

Temperature concepts for small, isolated systems; $1/t$ decay and radiative cooling

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Abstract. We report on progress in our investigations of cluster cooling. The analysis of measurements is based on introduction of the microcanonical temperature and a statistical description of the decay of an ensemble with a broad distribution in temperature. The resulting time dependence of the decay rate is a power law close to t^{-1} , replaced by nearly exponential decay after a characteristic time for quenching by radiative cooling. We focus on results obtained for fullerenes, both anions and cations and recently also neutral C_{60} .

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1 Introduction

It is an interesting aspect of clusters that they form a bridge between atomic and molecular systems and macroscopic matter. With increasing cluster size there is a transition not only in the physical properties, as from the sharp electronic levels of an atom to the energy bands of a solid, but also in the concepts applied to describe the state and the dynamics of the systems. We focus here on the concepts of energy and temperature. For reactions of a small cluster the total excitation energy is the key quantity. With increasing size it becomes more and more important that the energy is distributed over many degrees of freedom and the probability for concentration of the energy on a single degree of freedom is very small. Thus, the apparent threshold for reactions becomes much higher than the reaction barrier ('kinetic shift'). In the macroscopic limit it is the energy per degree of freedom which determines the reaction rate, and the state is characterized by a thermodynamic temperature. It therefore seems natural to define the temperature also for a cluster of finite size by setting the excitation energy equal to the average energy of a system in statistical equilibrium with surroundings at that temperature, and the introduction of such a 'canonical temperature' has been supported by more detailed theoretical arguments [1].

However, the dynamics of an isolated system with conserved energy is fundamentally different from that of a system in thermal equilibrium with the surroundings. A closer analysis shows that it is a different concept of temperature that is relevant for an isolated system, the microcanonical temperature, defined as for a macroscopic heat bath in terms of the logarithmic derivative of the level density [2]. The system can be regarded as a (finite) heat bath for the degrees of freedom involved in a reaction. This is the basic idea in Klotz' finite-heat-bath theory [3,4] but he does not introduce the microcanonical temperature. Instead he defines a temperature for a given reaction with reference to the same reaction in a system in thermal equilibrium with a macroscopic heat bath ('isokinetic temperature'). We find a description based on the microcanonical temperature much simpler. For small systems this temperature is significantly different from the canonical temperature defined above since the corresponding heat capacities differ by about k_B , Boltzmann's constant.

As an example of application of the temperature concept we discuss statistical photon emission. Emission from infrared-active vibrations and its influence on chemical reactions has been studied extensively, in particular by Dunbar and his group [5], and more recently also cooling by electronic emission has been identified and described [6,7]. Radiative cooling violates the conservation of energy for individual clusters and can play an important role in the analysis of experiments on cluster dynamics [8,9]. The spectrum of radiation and hence the origin

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of the radiation can be studied by direct detection of the emitted photons [10–13] but it is difficult to get quantitative information on the radiation power. Several other methods have been applied for this purpose, for example measurement of decay after absorption of two photons with a variable delay of the second photon [14,15]. We have developed a method based on observation of the decay of an ensemble of clusters with a broad distribution in excitation energy. The time dependence follows a power law until a characteristic cooling time when the decay is quenched by radiative cooling [16]. We focus here on a comprehensive study of fullerenes. Both anions and cations have been investigated at an ion storage ring and the cooling appears to be described quite well by a dielectric model [17–19]. Very recently we have also studied cooling of neutral C_{60} molecules with a time-of-flight apparatus [20].

2 Canonical and microcanonical temperature

Although the concepts of canonical and microcanonical temperature are fundamentally different the distinction is not always made. Consider the basic situation in thermodynamics, a system in contact with a heat bath characterized by a level density Ω . At excitation energy E_0 the microcanonical temperature T of the heat bath is defined through the relation

$$\frac{1}{k_B T} = \frac{d}{dE_0} \ln \Omega(E_0). \quad (1)$$

With the statistical definition of entropy, $S = k_B \ln \Omega$, this definition corresponds to the thermodynamic relation $dE = TdS$ when no work is performed. In statistical equilibrium all states are occupied with equal probability and we obtain for the distribution in excitation energy E of the system with level density $\rho(E)$,

$$P(E) \propto \rho(E) \frac{\Omega(E_0 - E)}{\Omega(E_0)} \simeq \rho(E) e^{-E/k_B T}, \quad (2)$$

where we have expanded the logarithm of the ratio of level densities to first order. In the limit $E/E_0 \rightarrow 0$ the terms of higher order vanish and the energy distribution becomes canonical. Thus T plays the double role of microcanonical temperature of the heat bath and canonical temperature for the system. For macroscopic systems the distinction between the two concepts is unimportant and it is often mathematically convenient to represent an isolated macroscopic system by a canonical distribution.

For a microscopic system the situation is different. The dynamics is quite different for isolated systems and for systems in thermal equilibrium with the surroundings, even if the initial energy distribution is the same (see Fig. 1 of Ref. [9] for an example). As often discussed by Bohr and Heisenberg, the relation between the classical concepts of energy and temperature exhibits some of the features of complementarity encountered in quantum mechanics. The concepts refer to mutually exclusive experimental situations with different relations of the small system to its

macroscopic surroundings. It is even possible to derive an analogue to Heisenberg's uncertainty relation [21]. It would therefore seem ill advised to introduce temperature into the description of the dynamics of isolated molecules and clusters.

This objection disappears when we introduce the microcanonical and not the canonical temperature [2]. To demonstrate that the microcanonical temperature is the appropriate concept we consider the statistical decay of a cluster with excitation energy E . Based either on considerations of detailed balance or on transition state theory the rate constant may be expressed as (see Ref. [9] and references therein)

$$k(E) = \nu \frac{\rho(E - E_b)}{\rho(E)}, \quad (3)$$

where E_b is an energy barrier, for example an electron binding energy, and the frequency factor ν varies slowly with E compared with the ratio of level densities. In the derivation, the numerator is at first the level density of the daughter system in the decay, and we have assumed that the ratio between the daughter and parent level densities at energy $E - E_b$ can be included in ν . The analogy of the ratio in equation (3) to the expression in equation (2) suggests an expansion of the logarithm. With the choice of the average of the initial and final state energies as the point of expansion we obtain to second order

$$k \simeq \nu e^{-E_b/k_B T_e}. \quad (4)$$

Here the temperature T_e differs from the microcanonical temperature in the initial state, defined as in equation (1), by a so-called finite-heat-bath correction, $T_e \simeq T - E_b/2C$, where C is the microcanonical heat capacity, $C = dE/dT$. The temperature T_e is to this order the average of the microcanonical temperatures in the initial and final states.

The picture of the system as a heat bath for the degree(s) of freedom active in the decay is the same as that elaborated in Klotz's finite-heat-bath theory [3,4], but in our view many aspects of the description are much easier to derive and to understand with the microcanonical temperature than with the 'isokinetic temperature'. For example, the temperature T_e in equation (4) is relevant only for the expression of the ratio in equation (3) as a Boltzmann factor. The evaluation of the frequency factor involves a sum over kinetic energies of the emitted particle and it may be useful also in this context to introduce an effective temperature. From an expansion analogous to that leading to equation (4) it is found that this temperature is not T_e but the final microcanonical temperature of the system after the emission, $T_f \simeq T - E_b/C$ [9].

The most common definition of a temperature for a small isolated system is the temperature at which the average energy in the canonical distribution in equation (2) equals the excitation energy E of the system and we may denote this value the 'canonical temperature'. An interesting attempt to justify this definition was made by Dunbar [1]. He considered a model system consisting of a

number of harmonic oscillators in statistical equilibrium at a well defined total energy and derived an approximate formula for the probability for the j th oscillator with spacing ε_j to be excited to the n th level. We have examined the derivation of this formula and have found that an improved approximation procedure leads to the same formula but with the microcanonical values of the temperature and heat capacity. With this reinterpretation the accuracy of the formula is much improved [2].

3 Radiation

A good example of the usefulness of the microcanonical temperature is the evaluation of the rate of photon emission. From detailed balance between emission and absorption in a statistical equilibrium with fixed total energy an expression is obtained which contains the ratio between the level densities of the system after and before emission, as in equation (3). The microcanonical temperature is then introduced through an expansion of the logarithm of this ratio, and to a good approximation one obtains for the radiation power at frequency ω [9,19],

$$I_r(E, \omega) d\omega \simeq \frac{\hbar \omega^3}{\pi^2 c^2} \sigma(E - \hbar \omega, \omega) \times \frac{d\omega}{\exp(\hbar \omega / k_B (T - \hbar \omega / 2C)) - 1}. \quad (5)$$

The cross-section σ is here the net cross-section for absorption of a photon with frequency ω , *i.e.*, the cross-section for absorption minus the cross-section for stimulated emission. The arguments for introducing this quantity are twofold: first, this is the cross-section measured in a transmission experiment and, second and most important, this is the quantity fulfilling the sum rules for the oscillator strength, independent of the excitation energy [19].

The simplest example is emission from infrared-active vibrations, which usually dominates the statistical photon emission at low temperatures ($T < 1000$ K). For a three dimensional harmonic oscillator with mass M and charge Q the cross-section is given by (see, for example, Ref. [19], Chap. 4)

$$\int \sigma(\omega) d\omega = \frac{2\pi^2 Q^2}{Mc}. \quad (6)$$

For a harmonic oscillator in level n only transitions to levels $n+1$ and $n-1$ contribute and the difference between the two cross-sections is independent of n .

For electronic transitions the distribution of oscillator strength is often dominated by a plasma resonance [19, 22–24], and one obtains for the cross-section [9]

$$\sigma(\omega) \simeq \pi r_N^2 \frac{4\omega r_N}{c} \frac{3\gamma\omega}{\omega_p^2}. \quad (7)$$

Here r_N is the cluster radius and ω_p is the plasma frequency and γ the damping constant in the dielectric function, $\varepsilon(\omega) = 1 - \omega_p^2 / (\omega(\omega + i\gamma))$.

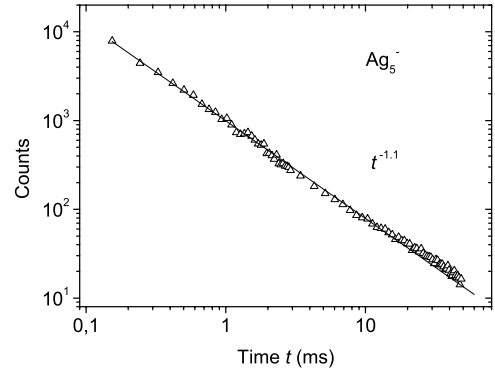


Fig. 1. Yield of neutrals detected turn by turn after injection of Ag clusters into ELISA from a sputter source. For $t > 3$ ms the yield has been averaged over 10 revolutions to improve statistics. The curve through the points is proportional to $t^{-1.1}$.

4 The $1/t$ decay law

In experiments on decay of clusters it is often difficult to define or determine the excitation energy accurately and instead the decay of an ensemble of clusters with a broad distribution in excitation energy — or temperature — is observed. As we shall see, we may even benefit from such a broad distribution because it allows simultaneous observation of the decay on different time scales and thereby identification of a characteristic time for radiative cooling [16].

At first we neglect radiation. The initial energy distribution $g(E)$ for the ensemble is then only changed by depletion with rate constant $k(E)$ and the decay rate at time t is given by

$$I(t) = \int dE g(E) k(E) \exp(-k(E)t). \quad (8)$$

The rate constant $k(E)$ varies rapidly with energy and the weight function $k(E) \exp(-k(E)t)$ therefore peaks sharply at the energy E_m where $kt = 1$. The integral may be approximated by the area of this peak multiplied by the value of the distribution function at E_m ,

$$I(t) \simeq \frac{1}{t} g(E_m) \frac{k(E_m)}{k'(E_m)}. \quad (9)$$

The energy E_m and hence also the last two factors in equation (9) vary slowly with time and the decay rate is approximately proportional to $1/t$. According to equation (4) and the relation $kt = 1$ the temperature of the decaying molecules decreases logarithmically with time,

$$T_e \simeq \frac{E_b}{k_B \ln(\nu t)}. \quad (10)$$

The $1/t$ decay law for ensembles with a broad distribution in excitation energy has been demonstrated by experiments with ions stored in the electrostatic ring ELISA [25]. One result is shown in Figure 1. The silver cluster anions were produced by a sputter source and after acceleration

to 22 keV and mass separation in a magnet they were injected into the ring, and the rate of decay by electron emission was monitored by detection of neutrals. Over three decades the rate follows a power law t^{-n} with $n \simeq 1.1$. As discussed in reference [16], the small deviation of n from unity can be explained as a contribution from the last factor in equation (9).

5 Quenching by radiative cooling

Photon emission is always a competing decay channel and since the lowest photon energies are typically much lower than the barrier E_b for the decay process under investigation, the dependence on energy for the rate of photon emission (Eq. (5)) is usually weaker than the exponential dependence of the decay rate (Eq. (4)). Photon emission therefore dominates at low excitation energies, corresponding to long times in the $1/t$ decay law, and this leads to quenching of the decay. For large clusters, the emission of a single photon leads to a fairly small change in temperature and the effect of the radiation may be described as continuous cooling. This can be introduced into equation (8) if the rate constant is represented by the Arrhenius expression in equation (4). We assume that the cooling rate is approximately constant in the range of interest, $T_e \rightarrow T_e/(1 + t/\tau_c)$, and obtain

$$\begin{aligned} I(t) &= \int dE g(E) \nu \exp\left(-\frac{E_b(1 + t/\tau_c)}{k_B T_e}\right) \\ &\times \exp\left(-\int_0^t dt' \nu \exp\left(-\frac{E_b(1 + t'/\tau_c)}{k_B T_e}\right)\right) \\ &= e^{-t/\tau} \int dE g(E) \nu \exp\left(-\frac{E_b}{k_B T_e}\right) \\ &\times \exp\left(-\nu \exp\left(-\frac{E_b}{k_B T_e}\right) \tau (1 - e^{-t/\tau})\right). \quad (11) \end{aligned}$$

Here $\tau = \tau_c/G$, where the Gspann parameter G for the decay is the absolute value of the exponent in equation (4). One then finds that the power law is replaced by

$$I(t) \propto \frac{1}{\tau(e^{t/\tau} - 1)}. \quad (12)$$

For times shorter than a quenching time τ the rate still follows the $1/t$ law but it approaches exponential decay at longer times. From a measurement of τ the cooling rate can be inferred if the value of the Gspann parameter is known. The time dependence in equation (12) is only valid within a limited time range, $t < \tau$; for longer times the variation of the radiation power and hence also of τ with temperature must be included [17].

The most detailed studies have been performed for electron emission from fullerene anions [7,16,17], and an example is shown in Figure 2. At times $t > 1$ ms the decay of hot molecules is quenched by radiative cooling, and for $t > 20$ ms the signal is dominated by neutrals produced in collisions with the rest gas in the ring. Since

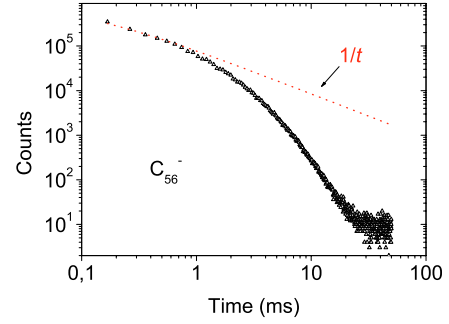


Fig. 2. Observation of electron emission from C_{56}^- ions in the storage ring ELISA. The ions were produced in a hot plasma source, and the yield of neutrals was recorded as a function of the storage time t .

both the electron binding and the factor ν in equation (4) are known fairly well for electron emission from fullerene anions, the decay temperature is known as a function of time from equation (10) and hence the radiation power as a function of temperature can be derived from the measurement. The result is well reproduced by equation (5) with a cross-section quite similar to equation (7) [19]. In fact, within about a factor of two such a description reproduces the quenching times measured for a sequence of fullerene anions with an even number of carbon atoms from 36 to 96 [17].

The dielectric model for fullerenes developed in reference [19] leads to a prediction of the radiative cooling as a function of temperature which can be used to estimate the temperature of decaying molecules from the observed cooling rate. This ‘thermometer’ is quite sensitive since the characteristic cooling time τ_c in equation (11) is predicted to be proportional to T^{-5} . We have applied this to C_2 emission from fullerene cations stored in ELISA [18]. The ions were produced with high internal excitation in a plasma source, and inside ELISA they were illuminated with a high-intensity pulse from a Nd:YAG laser, creating an ensemble with a high-energy cut off determined only by depletion due to dissociation. The quenching times are tens of microseconds and since the revolution time in ELISA is about 100 μ s, only the exponential tail of the quenched decay is observed.

This is illustrated in Figure 3 showing the measured dissociation yield as a function of time for C_{56}^+ and C_{60}^+ , together with curves calculated from the predicted radiation power as a function of temperature and with an optimum choice of dissociation energy. This energy determines the decay temperature as a function of time according to equation (10) with E_b replaced by E_d . The faster quenching of the signal for C_{60}^+ implies that this molecule has the higher decay temperature and hence also the higher dissociation energy, provided that the values of ν are nearly the same. With this method we have determined the dissociation energy for cations of a sequence of fullerenes, from C_{50}^+ to C_{70}^+ , and for a couple of heavier molecules. We have applied a frequency factor $\nu = 2 \times 10^{19} \text{ s}^{-1}$ for all the dissociation processes, and with this choice the sum of the dissociation energies for C_{62} , C_{64} , C_{66} , C_{68} and C_{70} is in

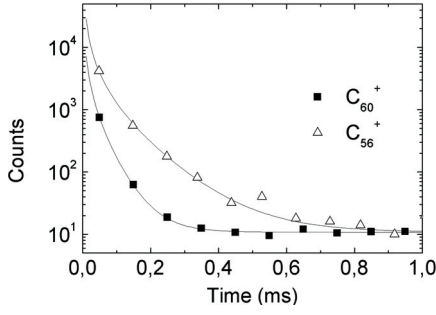


Fig. 3. Decay curve for C_{56}^+ ($\triangle$) and C_{60}^+ ($\blacksquare$) after injection into ELISA from a plasma source and excitation by a pulse from a Nd:YAG laser. The lines represent simulations with the calculated radiation power as a function of temperature and optimum values of the dissociation energy. A constant yield from dissociation induced by rest gas collisions is also included.

good agreement with an independent determination from the heats of formation of C_{60} , C_{70} and C_2 [26].

An important assumption in this analysis is that the radiation power as a function of temperature is given accurately by the theoretical model. As illustrated by examples in reference [19], deviations from the model are most likely for the magic fullerenes due to their electronic shell structure. However, for the cations the closed-shell structure is broken and the radiation power should not be far from the model prediction. The analysis of the measurement for C_{60}^+ illustrated in Figure 3 gives a dissociation energy $E_d = 10.3$ eV for the neutral C_{60} molecule, which is in good agreement with other recent determinations [27].

6 Decay through a weak channel

Our method for determination of the dissociation energy for fullerenes is free of some of the problems of previous measurements which have created considerable uncertainty in the literature [8, 27], but it still relies upon an assumption of equal magnitude of the frequency factors ν in equation (4). The only method which is free from such weakness appears to be the observation of delayed ionisation of C_{60} in reference [28]. In this experiment the yields of ions and electrons were measured as functions of time after multiphoton excitation with an intense laser pulse. Although the ionisation energy, $E_i = 7.6$ eV, is lower than the dissociation energy E_d , ionisation is the weaker channel of decay. This implies that the ionisation rate can be written as in equation (8), with an exponential depletion determined by the dissociation rate constant k but with the front factor k replaced by the rate constant k_i for ionisation. Ignoring the small difference between the finite-heat-bath corrections for the two channels we find that k_i may be expressed as

$$k_i = \nu_i e^{-E_i/k_B T_e} \propto \left(e^{-E_d/k_B T_e} \right)^{E_i/E_d} \propto k^{E_i/E_d}. \quad (13)$$

The argument leading from equation (8) to equation (9) now gives a different power law,

$$I_i(t) \propto t^{-E_i/E_d}. \quad (14)$$

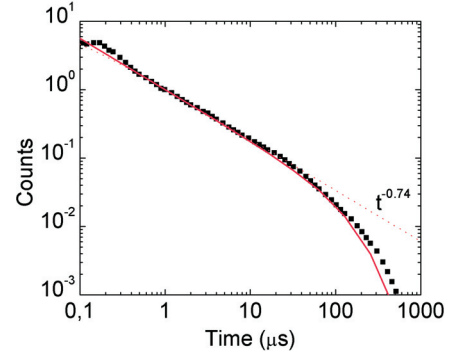


Fig. 4. Electron yield as a function of time after multi-photon excitation of C_{60} with a pulse of third-order-harmonic radiation from a Nd:YAG laser. The curve is from a numerical evaluation of equation (8) with the modification in equation (13) and with a constant energy distribution $g(E)$. The rate constants are given by equation (4) with $\nu = 2 \times 10^{20} \text{ s}^{-1}$ and $E_d = 11$ eV for C_2 emission and $\nu = 2.5 \times 10^9 \times (T_f [\text{K}]) \text{ s}^{-1}$ and $E_i = 7.6$ eV for ionisation. Radiative cooling is included with a rate of about 20% of that predicted from the dielectric model in reference [19].

Fitting their measurements with such a time dependence, Hansen and Echt obtained a very high value of the dissociation energy for C_2 emission from C_{60} , $E_d = 11.9 \pm 1.9$ eV [28].

Recently these measurements have been repeated and extended by Campbell's group, and the experimental results appear to be consistent with the previous measurements [29]. However, it is argued that an observed strong decrease of the yield for times approaching $100 \mu\text{s}$ cannot be accounted for by radiative cooling alone. An important role of long-lived triplet states is suggested and the strong decrease of the decay rate is interpreted as decay of these states.

We have performed similar time-of-flight experiments in a different geometry [20]. We have detected both ions and electrons from a beam of C_{60} molecules from an oven, excited by a laser beam. The two beams were nearly anti-parallel and this ensures that there are no geometrical effects on the detection efficiency at long times, due to the motion of the molecules. A preliminary result is shown in Figure 4. As in earlier measurements, the logarithmic slope is about 0.7, corresponding to $E_d \simeq 11$ eV in equation (14), and the data are compared with a curve obtained from a numerical calculation including radiative cooling. The corresponding radiation power is lower than the power calculated from the dielectric model in reference [19] but, as discussed there, a large reduction is expected due to the large HOMO-LUMO gap for C_{60} .

The frequency factor ν for C_2 emission used in this calculation is an order of magnitude higher than in our analysis of the experiments on cations. With this higher value of ν the measurement for C_{60}^+ illustrated in Figure 3 gives a dissociation energy for the neutral molecule that is consistent with the preliminary value obtained from the time-of-flight spectrum in Figure 4. A higher value of ν for C_{60} also appears to be necessary to explain the yield

of C_{58}^+ relative to those of C_{56}^+ , C_{54}^+ , etc. observed in the time-of-flight experiment. There may be several factors contributing to this higher value of the frequency, all connected to the extraordinary stability of C_{60} . As noted below equation (3), ν is proportional to the ratio of the level densities for C_{58} and C_{60} at the same excitation energy. Owing to the large HOMO-LUMO gap for C_{60} , the electronic contribution to the level density is much smaller for this molecule. Also, the geometrical structure of C_{60} is very stable while for most fullerenes there are a number of isomers with nearly the same energy. Finally, the vibrational frequencies are slightly higher for C_{60} than for C_{58} , and this leads to a lower vibrational level density.

7 Concluding remarks

In this progress report we have emphasized the development of an effective theoretical description of cluster decay. The introduction of the microcanonical temperature and Arrhenius expressions for decay rates are essential elements in the formalism used to interpret experiments, and the power-law distributions resulting from decay of ensembles with a broad temperature distribution have been shown to be a very useful reference for determination of the influence of radiative cooling. In most of our investigations we have used a small electrostatic storage ring, which allows detection of the decay of excited clusters over several orders of magnitude in time, and we have studied a broad range of ions, including metal clusters, fullerenes, and recently also biomolecules. We have focussed here on the comprehensive results obtained on the radiative cooling of fullerenes. The recent results for the decay of neutral C_{60} in a time-of-flight apparatus have provided the first reliable measurement of radiative cooling of this ‘magic’ molecule. Owing to the closed-shell electronic structure there are no low-energy electronic excitations and the radiation power should be much lower than observed for the ions, even at the very high temperatures required for the decay (~ 4000 K). This has now been confirmed by experiment.

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