

## On the concept of temperature for a small isolated system

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The microcanonical temperature is shown to be a useful concept in calculations of the decay of a small isolated system with well defined energy. A simpler and more transparent description is obtained than in Klots' formulation of finite-heat-bath theory, where the system is represented by a canonical ensemble. As a further illustration of the utility of the microcanonical temperature concept, we discuss a formula derived by Dunbar for the probabilities for excitation of a single oscillator in a collection of harmonic oscillators with well defined total energy. This formula expresses the excitation probabilities in terms of the temperature for a canonical ensemble with mean energy equal to the energy of the system. However, a much improved accuracy is obtained if the canonical temperature and heat capacity are replaced by their microcanonical values. We justify this replacement through a modified derivation, in which the microcanonical temperature appears as the canonical temperature of a fictitious system with level density  $\rho'(E)$ , the derivative of the level density  $\rho(E)$  of the collection of oscillators. © 2001 American Institute of Physics.  
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### I. INTRODUCTION

For an isolated system the energy is conserved and in a statistical equilibrium, where all microstates with the same energy are equally probable, the state of the system may be identified with a microcanonical ensemble. However, in the calculation of the properties of the system it may be advantageous to approximate the state by a canonical ensemble because of the mathematical simplicity of this ensemble (see the introduction to Ref. 1). In this method, which was pioneered by Gibbs,<sup>2</sup> the energy of the system is identified with the average energy in the canonical ensemble. In an alternative description developed by Fowler,<sup>3</sup> the statistical weights were expressed as complex integrals, which were evaluated, in particular, in the steepest-descent approximation. In this case the temperature is defined by a relation determining the saddle point of the absolute value of the integrand, and, as it turns out, the microcanonical system is then in effect also here represented by a canonical distribution.

We consider systems which are large enough to warrant a statistical treatment but still have rather few degrees of freedom so that the relative width of the canonical energy distribution is significant. For such systems there is a latitude in the definition of temperature which may be seen as a consequence of a complementarity between the concepts of energy and temperature.<sup>4</sup> An alternative to the "canonical temperature" discussed above is the microcanonical temperature, defined in terms of the derivative of the logarithm of the level density. We argue that this temperature is useful in calculations of the statistical decay of excited molecules or clusters, and that one obtains a conceptually much simpler description by avoiding the standard canonical approximation scheme.

In this connection, we discuss a paper by Dunbar,<sup>5</sup> which has been cited as giving a justification for the representation of an isolated system by a canonical ensemble. The

paper deals with the probability  $P_j(n)$  for occupation of the  $n$ th level of the  $j$ th oscillator in a collection of harmonic oscillators in statistical equilibrium at fixed total energy. The evaluation of this probability is closely related to the problem of calculating the decay rate for an excited molecule or cluster since this rate depends on the probability for concentration of a large amount of energy on a single degree of freedom, the reaction coordinate, or on a few degrees of freedom. Applying Fowler's method, Dunbar derived an analytical formula expressing  $P_j(n)$  in terms of the canonical temperature and heat capacity of the collection of oscillators, and, on the basis of comparisons with exact calculations for a few model systems, he claimed the formula to be superior to the approximation by a Boltzmann factor. However, the comparisons were flawed by numerical errors. We find Dunbar's formula to give a rather poor representation of the exact  $P_j(n)$  values, hardly an improvement over the simple Boltzmann distribution.

We have analyzed the approximation made in the derivation of Dunbar's formula. We use a different but equivalent method, expressing the level density as an inverse Laplace transform of the partition function.<sup>6,7</sup> Dunbar's derivation is a perturbation calculation in which the integration path for a steepest descent evaluation of the level density of the total system is also used in the evaluation of the level density of a subsystem with one oscillator excluded. We find this procedure to be much more accurate when the level density is expressed in terms of the inverse Laplace transform of the partition function corresponding to the derivative of the level density, and this leads to Dunbar's formula with the microcanonical temperature and heat capacity.

In the following we first introduce the basic concepts, the canonical and microcanonical temperatures, and give a derivation of the relation between the corresponding heat capacities. We shall later consider a model system of harmonic oscillators and therefore quote some useful expres-

sions for such a system. In Sec. III we discuss the application of the microcanonical temperature in a statistical description of the decay of an isolated system, and as an example we consider particle emission from a cluster. The formalism is closely related to Klots' finite-heat-bath theory<sup>8,9</sup> but we argue that a conceptual simplification is obtained when reference to a fictitious canonical ensemble is avoided.

As a variation on this theme, we then discuss Dunbar's result, and in Sec. IV we give a derivation of his formula. In Sec. V we analyze the accuracy of Dunbar's calculation and show that one may eliminate the main error by the modified approximation procedure, which leads to Dunbar's formula with the microcanonical parameters. Finally, we apply this procedure to derive an expression for the rate of decay of a small isolated system. To lowest order in the finite-heat-bath correction, the result is equivalent to that given in Sec. III, but the derivation there based on a Taylor expansion is easier to extend to higher order and higher accuracy.

## II. MICROCANONICAL AND CANONICAL TEMPERATURE

A system in statistical equilibrium and with well defined energy is represented by a microcanonical ensemble. We consider a quantum system with excitation energy  $E$ . The system is characterized by a density of states,  $\rho(E)$ , smoothed over an energy interval larger than the spacing of the energy levels, and the microcanonical temperature  $T_m$  is defined through the relation

$$\frac{1}{k_B T_m} = \frac{d}{dE} \ln \rho(E), \tag{1}$$

where  $k_B$  is Boltzmann's constant. To calculate explicitly this relation between  $E$  and  $T_m$  for a system with density  $\rho(E)$  it is useful to consider the canonical energy distribution,  $P(\epsilon)$ , representing the system in equilibrium with a heat bath at temperature  $T_m$ ,

$$P(\epsilon) \propto \rho(\epsilon) e^{-\epsilon/k_B T_m}. \tag{2}$$

From differentiation of this distribution, the most probable value,  $\epsilon_p$ , is seen to be equal to the energy  $E$  of the system. However, as we shall illustrate below by an example [Eq. (14)], the average energy of a canonical ensemble is usually easier to calculate, and the quantity of interest, the most probable value, is then obtained when a small correction for the skewness of the energy distribution is included. From a second-order Taylor expansion of  $\ln P(\epsilon)$  around  $\epsilon_p$  we obtain a Gaussian approximation to the distribution,

$$P_0(\epsilon) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-(\epsilon - \epsilon_p)^2/2\sigma^2). \tag{3}$$

The width  $\sigma$  is found from differentiation of Eq. (1),

$$\sigma \approx \sqrt{k_B C_m T_m}, \tag{4}$$

where  $C_m$  is the derivative of  $E$  with respect to  $T_m$ , i.e.,  $C_m$  is the microcanonical heat capacity. Since  $\epsilon_p$  is of order  $C_m T_m$ , it is a condition for application of the Gaussian approximation that the heat capacity be large in units of  $k_B$ .

To include the skewness of the energy distribution, we carry out the Taylor expansion of  $\ln P$  to third order. This results in an energy distribution equal to  $P_0(\epsilon)$  multiplied by a skewness factor  $S(\epsilon)$  given by

$$S(\epsilon) \approx \exp\left(\frac{1}{6}(\epsilon - \epsilon_p)^3 \frac{d}{dE} \left(\frac{-1}{\sigma^2}\right)\right) \approx 1 + \frac{1}{6}(\epsilon - \epsilon_p)^3 \frac{d}{dE} \left(\frac{-1}{\sigma^2}\right). \tag{5}$$

For the corresponding average energy we find

$$\bar{\epsilon}(T_m) \approx \int_0^\infty d\epsilon \epsilon P_0(\epsilon) S(\epsilon) \approx E + k_B T_m \left(1 + \frac{T_m}{2C_m} \frac{d}{dT_m} C_m(T_m)\right). \tag{6}$$

The second term inside the parentheses is often small, and neglecting this term we have the desired relation on a simple form, which may also be expressed as a relation between the canonical and microcanonical heat capacities,  $C_c$  and  $C_m$ ,

$$C_m \approx C_c - k_B. \tag{7}$$

When the average energy of a system in contact with a heat bath is known, we can apply Eq. (7) to obtain the relation between the energy and the microcanonical temperature for the isolated system.

We now present an alternative derivation of the relation between peak energy and average energy for a canonical distribution. The skewness of the distribution is included in a less direct manner but along the way we obtain a result which we shall need in Sec. IV. If we introduce the symbol  $\beta_m = 1/k_B T_m$ , we may write the average energy for a canonical distribution with temperature  $T_m$  as a logarithmic derivative of the partition function  $Q(\beta_m)$ ,

$$\bar{\epsilon}(T_m) = -\frac{d}{d\beta_m} \ln \left( \int_0^\infty d\epsilon \rho(\epsilon) e^{-\beta_m \epsilon} \right) = -\frac{d}{d\beta_m} \ln Q(\beta_m). \tag{8}$$

To evaluate the integral, we approximate the integrand by a Gaussian as in Eq. (3), and with  $\epsilon_p = E$  the partition function becomes

$$Q(\beta_m) \approx \rho(E) e^{-\beta_m E} \sqrt{2\pi\sigma^2}. \tag{9}$$

Introducing the width  $\sigma$  from Eq. (4) we may write Eq. (9) as an expression for the level density, and this is the formula to be applied later,

$$\rho(E) \approx e^{E/k_B T_m} (2\pi k_B C_m T_m^2)^{-1/2} Q(1/k_B T_m). \tag{10}$$

A combination of Eqs. (4), (8), and (9) gives for the average energy of the canonical ensemble

$$\bar{\epsilon}(T_m) \approx -\frac{d}{d\beta_m} (\ln \rho(E) - \beta_m E - \ln \beta_m + 1/2 \ln C_m). \tag{11}$$

We ignore the last term, which gives the same correction for the temperature dependence of  $C_m$  as in Eq. (6), and we then obtain

$$\bar{\epsilon}(T_m) \approx -\frac{dE}{d\beta_m} \left[ \frac{d}{dE} \ln \rho(E) - \beta_m \right] + E + \beta_m^{-1} = E + k_B T_m, \quad (12)$$

since the quantity in square brackets vanishes according to the definition in Eq. (1). Thus we retrieve the relations in Eqs. (6) and (7).

As an example, we consider a model system to be discussed in Secs. IV and V. For  $J$  harmonic oscillators with level spacings  $\epsilon_j$  the partition function becomes

$$Q(\beta_m) = \prod_{j=1}^J [1 - e^{-\beta_m \epsilon_j}]^{-1}, \quad (13)$$

and, according to Eq. (8), the average excitation energy is then given by

$$\bar{\epsilon}(T_m) = \sum_{j=1}^J \frac{\epsilon_j}{e^{\epsilon_j/k_B T_m} - 1}. \quad (14)$$

From a second-order expansion in  $\epsilon_j/k_B T_m$  one finds that in the high temperature limit  $\bar{\epsilon}$  approaches the classical result  $Jk_B T_m - E_0$ , where  $E_0$  is the zero point energy of the oscillators, and Eq. (12) then leads to the relation  $E = (J - 1)k_B T_m - E_0$ . The classical level density at excitation energy  $E$  is proportional to  $(E + E_0)^{J-1}$ ,<sup>1</sup> and therefore one obtains the same relation between  $E$  and  $T_m$  directly from the definition in Eq. (1). The relation in Eq. (12) is also exact in the classical description of  $N$  free particles, with a level density proportional to  $E^{3/2N-1}$ .

### III. MICROCANONICAL DECAY AND FINITE-HEAT-BATH THEORY

In standard treatments of statistical mechanics, the relation in Eq. (1) is used to define the temperature of a very large system. One then proceeds to derive the fundamental result that a small subsystem of a large microcanonical system has a canonical energy distribution. We shall use the microcanonical temperature of a small system for the analogous purpose, to calculate the probability for concentration of a sufficient amount of energy in motion along a reaction coordinate to allow the system to overcome an energy barrier. The system then plays the role of a heat bath for the single degree of freedom (or for the few degrees of freedom of an emitted particle).

We consider emission of an electron or a small fragment from an atomic cluster. From the detailed-balance relation between emission and attachment, one obtains the following expression for the probability per unit time and unit energy for emission of a particle with energy  $\epsilon$ ,<sup>10</sup>

$$k(E, \epsilon) = A(\epsilon) \frac{\rho_d(E - E_b - \epsilon)}{\rho_p(E)}, \quad (15)$$

where  $E$  is the initial excitation energy of the cluster and  $E_b$  is the binding energy of the particle, while  $\rho_p$  and  $\rho_d$  are the level densities of the parent and daughter clusters. The front factor  $A(\epsilon)$  is proportional to the cross section for the re-

verse process, and for emission of a particle without internal degrees of freedom and with a constant cross section  $A(\epsilon)$  is proportional to  $\epsilon$ .<sup>10</sup> If we approximate the logarithm of the daughter level density by a first-order Taylor expansion in  $\epsilon$ , the decay rate,  $k(E, \epsilon)$ , becomes proportional to a Boltzmann factor  $\exp(-\epsilon/k_B T_d)$ , where  $T_d$  is the microcanonical daughter temperature,

$$\frac{1}{k_B T_d} = \frac{d}{dE} \ln \rho_d(E - E_b). \quad (16)$$

Thus it may be possible to determine the daughter temperature from a measurement of the distribution in released kinetic energy.<sup>11</sup> The total decay rate is obtained by integration of  $k(E, \epsilon)$  over  $\epsilon$ ,

$$k(E) = \nu(T_d) \frac{\rho_d(E - E_b)}{\rho_p(E)}. \quad (17)$$

We assume that there is no barrier for attachment and normally  $\nu(T_d)$  then varies much more slowly than the last factor. As an example, we obtain  $\nu \propto T_d^2$  for  $A \propto \epsilon$ .

When the transition from parent to daughter involves only a small change in the number of degrees of freedom, we may replace the level densities in Eq. (17) by a single function  $\rho$  and include the slowly varying correction factor in the frequency  $\nu$ . It then follows from the mean value theorem applied to  $\ln \rho(E)$  that with a temperature  $T_e$ , defined as in Eq. (1) for some energy between  $E - E_b$  and  $E$ , we may write the decay rate in Arrhenius form,

$$k(E) = \nu \exp\left(\frac{-E_b}{k_B T_e}\right). \quad (18)$$

To obtain an estimate of the ‘‘emission temperature’’  $T_e$  we expand the logarithm of the ratio of level densities in a Taylor series, and we choose the midpoint of the energy interval as the center of expansion to make the even-order terms vanish. When the heat capacity  $C_m$  can be considered constant in the differentiations we obtain to fourth order,

$$\begin{aligned} \ln\left(\frac{\rho(E - E_b)}{\rho(E)}\right) &\approx -E_b \frac{d}{dE} \ln \rho(E - E_b/2) \\ &\quad - \frac{1}{24} E_b^3 \frac{d^3}{dE^3} \ln \rho(E - E_b/2) \\ &= \frac{-E_b}{k_B(T_m - E_b/2C_m)} \\ &\quad \times \left(1 + \frac{E_b^2}{12C_m^2(T_m - E_b/2C_m)^2}\right), \quad (19) \end{aligned}$$

where  $T_m$  is the microcanonical temperature before emission. The emission temperature  $T_e$  is then given to first order in  $E_b/2C_m$  by

$$T_e \approx T_m - E_b/2C_m. \quad (20)$$

The second term is usually called the finite-heat-bath correction to the temperature. It has many analogs, for example in the application of semiclassical estimates to quantum processes, where there is a finite difference between the initial and final states.

Formulas very similar to Eqs. (18)–(20) are an essential element of the finite-heat-bath theory developed by Klots.<sup>8,9</sup> The emission temperature  $T_e$  corresponds in this formalism to an “isokinetic temperature” at which the decay rate in a canonical ensemble is equal to  $k(E)$ . In our opinion, the description becomes conceptually simpler and the approximations more transparent with the introduction of the microcanonical temperature. Klots’ formalism is complicated by the introduction of a fictitious system in thermal equilibrium and of auxiliary quantities which are unnecessary in the simple derivation above.

In Ref. 12 we have applied the description above in a detailed analysis of experiments on electron emission from clusters. For the very large fullerene molecules, the measured lifetimes of anions<sup>13,14</sup> are in good accord with predictions based on Eqs. (18) and (20), with parameters determined from independent measurements. For small clusters, it is necessary to apply the higher-order expansion in Eq. (19) and, as an example, we have analyzed experiments on small Nb clusters.<sup>15</sup> Over a limited range in energy, the expression in Eq. (19) is linear in  $1/T_m$ , and the value of  $E_b$  may therefore be obtained from a fit of Eq. (19) to the slope of the data in an Arrhenius plot of  $\ln k$  against  $1/T_m$ .

In the following we discuss the Dunbar problem, which is closely related to the evaluation of decay rates given by Eq. (17). Somewhat surprisingly, we find that also in this context the microcanonical temperature emerges as the most useful temperature concept. We give in Sec. IV a derivation of Dunbar’s formula with the level density represented by an inverse Laplace transform of the partition function. This is followed in Sec. V by a detailed discussion of the accuracy of Dunbar’s perturbation calculation and by a derivation of the microcanonical Dunbar formula.

#### IV. DUNBAR’S FORMULA

We shall here derive Dunbar’s formula for the excitation probability for a single oscillator in a collection of harmonic oscillators with well defined total excitation energy  $E$ .<sup>5</sup> Dunbar applied Fowler’s method of complex integration but it is equivalent to the Laplace transform used below.<sup>7</sup> The partition function in Eq. (8) is the Laplace transform of the level density,  $Q(\beta) = \mathcal{L}(\rho(E))$ , and the level density is hence given by the inverse Laplace transform of  $Q(\beta)$ ,

$$\rho(E) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} Q(\beta) e^{\beta E} d\beta, \quad (21)$$

where  $\gamma$  is an arbitrary positive real number. We shall evaluate this integral by the steepest-descent method. With the integrand written as  $\exp(f(\beta))$ , the first step is to determine the saddle point of the real part of  $f(\beta)$ , where the derivative of  $f$  vanishes,

$$\frac{\partial f}{\partial \beta} = \frac{\partial}{\partial \beta} (\ln Q(\beta) + \beta E) = 0. \quad (22)$$

According to Eq. (8), this equation is fulfilled for a real value  $\beta_c$  corresponding to a canonical ensemble with average energy  $E$ . The integration path is chosen through the saddle point, and the complex variable may then be written as  $\beta$

$= \beta_c + i\beta'$ . We expand  $f(\beta)$  to second order in  $\beta'$  and perform the integral over the resulting Gaussian. The second derivative of the logarithm of the partition function equals minus the first derivative of the average energy, and the width  $\sigma^*$  of the Gaussian is given by

$$\sigma^* = \sqrt{k_B/C_c} \beta_c. \quad (23)$$

The Gaussian integration therefore gives the following formula for the level density,<sup>7</sup>

$$\rho(E) \approx (2\pi)^{-1/2} \beta_c (k_B/C_c)^{1/2} e^{\beta_c E} Q(\beta_c). \quad (24)$$

The Gaussian approximation in Eq. (3) to the energy distribution in Eq. (2) led to the same formula for the level density in Eq. (10) but with the microcanonical value  $T_m$  in Eq. (1) for the temperature and with the microcanonical heat capacity  $C_m$ . The two formulas become identical for large systems, i.e., for  $k_B/C_c \rightarrow 0$ , and we have found them also to give nearly the same result for the small model system discussed below, with relative deviations from the exact result which are an order of magnitude smaller than  $k_B/C_c$ .

For a system of harmonic oscillators, Dunbar took the analysis one step further and considered the excitation probability for the individual oscillators, i.e., the probability  $P_j(n)$  for finding the  $j$ th oscillator in the  $n$ th excited state. The exact value is given by the ratio between the number of states available for the remaining  $J-1$  oscillators with excitation energy  $E - n\epsilon_j$  and the number of states of the total system with excitation energy  $E$ . An approximate value may be obtained from the ratio between the level densities  $\rho_j(E - n\epsilon_j)$  of the  $J-1$  oscillators and  $\rho(E)$  of the total system, estimated in the steepest-descent approximation. We apply Eq. (21) to calculate both level densities. Denoting the partition function for the total system by  $Q(\beta)$  and applying the expression in Eq. (13), we obtain

$$\rho_j(E - n\epsilon_j) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} Q(\beta) (1 - e^{-\beta\epsilon_j}) e^{\beta(E - n\epsilon_j)} d\beta. \quad (25)$$

Written in this way, the integrand is a difference between two terms which are identical apart from a replacement of  $n$  by  $n+1$ . Following Ref. 5, we estimate each of these terms by a perturbation calculation: We use the same integration path as for  $\rho(E)$ . When the Gaussian approximation for  $Q(\beta) \exp(\beta E)$  is introduced, the integrals are easily evaluated through completion of the square in the exponent, and we obtain Dunbar’s formula,

$$P_j(n) \approx e^{-n\epsilon_j/k_B T_c} \exp\left(-\frac{k_B}{2C_c} \left(\frac{n\epsilon_j}{k_B T_c}\right)^2\right) \times \left[1 - e^{-\epsilon_j/k_B T_c} \exp\left(-\frac{(2n+1)k_B}{2C_c} \left(\frac{\epsilon_j}{k_B T_c}\right)^2\right)\right], \quad (26)$$

where  $T_c$  denotes the canonical temperature of the total system. This formula has several nice features: The first factor is the usual Boltzmann factor, and for  $k_B/C_c \rightarrow 0$  the expression approaches a normalized exponential distribution. To first order in  $k_B/C_c$ , the second exponent corresponds to the finite-heat-bath correction of the first exponent, as given in

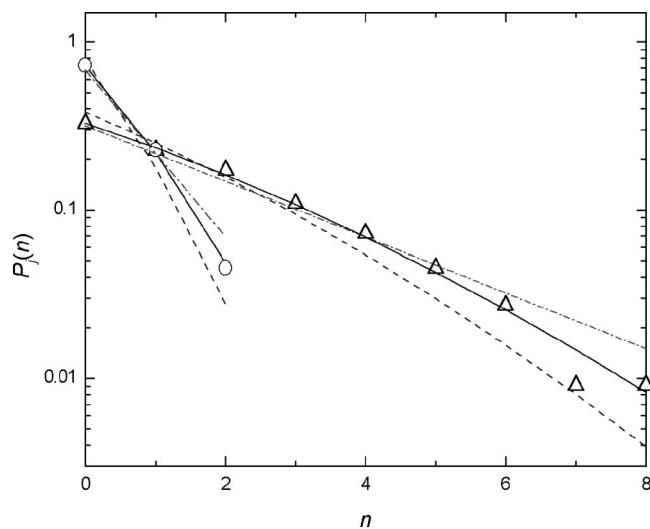


FIG. 1. Excitation probabilities for a single oscillator with level spacing  $500 \text{ cm}^{-1}$  ( $\Delta$ ) and  $1500 \text{ cm}^{-1}$  ( $\circ$ ) in a collection of six harmonic oscillators,  $2 \times (500 \text{ cm}^{-1}, 1000 \text{ cm}^{-1}, \text{ and } 1500 \text{ cm}^{-1})$ , with total excitation energy  $4000 \text{ cm}^{-1}$ . The total number of states is 110. The dashed curves indicate Dunbar's formula in Eq. (26) ( $T_c = 1552 \text{ K}$ ), the full-drawn curves the same formula with microcanonical parameters ( $T_m = 1889 \text{ K}$ ), and the dotted-dashed curves Boltzmann distributions at  $T_c$ .

Eq. (20). The expression in Eq. (26) is normalized also for a finite value of  $k_B/C_c$ : As noted above, the two terms with opposite sign are identical apart from the replacement of  $n$  by  $n+1$ . In the sum over  $n$  to infinity the terms therefore cancel in pairs, except for the term with  $n=0$  which is equal to unity. Although the sum includes small unphysical terms with  $n\epsilon_j > E$ , this is in most cases a satisfactory normalization.

On the basis of numerical calculations for a few model systems, Dunbar claimed Eq. (26) to be more accurate than a simple Boltzmann distribution. However, we find his comparisons to be flawed by numerical errors in the evaluation of the expression in Eq. (26). The error is most easily seen for  $n=0$  where it is clear that the value of this expression is larger than the corresponding term in a normalized Boltzmann distribution, and this relation is reversed in Fig. 3 of Ref. 5. We have recalculated the probabilities for the model system illustrated in this figure, and Dunbar's formula is in fact a rather poor approximation, as shown in Fig. 1. On the other hand, if we instead use the microcanonical temperature and the corresponding heat capacity, the agreement of the formula with the exact counting is excellent!

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In order to find an explanation for this observation, we analyze the derivation of Dunbar's formula in some detail. It is based on a second-order expansion of the logarithm of the two terms in the integrand in Eq. (25), but at the saddle point for the integrand in Eq. (21) rather than at the individual saddle points for the two terms. To estimate the error associated with this shift of the expansion points, we consider the value  $I(\gamma)$  obtained for the integral in Eq. (21) when the logarithm of the integrand is expanded to second order

around  $\gamma = \gamma_0 + \Delta\gamma$ , where  $\gamma_0$  is the saddle point. For the ratio  $I(\gamma)/I(\gamma_0)$  we obtain to second order in  $\Delta\gamma/\gamma_0$ ,

$$I(\gamma)/I(\gamma_0) \approx \left( 1 + \frac{C_c(\gamma_0)}{2k_B} \left( \frac{\Delta\gamma}{\gamma_0} \right)^2 \right) \times \left( 1 - \frac{C_c(\gamma_0)^2}{2k_B C_c(\gamma)} \left( \frac{\Delta\gamma}{\gamma_0} \right)^2 \right) \left( \frac{\gamma}{\gamma_0} \left( \frac{C_c(\gamma_0)}{C_c(\gamma)} \right)^{1/2} \right). \quad (27)$$

The first of the three factors is the ratio between the values of the integrand at  $\beta = \gamma$  and at  $\beta = \gamma_0$ . The second factor accounts for the fact that the first derivative of the integrand differs from zero at the expansion point  $\beta = \gamma$ . As a function of the imaginary part,  $\beta'$ , the logarithm of the integrand then contains an imaginary first-order term. By completion of the square as in the evaluation of Eq. (25) one finds that this leads to a reduction of the Gaussian integral by an exponential factor, which in Eq. (27) has been approximated to second order in  $\Delta\gamma/\gamma_0$ . The last factor in Eq. (27) stems from the  $\gamma$  dependence of the width of the Gaussian, derived as in Eq. (23) from the second derivative of the logarithm of the integrand. If the temperature dependence of the heat capacity can be neglected, the first two factors in Eq. (27) cancel to second order in  $\Delta\gamma/\gamma_0$ , and to this accuracy  $I(\gamma)$  is therefore proportional to  $\gamma$ .

The observation that apparently the microcanonical temperature should be used in Dunbar's formula inspired us to try to remedy the error in the evaluation of Eq. (25) by considering  $\rho'(E)$ , the derivative of the level density. According to the definition of the microcanonical temperature in Eq. (1), we have the exact relation  $\rho(E) = \rho'(E)/\beta_m$  and we may therefore as well consider approximate expressions for  $\rho'$ . From partial integration one obtains  $\mathcal{L}(\rho') = \beta\mathcal{L}(\rho)$ , and in the inverse transform analogous to Eq. (21) the integrand therefore contains an additional factor  $\beta$ . We apply again the steepest-descent approximation. The condition analogous to Eq. (22), determining the saddle point, now corresponds to the relation in Eq. (12), i.e., the saddle point is to a good approximation at  $\gamma = \beta_m$  if the heat capacity is nearly constant [Eq. (6)]. The second derivative of  $\ln(\beta Q(\beta))$  gives the width of the Gaussian, and one obtains the formula in Eq. (23) with  $\beta_c$  replaced by  $\beta_m$  and with  $C_c$  replaced by  $C_c - k_B$ . When only weakly dependent on temperature, this quantity equals the microcanonical heat capacity  $C_m$  according to Eq. (7). We then obtain the formula

$$\rho(E) \approx (2\pi)^{-1/2} \beta_m (k_B/C_m)^{1/2} e^{\beta_m E} Q(\beta_m). \quad (28)$$

This formula is identical to Eq. (10) and hence found to be as accurate as the formula in Eq. (24). We may therefore choose freely between the two estimates of the level density based on an evaluation of either  $\rho(E)$  or  $\rho'(E)$  by the steepest-descent approximation to the inverse Laplace transform.

We now apply these considerations to the evaluation of the level density  $\rho_j$  and show that with the alternative procedure based on a formula for the derivative of the level density, the error following from the linear dependence on  $\gamma$  can be avoided. To this end, we define a function  $F(\gamma)$  by the expression,

$$F(\gamma) = \frac{1}{\gamma} \frac{1}{2\pi i} \times \left( \int_{\gamma-i\infty}^{\gamma+i\infty} \beta Q(\beta) (1 - e^{-\beta\epsilon_j}) e^{\beta(E-n\epsilon_j)} d\beta \right)_{\text{Gauss}}, \quad (29)$$

where the integral is evaluated by a second-order expansion of the logarithm of the integrand. The product of the first three factors in the integrand is the partition function for the derivative of the level density for the  $J-1$  oscillators. We assume that the heat capacities can be considered constant. At the saddle point  $\gamma_0$ , which then is the microcanonical value of  $\beta$  for this subsystem at excitation energy  $E-n\epsilon_j$ , the integral divided by  $2\pi i$  gives an accurate approximation to the derivative of the level density for the subsystem. According to the definition in Eq. (1), the value  $F(\gamma_0)$  is then also an accurate approximation to  $\rho_j(E-n\epsilon_j)$ . For neighboring values of  $\gamma$ , the factor  $\gamma^{-1}$  in front cancels the linear dependence of the integral and the expression is independent of  $\gamma$  to second order. To obtain a simple formula for the probabilities  $P_j(n) = \rho_j(E-n\epsilon_j)/\rho(E)$  we therefore use the value  $\gamma = \beta_m$  corresponding to the saddle point for the analogous expression for  $\rho(E)$ , and we obtain

$$P_j(n) \approx e^{-n\epsilon_j/k_B T_m} (1 - e^{-\epsilon_j/k_B T_m}) \times \exp\left(-\frac{\epsilon_j^2}{2k_B C_{m,j} T_m^2} \left(\frac{1}{e^{\epsilon_j/k_B T_m} - 1} - n\right)^2\right) \left(\frac{C_m}{C_{m,j}}\right)^{1/2}, \quad (30)$$

where we have introduced the symbol  $C_{m,j}$  for the microcanonical heat capacity of the subsystem excluding the  $j$ th oscillator. To avoid this additional parameter, we may as in the evaluation of Eq. (25) replace the expression in Eq. (29) for  $\gamma = \beta_m$  by a difference between two terms, which are evaluated individually in the Gaussian approximation. We then obtain a formula identical to Dunbar's result in Eq. (26) but with the microcanonical values of the temperature and the heat capacity. The deviations from Eq. (30) are small, amounting to less than 6% for all the model calculations in Figs. 1 and 2.

The exact probabilities for the model illustrated in the figures were calculated from a recursion formula. If the oscillators are enumerated from 1 to  $J$ , the following relation holds for the number of states  $N(E, K)$  of a system with excitation energy  $E$  and containing the first  $K$  oscillators,

$$N(E, K) = \sum_n N(E - n\epsilon_K, K - 1), \quad \text{for } K \leq J, \quad (31)$$

where the sum over  $n$  is restricted to non-negative values of  $E - n\epsilon_K$ . As shown in Fig. 1, the "microcanonical Dunbar formula" gives much better agreement with these exact probabilities than the original Dunbar formula, which gives too low probabilities for large  $n$ . In the light of our discussion, this discrepancy can be explained in the main by the linear dependence on  $\gamma$  of the expression in Eq. (27). For large  $n$  values, most of the energy is concentrated on the single oscillator and  $\gamma_0$  is therefore much larger than the

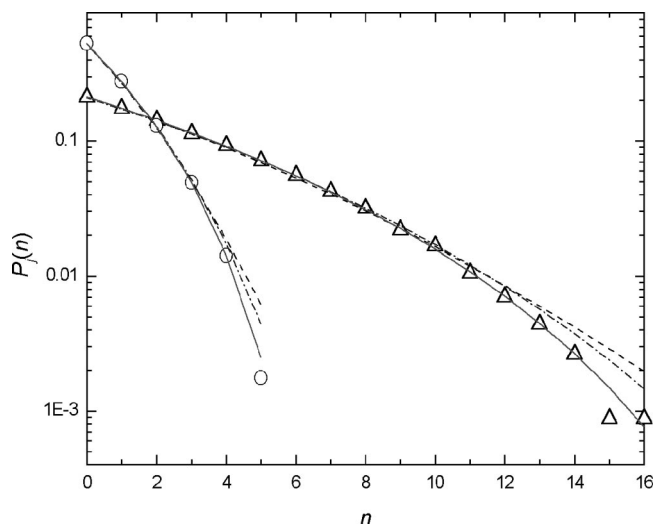


FIG. 2. Excitation probabilities for the same oscillators as in Fig. 1, but at a total excitation energy of  $8000 \text{ cm}^{-1}$  where the number of states is 1136. Dunbar's formula with microcanonical parameters is now illustrated by the dashed curves, while the dotted-dashed curves result from an expansion to second order of the logarithm of the expression in Eq. (34), in analogy to Eqs. (18) and (20). The more accurate, full-drawn curves correspond to an expansion to fourth order, in analogy to Eq. (19). For the total system the microcanonical temperature is 3088 K, and for a system with the same energy but with one oscillator removed, 3790 K ( $500 \text{ cm}^{-1}$ ) and 3630 K ( $1500 \text{ cm}^{-1}$ ).

value  $\gamma = \beta_c$  at which the integral in Eq. (25) is evaluated. Figure 2 shows the excitation probabilities for the same six-oscillator model as in Fig. 1 but for a total excitation energy which is twice as large. The total number of states is then an order of magnitude larger and the excitation probabilities can be followed over a larger range. It is seen that then also the microcanonical Dunbar formula becomes inaccurate for the largest  $n$  values.

## VI. FINITE-HEAT-BATH THEORY

For the derivation of the analytical formula in Eq. (26), the simple mathematical form of the partition function for the harmonic oscillator is essential. However, as we shall now show, the most important feature of this formula, the Boltzmann factor with a finite-heat-bath correction, is more general. We apply the perturbation procedure based on a Laplace transform of  $\rho'$  to evaluate the ratio of level densities in Eq. (19). Assuming again the temperature dependence of the heat capacities to be weak, we may express the level densities in the form

$$\rho(E - \delta E) \approx \frac{1}{\beta_m} \frac{1}{2\pi i} \left( \int_{\beta_m - i\infty}^{\beta_m + i\infty} \beta Q(\beta) e^{\beta(E - \delta E)} d\beta \right)_{\text{Gauss}}, \quad (32)$$

where  $\beta_m$  is the microcanonical value at excitation energy  $E$ , and  $\delta E$  equals  $E_b$  or zero. The Gaussians representing the two integrands have the same width and the ratio of the peak values equals  $\exp(-\beta_m E_b)$ . The first derivative of the logarithm of the integrand differs from zero for  $\delta E = E_b$ , and taking this into account as before by completion of the square we obtain

$$\frac{\rho(E-E_b)}{\rho(E)} \approx \exp\left[-\beta_m E_b \left\langle 1 + \frac{k_B}{2C_m} \beta_m E_b \right\rangle\right]. \quad (33)$$

This expression corresponds to a Boltzmann factor with a modification that to first order is the same as the finite-heat-bath correction in Eq. (20). Hence the perturbation calculation can be considered an alternative derivation of this correction. However, the Taylor expansion is more straightforward and a variation with temperature of the heat capacity can easily be included.<sup>12</sup> Furthermore, it has the important advantage that it can be improved by inclusion of higher-order terms, as in Eq. (19).

This may be illustrated by an application of the Taylor expansion to estimate the excitation probabilities for a single oscillator in our model system. The other  $J-1$  oscillators constitute a finite heat bath, and the relative excitation probabilities are given by

$$P_j(n) \propto \frac{\rho_j(E - n\epsilon_j)}{\rho_j(E)}. \quad (34)$$

For the examples illustrated in Figs. 1 and 2, a second-order expansion of the logarithm of this ratio, analogous to Eqs. (18) and (20), leads to predictions which are close to the microcanonical Dunbar formula. For each oscillator  $j$ , the values of the temperature  $T_m$  and heat capacity  $C_m$  for the subsystem with  $J-1$  oscillators were obtained from Eqs. (7), (12), and (14), and the common constant on the ratio in Eq. (34) was determined from a normalization of the sum over  $n$  to unity. With the fourth-order expansion in Eq. (19) the exact statistical weights are reproduced quite well even for the highest excitations in Fig. 2.

We have seen that it can be convenient to consider the derivative of  $\rho(E)$  rather than the level density itself. Sometimes it can also be useful to introduce the integrated level density,  $w(E)$ .<sup>7,8</sup> Since the relation between  $w(E)$  and  $\rho(E)$  is the same as between  $\rho$  and  $\rho'$ , we have from the definition in Eq. (1),

$$w(E) = k_B T_{m,w} \rho(E), \quad (35)$$

where  $T_{m,w}$  is the microcanonical temperature for a system with level density  $w$ . As before we may identify it with the canonical temperature  $T_c$  for the system with level density  $\rho$  if the heat capacity is nearly constant. The lowest-order correction for variation of the heat capacity may be obtained from Eq. (6), applied to the system with level density  $w$ . According to Eq. (8), the left-hand side equals  $\bar{\epsilon}(T_{m,w}) + k_B T_{m,w}$ , where the function  $\bar{\epsilon}$  refers to the system with level density  $\rho$ , and on the right-hand side we replace  $E$  by  $\bar{\epsilon}(T_c)$ . By expansion of the function  $\bar{\epsilon}$  to first order we then obtain the relation,

$$T_{m,w} - T_c \approx \frac{k_B}{2C_c} \frac{T_c}{C_c} \frac{d}{dT_c} C_c(T_c), \quad (36)$$

where we have replaced  $T_{m,w}$  by  $T_c$  and  $C_{m,w}$  by  $C_c$  on the right-hand side.

The formula in Eq. (35) with  $T_{m,w} = T_c$  was derived in Ref. 7 but with little attention to accuracy. In Ref. 8 an attempt was made to improve the argument because the relation played an important role in the discussion of finite-

heat-bath theory, but a relative uncertainty of order  $k_B/C_c$  remained. Here we have established the relation to first order in  $k_B/C_c$ . Temperature corrections like the one in Eq. (36) would also appear in the microcanonical Dunbar formula if the variation with temperature of the heat capacity were included. However, the corrections are usually quite small, of order 1% or smaller in the model examples illustrated in Figs. 1 and 2.

## VII. CONCLUDING REMARKS

We have discussed the concept of temperature for an isolated finite system with well defined energy. As an approximation, the system may be represented by a canonical energy distribution with mean value equal to the energy of the system, and the corresponding temperature is denoted the "canonical temperature." An alternative is the microcanonical temperature, defined in terms of the derivative of the logarithm of the level density, and for small systems there is a significant difference between the two temperatures. We have argued that the microcanonical temperature is the most useful concept when decay by particle emission from a cluster is considered. An Arrhenius formula may be derived from the statistical expression for the decay rate by a Taylor expansion of the logarithm of the level density, and the resulting effective decay temperature equals the initial microcanonical temperature with a correction depending on the size of the system. In our opinion, this is a simpler conceptual framework for a finite-heat-bath theory than the one applied by Klots, where the system is represented by a canonical ensemble.<sup>8,9</sup>

The level density of a system may be expressed as the inverse Laplace transform of the partition function, and the canonical temperature appears as the characteristic temperature when this transform is evaluated by the saddle point method. In this connection, we have discussed an analytical formula, derived by Dunbar,<sup>5</sup> for the excitation probabilities of one oscillator in a collection of harmonic oscillators with well defined and statistically distributed total excitation energy. A much improved accuracy of this formula is obtained when the canonical temperature and heat capacity of the system are replaced by the microcanonical values, and we have found a justification for this replacement in a modification of the derivation. The modified procedure is not limited to harmonic oscillators and it has also been applied to particle emission from a cluster. This gives an alternative derivation of an Arrhenius formula with an effective decay temperature equal to the microcanonical temperature with a finite-heat-bath correction.

However, the description based on a Taylor expansion of the logarithm of the level density is simpler and has the advantage that it can be extended to higher order. This is important for small molecules or clusters, where also the distinction between the microcanonical and the canonical temperature is significant. For larger systems, consisting of tens of atoms or more, only the first-order term in the Taylor expansion need be retained, but the corresponding finite-heat-bath correction remains important even for quite large systems like the buckminsterfullerene molecule  $C_{60}$ .<sup>12</sup>

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