Eur. Phys. J. D **43**, 101–104 (2007)
DOI: 10.1140/epjd/e2007-00123-8

THE EUROPEAN PHYSICAL JOURNAL D

Energy distributions of clusters cooled by thermal radiation

J. Stenfalk[1] and K. Hansen[2,a]

[1] Niels Bohr Institute, Ørsted Laboratory, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark
[2] Department of Physics, Göteborg University, 412 96 Göteborg, Sweden

Received 21 September 2006 / Received in final form 3rd November 2006
Published online 24 May 2007 –

Abstract. Particles that cool radiatively in vacuum reach a limiting energy distribution, defined by the low energy dielectric function, the heat capacity and time. We find that in a finite time, both mean temperature and the width of the distribution converge to powerlaws in time, and that the ratio of the two reach a constant value which depends on the heat capacity and the photon absorption cross section. Further, both the photon emission rate and the ratio of width to mean energy of the distribution show surprising similarities with the analogous results for cooling by particle evaporation.

PACS. 36.40.-c Atomic and molecular clusters – 61.46.Bc Clusters – 61.46.Df Nanoparticles

1 Introduction

Clusters and molecules which have reached internal equilibrium in vacuum emit excess energy predominantly in reactions where bonds are broken and one or more atoms are emitted. Reactions of this kind involve an activation energy and thus effectively a Boltzmann factor which suppresses them very strongly when the internal energy content becomes sufficiently low. Emission of thermal radiation, in contrast, does not necessarily suffer from this cutoff because there is no intrinsic activation energy for photon emission, only the photon energy is carried away in the process. This will generally cause cooling by evaporation or thermionic emission to dominate at high energy and radiative cooling to dominate at low excitation energy. The cross-over from emission of massive to massless particles is most easily observed for highly refractory materials. Thermal photon emission has indeed been observed from clusters of several different materials [1–4]. The influence of radiation on unimolecular decay in the cross-over region has already been investigated, mainly experimentally, in connection with emission of infrared radiation from molecules [5–7] and with emission from fullerenes [8–12].

It is the purpose of this work to derive the energy distribution determined from the features specific to photon emission, and to provide simple analytical results for the case of a photon absorption cross section that varies as a power of the photon energy. Apart from the replacement of massive particles with an activation energy with massless photons without, the situation is analogous to the decay cascades described in the evaporative ensemble [13], and in effect we will describe a radiative ensemble. We are aware that this cross section will not cover all physical situations by far, but think that the simplicity gained will offset the loss of generality.

2 Emission rates and temperature

Thermal photons are emitted with the rate constant [14]

$$k(E,\nu) = \frac{8\pi\nu^2}{c^2}\sigma_{ph}(\nu)\frac{e^{-\frac{h\nu}{T_{e1}}}}{1-e^{-\frac{h\nu}{T_{e2}}}}, \tag{1}$$

where σ_{ph} is photon absorption cross section.

The two temperatures, T_{e1}, T_{e2} are the microcanonical temperatures at the energies $E - h\nu/2$ and $E - 3h\nu/2$. The microcanonical temperature is defined as [15,16]

$$T^{-1} \equiv \frac{\mathrm{d}\ln(\rho(E))}{\mathrm{d}E}, \tag{2}$$

where $\rho(E)$ is the density of states, or level density, of the system at energy E. For a particle with sufficiently large heat capacity relative to k_B, the corrections of $h\nu/2$ and $3h\nu/2$ in equation (1) can be neglected, one can use equation (1) with the uncorrected values $T_{e1} \approx T_{e2} \approx T(E)$. We will use this approximation throughout. We will furthermore assume that the canonical heat capacity is constant, equal to $C = sk_B$. In the high temperature limit of harmonic oscillator degrees of freedom, s is equal to the number of oscillators. We will use it more generally as the heat capacity in units of k_B. The microcanonical temperature is then $T = (E + E_0)/(s-1)$. For vibrations which can be described as harmonic oscillators, E_0 is the sum of all zero point energies of the oscillators. The level density and microcanonical temperature used here holds

[a] e-mail: klavs@physics.gu.se

for harmonic oscillators above an energy corresponding to the sum of vibrational quanta, i.e. we require $E \gtrsim 2E_0$. For these energies the constant E_0 does not have any influence on the results and can be set to zero without loss of generality. Hence we will use the relation $T = E/(s-1)$ and interchange freely between T and E. The results here are limited to an energy window below the unimolecular regime and the one where the energy per degree of freedom is above the typical vibrational quantum.

For the photon absorption cross section we will use

$$\sigma_{ph}(\nu) = \alpha(h\nu)^n. \tag{3}$$

The motivation for this choice is the behavior of a metallic particle. In these, the low photon energy absorption cross section gets a strong contribution from the surface plasmon resonance, for which $n = 2$, and α is given by parameters such as the width of the resonance etc. The value $n = 0$ corresponds to a Planck-like spectrum. In the interest of treating the more general problem, however, we shall leave n and α unspecified in the following.

Except where otherwise noted we will use $k_B = 1$, i.e use energy units for temperature.

3 Time development equation

A master equation for the problem has been used previously and solved for the specific case of fullerene cooling [17]. But even with the simplifications mentioned above a complete analytical solution for the energy distribution for all times is beyond the scope of this paper. We will instead consider analytically the development of the first two moments of the energy distribution.The first two moments will provide a good description for relatively narrow distributions, corresponding to large heat capacities.

The time derivative of the m'th moment is given by

$$\frac{\mathrm{d}\overline{E^m}}{\mathrm{d}t} = \int_0^\infty f(E) \int_0^E k(E,\nu)\left((E-h\nu)^m - E^m\right)\mathrm{d}\nu\mathrm{d}E, \tag{4}$$

where $f(E)$ is the normalized energy distribution. The upper limit of the inner integral can be replaced by infinity with little error. The integrals over the photon emission rate constant and a power of the photon energy can be calculated with standard techniques:

$$\int_0^\infty k(E,\nu)(h\nu)^p \mathrm{d}\nu = \frac{8\pi}{h^3c^2}\alpha\zeta(n+p+3)\Gamma(n+p+3)T^{n+p+3}. \tag{5}$$

The remaining integral in equation (4) is over the energy distribution. With the integrals in equation (5) they reduce to moments of the energy, $\overline{E^m}$ and be calculated term by term with an expansion of the energy around the mean energy, $\overline{E}$. The first two terms in this expansion includes the mean energy and the variance in energy, $\sigma_E^2 \equiv \langle(E-\overline{E})^2\rangle$. For the first two moments one gets equations of the form

$$\frac{\mathrm{d}\overline{E^p}}{\mathrm{d}t} = -d_p\left(\overline{E}^{n+p+3} + g_p\sigma_E^2\overline{E}^{n+p+1}\right), \tag{6}$$

where $p = 1, 2$, $g_p = (n+p+2)(n+p+3)/2$ and d_p are known constants. From the equation for $\mathrm{d}\overline{E^2}/\mathrm{d}t$ one calculates the time derivative of σ_E^2 by subtraction of $2\overline{E}\mathrm{d}\overline{E}/\mathrm{d}t$. After conversion from energy to temperature one arrives at the equations (with $\sigma_T \equiv \sigma_E/(s-1)$)

$$\begin{aligned}\frac{\mathrm{d}\overline{T}}{\mathrm{d}\tau} &= -a_0\overline{T}^{n+4} - a_1\sigma_T^2\overline{T}^{n+2}\\ \frac{\mathrm{d}\sigma_T^2}{\mathrm{d}\tau} &= a_2\overline{T}^{n+5} + a_3\sigma_T^2\overline{T}^{n+3},\end{aligned} \tag{7}$$

where the time has been scaled as $\tau = t\alpha\frac{8\pi}{h^3c^2}\zeta(n+4)\Gamma(n+4)/(s-1)$. There is no natural scaling of the time in the problem and the scaled time has a mixed dimension of energy and physical time.

The coefficients in the equation are

$$\begin{aligned}a_0 &= 1, \quad a_1 = \frac{1}{2}(n+3)(n+4), \quad a_2 = \frac{(n+4)}{(s-1)}\frac{\zeta(n+5)}{\zeta(n+4)}\\ a_3 &= -2(n+4) + \frac{1}{2}\frac{\zeta(n+5)}{\zeta(n+4)}\frac{(n+4)^2(n+5)}{s-1}.\end{aligned} \tag{8}$$

This equation is obviously obtained by a truncation of the expansion of the equations of motion in terms of the moments. The justification for considering it is that it will provide a guide to the asymptotic solutions and the ratio $\overline{T}/\sigma_T$ in terms of the parameters of the problem.

4 Solution of the time development equations

Equations (7) have the asymptotic solutions

$$\overline{T} = b_0\tau^{-1/(n+3)}, \quad \sigma_T^2 = b_1^2\tau^{-2/(n+3)}, \tag{9}$$

which can be seen by inspection. Furthermore, no other powers of τ are solutions. We note that the terms involving higher moments, left out in equation (7), as well as the equations for these moments, have the same structure as those given. Specifically, the equations for $\mathrm{d}\overline{E^p}/\mathrm{d}t$ involve terms of the form $T^a(\sigma_T^2)^b\overline{E^3}^c...$ with $a + b/2 + c/3 + ... = p + n + 3$. We therefore expect this power dependence to survive a more exact treatment. This is indeed borne out by numerical simulations which will be treated in detail elsewhere.

The solution of equation (7) also provides an equation for the ratio b_0/b_1, i.e. the average temperature vs. the spread in temperature

$$r \equiv \frac{b_0^2}{b_1^2} = -\frac{1}{2}\frac{a_3+2a_0}{a_2} \pm \sqrt{-\frac{2a_1}{a_2} + \frac{1}{4}\left(\frac{a_3+2a_0}{a_2}\right)^2}. \tag{10}$$

The heat capacity enters this equation through the coefficients a_2 and a_3. The equation has no real solution below a

critical value of a certain heat capacity, s_{crit}, and two real solutions above this. s_{crit} depends on n and for $n = 0, 1, 2$ the values are $s_{crit} = 17, 22, 28$. Numerical simulations suggest that the existence of s_{crit} is likely to be an artefact of the simplified equation of motion and we will not go into further details on the subject. For heat capacities above s_{crit}, however, the value calculated here for b_0/b_1 will give a reasonable estimate for the true value.

When equation (10) has real solutions, one is stable and one is unstable. The stability of the solutions was investigated by adding a small perturbation, δT, $\delta\sigma_T$, to the solutions in equation (9), inserting these in equation (7) and linearizing the resulting time development equations for the perturbations. A technical remark is in place here: The variables to be studied for this calculation are most convenient chosen as $\overline{T}$ and σ_T vs. $\overline{T}$ and σ_T^2. The latter choice requires the solution of two second order differential equations to find the stability.

The resulting 2×2 matrix has a time dependence of τ^{-1} which can be factored out in front of a constant matrix. There is one matrix for each of the solutions of the ratio b_0/b_1. To represent stable solutions both eigenvalues of a matrix must be negative, and the convergence rate is determined by the numerically smallest of these.

The general solution of the problem is very tedious and not much insight is gained from the exact expression which is very involved. We will apply the limit of large heat capacity and consider the leading order in $s - 1$. In this limit we find that the stable solution is given by the positive-sign solution in equation (10), which corresponds to the solution with the lowest ratio $\sigma_T/\overline{T}$ of the two. The two Eigenvalues for this solution are

$$\lambda_1 = -\frac{n+4}{n+3}, \quad \lambda_2 = -\frac{2n+7}{n+3}. \tag{11}$$

The equation for the decay of the perturbation included a factor $1/\tau$ in front of the matrix, and the decay of a perturbation from the asymptotic solutions is therefore not exponential. Rather, it follows the powerlaw

$$\delta\overline{T} \propto \tau^{\lambda_1} = \tau^{-\frac{n+4}{n+3}}, \tag{12}$$

and a similar one for σ_T with the same power. Although not exponential, the power of τ is still a factor of $n + 4$ larger than the corresponding power for the development of the mean values. The convergence towards $\overline{T}$ and σ_T is thus more rapid than the rate of change of the quantities themselves.

In the large s limit we can also calculate $\overline{T}/\sigma_T$ for the asymptotic solutions. The next-to-leading order gives

$$r = 2(s-1)\frac{n+3}{n+4} - \frac{1}{2}(n+3). \tag{13}$$

The value of b_0 and b_1 can be found from this value and the algebraic equation obtained when inserting equation (9) into equation (7). The results are, to leading order in $s-1$ and ignoring the ratios of the ζ-functions which are close to unity,

$$b_0 = (n+3)^{\frac{-1}{n+3}}, \quad b_1 = (n+3)^{\frac{-1}{n+3}} \left(\frac{n+4}{n+3}\right)^{1/2} \frac{1}{\sqrt{2(s-1)}}. \tag{14}$$

Numerical solutions of equation (7) are shown in Figure 1 and compared to these approximate values for $s = 1000$. Figure 2 shows similar curves for $s = 30$ and $n = 0, 2$. It can be seen that even for $s = 30$, which is close to the critical heat capacity for these equations, do the large heat capacity solutions agree fairly well with the numerical solutions. The simulated time range is only illustrative. It is not indicative of the range of times for which the physical assumptions used in the derivation can be expected to hold.

The result in equation (13) is intuitively acceptable: For large heat capacities the width decreases relative to the mean energy. The functional form is also

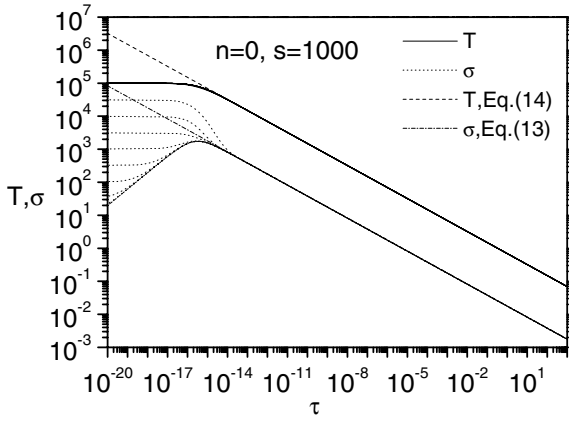

Fig. 1. Comparison of large heat capacity, asymptotic solutions for $\overline{T}, \sigma_T$ with numerical solutions of the differential equations (7). The latter are started with different values of σ_T and $\overline{T} = 10^5$ in scaled units. The dashed and dash-dotted lines are the approximations to the asymptotic values in equations (13, 14).

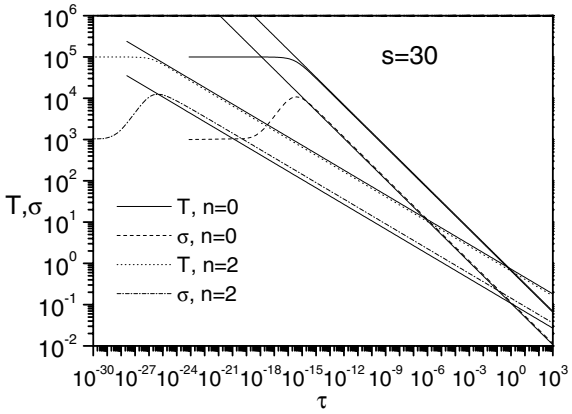

Fig. 2. The same comparison as in Figure 1 but for a small cluster, $s = 30$, and two different values of n. Only one initial value for σ_T is shown. The straight lines are the asymptotic solutions of equations (13, 14), in all cases corresponding to the numerical solution which is closest in the figure.

understandable. The cooling through a given temperature interval requires a number of photons which is proportional to the heat capacity. The variance of this number of photons thus increases proportional to the heat capacity and hence the relative variance *decreases* with the number of photons, i.e. with the heat capacity.

What is less trivial is the fact that the width of the energy distribution is essentially $\sqrt{2}$ *less* than the canonical value. This is in fact precisely the same result one derives for cooling exclusively by particle emission in the evaporative ensemble [18], in spite of the very different cooling mechanisms.

Translating the time dependence calculated in scaled variables to physical values and introducing k_B gives the equation for the mean

$$\overline{T} = \frac{1}{k_B}\left(\frac{\alpha 8\pi}{h^3c^2}\frac{(n+3)\zeta(n+4)\Gamma(n+4)}{s-1}\right)^{-\frac{1}{n+3}} t^{-1/(n+3)}. \tag{15}$$

For $n = 0, s = 100, \alpha = 100$ Å^2 the constant on the right hand side is calculated to 12.6 Ks$^{1/3}$. This value of n corresponds to a Planck-like emission spectrum. For a particle whose emission properties can be described with a classical dielectric function like the one used in [17,19,20] for fullerenes, the cross section is, in the low frequency regime and with some typical values,

$$\sigma_{ph} = \frac{q^2}{m_e c\varepsilon_0}\gamma N_e \frac{(2\pi\nu)^2}{\omega_s^4} = 5.10\times 10^{15}[\mathrm{J}^{-2}\,\mathrm{m}^2](h\nu)^2, \tag{16}$$

where q, m_e is the charge and mass of the electron, c the speed of light, $\hbar\gamma = 15$ eV, $\hbar\omega_s = 20$ eV the width and position of the resonance, and $N_e = 200$ the number of valence electrons. With these numbers the constant in equation (15) becomes 580 Ks$^{1/5}$.

Another interesting feature of the solutions is the temporal behavior of the photon emission rate constant integrated over photon energies. For sufficiently narrow energy distributions, i.e. for $2(s-1) \gg 1$, the mean also represents the integrated energy distribution fairly well. Use of equations (9, 14) and the scaling factor on time give the simple result

$$\int_0^\infty k(\overline{E}, h\nu)\mathrm{d}\nu = \frac{\zeta(n+3)}{\zeta(n+4)}\frac{s-1}{(n+3)^2}t^{-1} \approx \frac{s-1}{(n+3)^2}1/t. \tag{17}$$

This result is surprising for several reasons. It does not depend on the specific photon absorption cross section, only on the power of the photon energy dependence, n. Secondly, it varies with time as a powerlaw with the power -1, which is independent of the cross section. The third remark is that equation (17) is also very similar to the emission rate for massive particles in an evaporative ensemble which has been investigated both theoretically and experimentally [21–23]. The only difference is that the $n+3$ in the denominator here replaces the so-called Gspann parameter, which is a dimensionless number with magnitudes around 25–35. This connection was suggested in [24], albeit with a slightly different value, and not justified in any detail.

5 Summary

Clusters that cool radiatively with a Planck-like spectrum or with a spectrum given by the low energy tail of the surface plasmon resonance will develop certain characteristic features. One of these is a powerlaw decay of the mean energy with time, and a parallel decay of the width of the energy distribution. The ensemble shows striking similarities to ensembles of large clusters that cool by evaporation, viz. the relative width of the energy distribution is identical and is a squareroot 2 less than the canonical width at the same internal energy. Also, the integrated photon emission rate constant is similar, it varies as $1/t$, and has a prefactor which is proportional to the heat capacity The present results cover the rudiments of radiative cooling and more work is required to include the effects of the background Planck radiation, of non-constant heat capacity of the clusters, to demonstrate the generality of some of the suggestions made here, and to explore the possibility of scaled solutions to more general cases.

This work has been supported by the Swedish Research Council (VR). Conversations with B. Mehlig are gratefully acknowledged.

References

1. B. Weber, R. Scholl, J. Appl. Phys. **74**, 607 (1993)
2. R. Mitzner, E.E.B. Campbell, J. Chem. Phys. **103**, 2445 (1995)
3. U. Frenzel, A. Roggenkamp, D. Kreisle, Chem. Phys. Lett. **240**, 109 (1995)
4. G. Ganteför et al., Phys. Rev. Lett. **77**, 4524 (1996)
5. R.C. Dunbar, J. Chem. Phys. **90**, 7369 (1989)
6. R.C. Dunbar, C. Lifshitz, J. Chem. Phys. **94**, 3542 (1991)
7. M. Larsson et al., J. Phys. B **27**, 1397 (1994)
8. K. Hansen, E.E.B. Campbell, J. Chem. Phys. **104**, 5012 (1996)
9. J.U. Andersen et al., Phys. Rev. Lett. **77**, 3991 (1996)
10. J. Laskin, C. Lifshitz, Chem. Phys. Lett. **277**, 564 (1997)
11. A.A. Agarkov et al., Eur. Phys. J. D **9**, 331 (1999)
12. S. Tomita et al., Phys. Rev. Lett. **87**, 073401 (2001)
13. C.E. Klots, Z. Phys. D **21**, 335 (1991)
14. J.U. Andersen, E. Bonderup, K. Hansen, J. Phys. B **35**, R1 (2002)
15. J.U. Andersen, E. Bonderup, K. Hansen, J. Chem. Phys. **114**, 6518 (2001)
16. D. Gross, *Microcanonical Thermodynamics* (World Scientific, Lecture Notes in Physics, 2001), Vol. 66
17. J.U. Andersen et al., Eur. Phys. J. D **17**, 189 (2001)
18. U. Näher, K. Hansen, J. Chem. Phys. **101**, 5367 (1994)
19. J.U. Andersen, E. Bonderup, Eur. Phys. J. D **11**, 413 (2000)
20. M. Hedén et al., J. Chem. Phys. **123**, 044310 (2005)
21. K. Hansen, U. Näher, Phys. Rev. A **60**, 1240 (1999)
22. K. Hansen et al., Phys. Rev. Lett. **87**, 123401 (2001)
23. J.U. Andersen et al., Eur. Phys. J. D **25**, 139 (2003)
24. K. Hansen, E.E.B. Campbell, Phys. Rev. E **58**, 5477 (1998)