lift the degeneracy. However, it seems to be possible that the surface contribution and the contribution from the electronic shell structure to the entropy are comparable, as the corresponding contributions to the separation energies.

This question will be studied in a forthcoming paper. As mentioned above, it is straight forward to incorporate the electronic shell structure into the rate expression by using the shell correction approach to  $F$ , as suggested in ref. /citefp.

## 4 Conclusion

Starting from the Weisskopf statistical decay model and the saddle point approximation to the Darwin - Fowler expression for the level density we have derived the droplet rate for evaporation of neutral atom. It is completely determined by the free energy of the *isolated* cluster. The free energy can be calculated from the experimental thermodynamical properties of macroscopic droplets, if the validity of the scaling laws with respect to the mass number is assumed to hold down to some tens of atoms. Applying the droplet rate to the experimental evaporation rates allows to derive "experimental separation energies", which are expected to be smaller than the one found on the basis of Engelking's rate. It would be interesting to reanalyse the existing measurements in order to see whether the droplet rate leads to a consistent picture and more accurate separation energies. It is not obvious at this point whether it is sufficient to consider the electronic shell structure only for the separation energies. First estimates indicate that it may contribute in favorable cases up to 10% to the entropy difference that appears in the exponent of the decay rate. This number is comparable with the surface contribution to the entropy difference.

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$N$	$E^*$	$\log \Gamma$	$T$	$\log \Gamma_E$	$T_E$	$D$	$D_E$	$\log \Gamma_H$	$\log \Gamma_B$	$T_{HB}$
20	4.04		50		75					52
19	3.09	5.64	40	9.40	61	0.94	1.41	5.69	6.11	41
50	9.99		50		69					52
49	9.00	6.05	46	9.25	64	0.99	1.44	6.15	6.45	47
100	19.85		50		68					51
99	18.84	6.21	48	9.23	65	1.02	1.46	6.31	6.56	49
500	98.35		50		66					51
499	97.28	6.50	50	9.33	65	1.06	1.49	6.57	6.72	50
$10^3$	196.15		50		66					51
	195.07	6.62	50	9.43	65	1.08	1.50	6.68	6.80	50
$10^4$	1950.30		50		65					50
	1949.19	7.10	50	9.88	65	1.11	1.52	7.15	7.20	50

Table 1: Comparison of different evaporation rates. Temperature and thermal energy of mother and daughter cluster are added. The energies are given in  $eV$  and the temperatures in  $meV$ . The decimal logarithm of the rates is quoted, where the rates are in units  $s^{-1}$ . The expression (14) is used to calculate the droplet rate. The columns with subscript  $E$  denote Engelking's values [5] that base on the level density of  $3N - 6$  harmonic oscillators. The column  $D_E$  quotes the separation energies that are necessary to make  $\Gamma_E = \Gamma$ . The columns with the subscripts  $H$  and  $B$  quote the rates obtained from the droplet rate of Hervieux and Gross [12] and Brink and Stringari [10]. The temperatures are equal for these two approaches. The same separation energies as given by the zero temperature liquid drop expression (27) are used.