The effective temperature in microcanonical rate constants

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Abstract

Microcanonical rate constants can be parameterized in terms of an effective temperature. We show here that for fairly general level densities of the involved species it is possible to make this parametrization with a temperature independent heat capacity and a rate constant of the Arrhenius form. This is a major simplification in the interpretation of many experiments on unimolecular decay in vacuum. The results show that activation energies and heat capacities measured in microcanonical experiment differ from their canonical analogues.

Key words: Unimolecular reactions, emission temperature, activation energy, frequency factor

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Introduction

Unimolecular reactions that occur under conditions where the reactants do not exchange energy with the surroundings and where the application of the microcanonical ensemble is therefore mandatory, can nevertheless often be described in terms of an effective temperature. The issue is particularly important for clusters and molecules because a large number of experiments are performed in vacuum. Examples spanning from helium droplets to thermally assisted ionization are given in [1–6]. In several situations a description in terms of a temperature has significant advantages compared to a constant energy description. One is the modelling of the kinetic energy release ϵ which, for spherical particles of not too small moments of inertia of the reacting particle, takes the simple form $\epsilon\sigma(\epsilon)\exp(-\epsilon/T_d)$, where σ is the capture cross section of the inverse process and T_d is the microcanonical temperature of the product particle (here and in the following k_B is set to unity) [7,8]. Another is the use of Arrhenius plots to extract activation energies and frequency factors. Yet another is the use of metastable decays to extract activation energies [9] or heat capacities [10]. Another, related, is the interpretation of abundances of freely evaporating clusters for the same purpose [11]. Also the quantitative interpretation of non-exponential decays in the presence of competing channels, e.g. unimolecular decay vs. radiative cooling [12], benefits from the definition of a temperature and a precise definition of the heat capacity.

Apart from the analysis of the kinetic energy release, all the applications rely implicitly on the assumption that the (microcanonical) heat capacity is constant in order to make the equations tractable. The basic reason is that mass distributions can be considered mappings of energy distributions, whereas decays are governed by the temperature, and the connection between energy and temperature is the heat capacity.

Given the functional form of a rate constant, $k(E)$, there is a large degree of freedom in the definition of emission temperature, activation energy and frequency factor. In general, changes in the definition of the temperature, say, can be absorbed into the definition of the frequency factor and *vice versa*. The constraint that the heat capacity be constant, however, uniquely fixes all the parameters that enter a microcanonical rate constant of the Arrhenius type. Since the exponential form of this rate constant also greatly simplifies analytical manipulations, we will use it here.

The question of an effective temperature was treated in [13]. This work uses the microcanonical temperature as the starting point. The earlier alternative by Klots [14] defines a so-called isokinetic temperature corresponding to the temperature of a canonical ensemble which has the same thermally averaged rate constant as microcanonical, which definition thus relates the energy and temperature. The present work will use the idea in [13] and apply it to a slightly less general situation but with a considerable higher degree of precision.

Rate constants

The microcanonical rate constant has the general form

$$k(E,\epsilon)\mathrm{d}\epsilon = f'\frac{\rho_t(E-E_a-\epsilon)}{\rho_r(E)}\mathrm{d}\epsilon, \tag{1}$$

where ρ_r is the level density of the reactant, ρ_t that of the transition state, and f' is a weakly energy dependent function that has the dimension of a frequency factor. E_a is the activation energy which, in the absence of a reverse activation barrier, is the difference in ground state energies of the product and the reactant, and ϵ the kinetic energy release. Eq.(1) is based on the detailed balance expression, which also fixes f [15]. Integration over the kinetic energy release can be performed by expanding the logarithm of the transition state level density to first order in ϵ and integrating. It gives

$$k(E) = f\frac{\rho_t(E - E_a)}{\rho_r(E)}, \tag{2}$$

where f includes the transition state microcanonical temperature.

The RRKM rate constant is probably more familiar to many readers. It can be derived from detailed balance by integrating Eq.(1) over the kinetic energy release in a transition state that has negative curvature in one direction:

$$k(E) = f'\frac{\int_0^{E-E_a} \rho_t(E - E_a - \epsilon)\mathrm{d}\epsilon}{\rho_r(E)} = f'\frac{N(E - E_a)}{\rho_r(E)}, \tag{3}$$

where $N(E)$ is the total number of quantum states up to energy E.

The differences between Eqs.(2) and (3) have only very minor numerical consequence here and we will use Eq.(2). Similarly, the weak energy dependence of f permits us to set it to a constant.

We need to specify the level densities to proceed. The same form will be used for both reactant and transition state:

$$\rho_i(E) = a_i(E + E_i)^{s_i}, \qquad i = r, t. \tag{4}$$

This is similar to the high energy level density of $s_i + 1$ harmonic oscillators, although the expression is in no way limited to this type of degrees of freedom.

We can read off the canonical heat capacity to (s_i+1) and the canonical caloric curve to $\overline{E} = (s_i+1)T - E_i$, both for energies $E \gtrsim E_i$. The canonical entropy is given by $S = (\overline{E} - E_i)/T + \ln(a_i T^s)$. Hence the three parameters a_i, E_i, s in the level density give essentially the zero'th, first and second derivatives wrt. temperature of the corresponding canonical partition function. It will therefore be a decent approximation for most systems, exceptions including melting/freezing transitions. If the three quantities are unknown, bulk values per degree of freedom may be used.

The identity used to establish the effective emission temperature, T_e, is then

$$k = \omega e^{-E_a^*/T_e} = f \frac{a_t}{a_r} \frac{(E - E_t - E_a)^{s_t}}{(E + E_r)^{s_r}}, \tag{5}$$

where we require that the caloric curve is linear,

$$E = C_v T_e - E_0. \tag{6}$$

E_0 is also known as the finite heat bath correction. The energy E_a^* is introduced because it is not obvious, and indeed not the case, that the best choice of activation energy in the Arrhenius expression is E_a.

It is not possible to satisfy Eq.(5) for all energies with constant values of ω, E_a^* and the required linear caloric curve. We note that s_t and s_r are not too different under usual circumstances. The average and difference are denoted as

$$\overline{s} \equiv {}^1\!/_2 \left(s_r + s_t\right), \qquad \Delta s \equiv s_r - s_t. \tag{7}$$

Typically $\Delta s/\overline{s} \approx 1/N$ where N is the number of atoms in the particle. Then it is meaningful to express the right hand side of Eq.(5) in terms of the average and the difference:

$$\omega e^{-\frac{C_v E_a^*}{E+E_0}} = f\frac{a_t}{a_r}\left[\left(E+E_t-E_a\right)\left(E+E_r\right)\right]^{-\Delta s/2}\left(\frac{E+E_t-E_a}{E+E_r}\right)^{\overline{s}}. \tag{8}$$

The factor in the square bracket will be included into the frequency factor. With the definition, which will soon prove useful,

$$E_a' \equiv E_a + E_r - E_t, \tag{9}$$

we have

$$\omega = f\frac{a_t}{a_r}\left[\left(E+E_r-E_a'\right)\left(E+E_r\right)\right]^{-\Delta s/2}. \tag{10}$$

Usually Δs is positive, e.g. equal to 3 for harmonic oscillators and single atom evaporation, and f includes a factor which is also a small power of the energy, typically E^2 [15]. The definition therefore gives an approximately constant frequency factor.

We then need to find $C_v E_a^*$ and E_0 from the equation

$$e^{-\frac{C_v E_a^*}{E+E_0}} = \left(\frac{E+E_r-E_a'}{E+E_r}\right)^{\overline{s}}. \tag{11}$$

Attempts to solve this by algebraic methods to a sufficient accuracy have proven very difficult. It is more advantageous to use the scaling properties of the equation. Define the scaled energies

$$\begin{aligned} \varepsilon &\equiv \frac{E+E_r}{E_a'}, \\ \varepsilon_0 &\equiv \frac{E_0-E_r}{E_a'}. \end{aligned} \tag{12}$$

With these definitions we get, after taking the $\overline{s}$th root and the logarithm, that

$$-\frac{C_v E_a^*}{\overline{s}E_a'}\left(\varepsilon+\varepsilon_0\right)^{-1} = \ln\left(1-\varepsilon^{-1}\right). \tag{13}$$

For $\varepsilon \to \infty$, ε_0 and $C_v E_a^*/\overline{s}E_a'$ approach 0.5 and 1, respectively. For more realistic excitation energies both of these values are larger. They can be calculated with an expansion of $(\ln(1-\varepsilon^{-1}))^{-1}$ to first order in ε;

$$-\frac{\overline{s}E_a'}{C_v E_a^*}(\varepsilon+\varepsilon_0) \approx \frac{1}{\ln(1-\varepsilon'^{-1})} - \frac{1}{(\ln(1-\varepsilon'^{-1}))^2(1-\varepsilon'^{-1})\varepsilon'^2}(\varepsilon-\varepsilon'), \quad (14)$$

where ε' is the expansion point. The choice of expansion point is equivalent to a choice of a rate constant and thereby an experimental time scale. From Eq.(8), we find that the left hand side of Eq.(14) at the expansion point is equal to

$$-\frac{\overline{s}E_a'}{C_v E_a^*}(\varepsilon+\varepsilon_0) = -\frac{\overline{s}}{\ln(\omega/k)} = \frac{1}{\ln(1-\varepsilon'^{-1})}. \quad (15)$$

Identifying k with $1/t$ we can replace $\ln(\omega/k)$ with $\ln(\omega t) \equiv G$ if k is not known. The approximations derived are then valid for the highest rate constant one can have in the beam at that specific time. Due to the large value of the argument of the logarithm, G can be considered constant over a fairly large range of times/rate constants. Typically it varies less than 10% if the time varies a factor 10.

From Eq.(15) we find the terms on the right hand side of Eq.(14):

$$\frac{E+E_0}{C_v E_a^*} = \frac{1}{G} + \frac{\overline{s}}{G^2}e^{G/\overline{s}}\left(1-e^{-G/\overline{s}}\right)^2\left(\frac{E+E_r}{E_a'} - \frac{1}{1-e^{-G/\overline{s}}}\right). \quad (16)$$

Identifying coefficients give

$$C_v E_a^* = E_a'\frac{G^2}{\overline{s}}e^{-G/\overline{s}}\left(1-e^{-G/\overline{s}}\right)^{-2}, \quad (17)$$

and

$$\begin{aligned} E_0 &= E_a'\frac{G}{\overline{s}}e^{-G/\overline{s}}\left(1-e^{-G/\overline{s}}\right)^{-2} - E_a'\left(1-e^{-G/\overline{s}}\right)^{-1} + E_r \quad (18)\\ &\approx -E_a'\left(\frac{1}{2}+\frac{G}{6\overline{s}}\right) + E_r + \mathrm{O}\Big(\Big(\frac{G}{\overline{s}}\Big)^3\Big). \end{aligned}$$

The last approximation can be used for $G = 25$ and $\overline{s} > 9$ to an accuracy better than 1%.

This calculation only gives the product $C_v E_a^*$. To disentangle the two factors, we calculate the canonical rate constant at temperature T:

$$\begin{aligned} k(T) &= \int_0^\infty k(E) \frac{\rho_r(E)}{Z_r(T)} e^{-E/T} \mathrm{d}E \\ &= \int_0^\infty f a_t \frac{(E+E_t-E_a)^{s_t}}{(E+E_r)^{s_r}} \times \frac{(E+E_r)^{s_r}}{Z_r(T)} e^{-E/T} \mathrm{d}E \\ &= f \frac{Z_t(T)}{Z_r(T)} e^{-E_a/T}. \end{aligned} \tag{19}$$

The partition functions are given by

$$Z_i = \int_0^\infty a_i (E+E_i)^{s_i} e^{-E/T} \mathrm{d}E \approx a_i e^{E_i/T} T^{s_i+1} s_i! \tag{20}$$

The approximation is valid when the canonical thermal energy is higher than E_i by, say, two standard variations, or $T \gtrsim 2E_i/(s_i - 2\sqrt{s_i})$. The canonical rate constant is then

$$k(T) \propto e^{-E_a'/T}. \tag{21}$$

Because this is a calculation of the rate constant on the right hand side of Eq.(8) and the activation energy is the same on both sides of the equation, this shows that the apparent activation energy E_a^* is equal to E_a'. Then

$$C_v = \frac{G^2}{\overline{s}} e^{-G/\overline{s}} \left(1 - e^{-G/\overline{s}}\right)^{-2} \approx \overline{s} + \frac{G^2}{12\overline{s}} + \mathrm{O}\left(\frac{G^3}{\overline{s}^2}\right). \tag{22}$$

The approximation is better than 1% for $\overline{s} > 20$ and $G = 25$. For smaller values of $\overline{s}$ it is recommended to use the full expression.

Eqs.(9,10,18,22) used together with Eq.(8) are the main results of this work. They define the parameters one extracts from measurements of metastable decays, cluster abundances etc. For clusters the frequency factor can often be estimated from the detailed balance equation with quantities extrapolated from bulk properties. This allows one to extract $\overline{s}$ from the measured effective values of C_v. The dependence of C_v is monotonous and the inversion to find $\overline{s}$ can then be made unambiguously with a numerical procedure.

A numerical check of the calculations is shown in Fig.(1). The figure shows the exact and the approximated rate constants for loss of a single atom for the sizes $N = 5, 10$ and 20. The parameters used are those of copper clusters with dissociation energies of 3 eV and vibrational frequencies of 0.02 eV, except for $N = 5$ where they were set to 0.005 eV to compensate for the reduction in the heat capacity at the very low product temperature. In the calculation of G the frequency factor was set to 10^{15} s^{-1}. The bulk atomic radius of 1.57 Å and a geometric cross section for the inverse reaction was used and f calculated with the detailed balance expression [15]. For $N = 4$, i.e. a product composed of three atoms, the approximations are only valid over a rather small energy

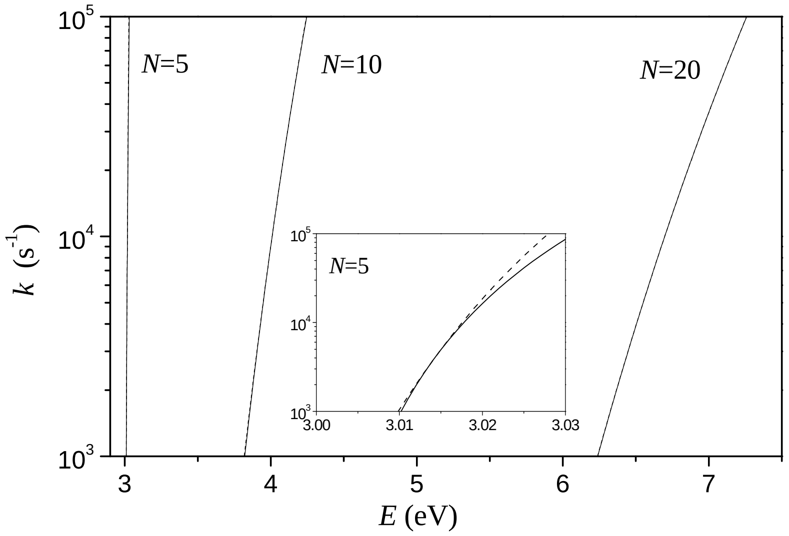

Fig. 1. The exact (full lines) and approximate (dotted lines) rate constant for the three cluster sizes indicated. The parameters of the systems are given in the main text. The inset shows an expanded view of the $N = 5$ curve.

interval. For $N = 10, 20$, however, the approximated rate constant can hardly be distinguished from the exact on the scale used in Fig(1). For large clusters the agreement is even better.

In summary, we have seen that activation energies and heat capacities derived from measurements of rate constants do not necessarily reflect those of the molecular properties, and the connections between them have been derived. Also the effective frequency factor has been calculated in terms of the detailed balance or RRKM frequency factor.

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