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# Derivation of thermal equations of state for quantum systems using the quasi-Gaussian entropy theory

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In this article, the quasi-Gaussian entropy theory is derived for pure quantum systems, along the same lines as previously done for semiclassical systems. The crucial element for the evaluation of the Helmholtz free energy and its temperature dependence is the moment generating function of the discrete probability distribution of the quantum mechanical energy. This complicated moment generating function is modeled via two distributions: the discrete distribution of the energy-level order index and the continuous distribution of the energy gap. For both distributions the corresponding physical-mathematical restrictions and possible systematic generation are discussed. The classical limit of the present derivation is mentioned in connection with the previous semiclassical derivation of the quasi-Gaussian entropy theory. Several simple statistical states are derived, and it is shown that among them are the familiar Einstein model and the one-, two-, and three-dimensional Debye models. The various statistical states are applied to copper,  $\alpha$ -alumina, and graphite. One of these states, the beta-diverging negative binomial state, is able to provide an accurate description of the heat capacity of both isotropic crystals, like copper, and anisotropic ones, like graphite, comparable to the general Tarasov equation. © 1999 American Institute of Physics. [S0021-9606(99)51633-4]

## I. INTRODUCTION

At the end of the last and the beginning of this century, the fundamentals of classical physics were severely attacked, when more and more experimental evidence pointed to the fact that the energy of a system apparently could not just assume any value in a continuous way. Instead, the energy seemed to be discretized, showing specific energy gaps.

This was most apparent from spectroscopic data, which clearly showed specific emission lines instead of a continuous spectrum. Also, the heat capacity of solids at low temperature clearly deviated from the "classical" Dulong and Petit value,<sup>1</sup> which follows from the equipartition principle of a set of classical harmonic oscillators.

Einstein<sup>2</sup> was actually the first one to recognize that Planck's revolutionary idea of quantized energy could very well explain the strange thermodynamic behavior of solids at relatively low temperature. A few years later, Debye<sup>3</sup> significantly refined Einstein's ideas, and up to now the Debye theory is still a successful theory to describe the thermodynamics of (simple) isotropic solids. Extensions of the Debye approach to anisotropic and more complicated molecular or polymer crystals are, e.g., the Tarasov equation.<sup>4</sup> Note that the Einstein and Debye models and extensions are all based

on a quantum harmonic oscillator Hamiltonian.

In this paper we will set up a "macroscopic" statistical mechanical theory to describe the thermodynamics of quantum mechanical systems, solids in particular, based on a few simple physical principles. Without relying on a specific Hamiltonian, we simply use the fact that the energy can assume only discrete values. Combining this with the general definition of the canonical partition function and the Helmholtz free energy, we develop a theory which employs the properties of the underlying energy distribution function to model the thermodynamics. Along the same lines we previously<sup>5-10</sup> set up such a theory, the quasi-Gaussian entropy theory, for semiclassical systems. In that case we showed that for fluid systems already a simple continuous model distribution (e.g., a Gamma distribution) is able to describe accurately the thermodynamics of polar and apolar molecules like water<sup>6,11</sup> and the Lennard-Jones fluid<sup>12,13</sup> over a large temperature range.

The paper is organized as follows. In Sec. II we derive how the Helmholtz free energy can be expressed in terms of the distribution functions of the order index  $l$  of the energy levels and the energy gap  $\Delta\epsilon$ . In Sec. III we describe possible models for these distributions and their physical-mathematical restrictions. In Sec. IV we present some statistical states, i.e., the thermodynamics of various combinations of distribution functions of  $l$  and  $\Delta\epsilon$ . These statistical states

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will be applied to copper,  $\alpha$ -alumina, and graphite in Sec. V. Conclusions are given in Sec. VI.

## II. GENERAL FRAMEWORK

The Helmholtz free energy in the canonical ensemble is

$$A = -kT \ln Q, \quad (1)$$

where the quantum mechanical canonical partition function is given by<sup>14,15</sup>

$$Q = \sum_n e^{-\beta \varepsilon_n} = \sum_L e^{-\beta \varepsilon_L} \Omega(\varepsilon_L). \quad (2)$$

In this expression,  $\varepsilon_n$  are the energies of the different physical states of the system, and  $\varepsilon_L$  is the  $L$ th energy level, ordering the possible energies of the system in increasing magnitude from the ground state, where  $L$  is the order index, and  $\Omega(\varepsilon_L)$  is the corresponding degeneracy factor. As usual,  $\beta = 1/kT$  with  $k$  the Boltzmann constant.

The excess free energy with respect to a system at “temperature”  $\beta_0$  can be expressed as<sup>7,8</sup>

$$\begin{aligned} \Delta(\beta A) &= \beta A - \beta_0 A_0 \\ &= -\ln \frac{\sum_L e^{-\beta \varepsilon_L} \Omega(\varepsilon_L)}{\sum_L e^{-\beta_0 \varepsilon_L} \Omega(\varepsilon_L)} \\ &= -\ln \frac{\sum_L e^{-\Delta\beta \varepsilon_L} e^{-\beta_0 \varepsilon_L} \Omega(\varepsilon_L)}{\sum_L e^{-\beta_0 \varepsilon_L} \Omega(\varepsilon_L)} = -\ln \langle e^{-\Delta\beta \varepsilon_L} \rangle_{\beta_0} \end{aligned} \quad (3)$$

$$= -\ln \frac{\sum_L e^{-\beta \varepsilon_L} \Omega(\varepsilon_L)}{\sum_L e^{\Delta\beta \varepsilon_L} e^{-\beta \varepsilon_L} \Omega(\varepsilon_L)} = \ln \langle e^{\Delta\beta \varepsilon_L} \rangle_{\beta}, \quad (4)$$

where  $\Delta\beta = \beta - \beta_0$  and  $\langle \cdots \rangle_{\beta}$  and  $\langle \cdots \rangle_{\beta_0}$  are canonical ensemble averages in the  $\beta$  and  $\beta_0$  ensemble. Note that

$$\langle e^{-\Delta\beta \varepsilon_L} \rangle_{\beta_0} = \sum_L e^{-\Delta\beta \varepsilon_L} p_0(\varepsilon_L) \equiv G_{\varepsilon_L}^0(-\Delta\beta), \quad (5)$$

$$\langle e^{\Delta\beta \varepsilon_L} \rangle_{\beta} = \sum_L e^{\Delta\beta \varepsilon_L} p(\varepsilon_L) \equiv G_{\varepsilon_L}(\Delta\beta) \quad (6)$$

are the moment generating functions<sup>16–18</sup> (MGF) of the discrete probability distribution functions  $p_0(\varepsilon_L)$  and  $p(\varepsilon_L)$  of the energy  $\varepsilon_L$ . Here, the zero subscript on  $p_0(\varepsilon_L)$  and superscript on  $G_{\varepsilon_L}^0(-\Delta\beta)$  denote that the distribution and MGF are evaluated at fixed temperature  $\beta_0$ .

In general, the moment generating function of a discrete probability distribution  $p(x)$  is defined as  $G_x(t) = \sum_i e^{tx} p(x_i) = \langle e^{tx} \rangle$ , and for a continuous probability distribution  $p(x)$  as  $G_x(t) = \int e^{tx} p(x) dx = \langle e^{tx} \rangle$ . It corresponds to the Laplace transform of the distribution. For reasons that will become clear later on, instead of Eq. (4) we prefer to use Eq. (3). From this equation it follows that the free energy difference is defined once the distribution of the energy at one temperature  $\beta_0$  is known. The key point is therefore the evaluation of the corresponding MGF  $G_{\varepsilon_L}^0(-\Delta\beta)$ .

As the system is a macroscopic thermodynamic system, it may be decomposed into a very large number ( $N_e$ ) of identical and statistically independent “elementary

systems.”<sup>5</sup> Clearly, the energy  $\varepsilon_L$  is the sum of the energies  $\varepsilon_l$  of the elementary systems. The distribution  $p_0(\varepsilon_L)$  is therefore the  $N_e$ -fold convolution of the “elementary distribution”  $p_0(\varepsilon_l)$ , and hence<sup>17</sup>

$$G_{\varepsilon_L}^0(-\Delta\beta) = [g_{\varepsilon_l}^0(-\Delta\beta)]^{N_e}, \quad (7)$$

where  $g_{\varepsilon_l}^0(t)$  is the MGF of  $p_0(\varepsilon_l)$ . From the central limit theorem,<sup>16</sup>  $p_0(\varepsilon_L)$  must be a unimodal distribution.

In contrast to the semiclassical case,<sup>8</sup> where the instantaneous energy  $\mathcal{U}$  is a continuous variable, for quantum systems  $\varepsilon_L$  and  $\varepsilon_l$  are in principle discrete variables. However, since the energy levels are in general not equidistant, it is not appropriate to model  $p_0(\varepsilon_l)$  merely by a simple “lattice distribution,” which is defined on equally spaced intervals.<sup>17</sup> We assume that the overall distribution  $p_0(\varepsilon_L)$  is “quasi-Gaussian,” implying that the elementary distribution can be modeled by analytical, relatively simple (unimodal) curves. Hence, we will make the following two very reasonable assumptions.

(1) We assume that the MGF  $g_{\varepsilon_l}^0(-\Delta\beta)$  in Eq. (7) can in turn be factorized into  $N_s$  “subelementary” MGFs. This means that the energy per elementary system can be written as a sum of energies  $\varepsilon_{l_i}$  of the subelementary distributions. Each of these subelementary MGFs is characterized by some specific fixed energy gap  $\Delta\varepsilon_i$  ( $i = 1 \cdots N_s$ ). Hence we can write the energy  $\varepsilon_{l_i}$  as

$$\varepsilon_{l_i} = \varepsilon_{0,i} + \Delta\varepsilon_i \cdot l_i \quad l_i = 0, 1, \dots, \quad (8)$$

with  $\varepsilon_{0,i}$  the temperature-independent ground-state energy,  $l_i$  the level order index, and  $\Delta\varepsilon_i$  the energy gap of the  $i$ th subelementary distribution. Therefore we have

$$\begin{aligned} g_{\varepsilon_l}^0(-\Delta\beta) &= \prod_{i=1}^{N_s} \tilde{g}_{\varepsilon_{l_i}}^0(-\Delta\beta) \\ &= e^{-\Delta\beta \varepsilon_0} \prod_{i=1}^{N_s} \tilde{g}_{l_i}^0(-\Delta\beta \Delta\varepsilon_i), \end{aligned} \quad (9)$$

where  $\varepsilon_0 = \sum_{i=1}^{N_s} \varepsilon_{0,i}$ . Note that since  $\Delta\varepsilon_i$  is constant for each  $i$ , it now appears inside the argument of the subelementary MGF  $\tilde{g}_{l_i}^0(t)$ , as for any constants  $c_1$  and  $c_2$  we have<sup>17</sup>  $G_{c_1+c_2x}(t) = \langle e^{t(c_1+c_2x)} \rangle = e^{tc_1} G_x(tc_2)$ . Using Eqs. (3), (5), (7), and (9), the free energy difference is therefore

$$\begin{aligned} \Delta(\beta A) &= -N_e \ln g_{\varepsilon_L}^0(-\Delta\beta) \\ &= N_e \varepsilon_0 \Delta\beta - N_e \sum_{i=1}^{N_s} \ln \tilde{g}_{l_i}^0(-\Delta\beta \Delta\varepsilon_i). \end{aligned} \quad (10)$$

Note that Eq. (9) corresponds to a special “clustering” of the physical states of the elementary system, such that the partition function can be factorized in an inhomogeneous way. Such a factorization cannot be exact, as in the “infinite” temperature limit any partition function can, if possible, only be homogeneously factorized. (Note that a homogeneous factorization of the elementary system should lead to a new definition of the elementary system.) It is therefore likely that this first assumption is reasonable for solid systems.

(2) We furthermore assume that the distribution of the order index  $l_i$  is the same for each  $i$  and hence independent of the value of  $\Delta\varepsilon_i$ . For an elementary system which contains still an “infinite” number of molecules, we can safely say that the value of the energy gap varies in an almost continuous way. We can therefore rewrite the sum in Eq. (10) also in terms of the (continuous) probability density of the energy gap  $\rho(\Delta\varepsilon)$ ,

$$\Delta(\beta A)$$

$$\begin{aligned} &= \mathbb{N}_e \varepsilon_0 \Delta\beta - \mathbb{N}_e \mathbb{N}_s \int_0^\infty \ln\{\tilde{g}_l^0(-\Delta\beta\Delta\varepsilon)\} \rho(\Delta\varepsilon) d\Delta\varepsilon \\ &= E_0 \Delta\beta - \mathbb{N} \int_0^\infty \ln\left\{ \sum_{l=0}^\infty e^{-\Delta\beta\Delta\varepsilon \cdot l} p_0(l) \right\} \rho(\Delta\varepsilon) d\Delta\varepsilon, \end{aligned} \quad (11)$$

where we defined  $E_0 = \mathbb{N}_e \varepsilon_0$  and  $\mathbb{N} = \mathbb{N}_e \mathbb{N}_s$ .

We see that the free energy difference for quantum mechanical systems can be described by two distribution functions: one being the discrete probability distribution  $p_0(l)$  of the order index  $l$  of the subelementary energy levels, and the other being the continuous probability density function  $\rho(\Delta\varepsilon)$  of the energy gap  $\Delta\varepsilon$  within each elementary system.

The free energy difference is therefore completely defined by the *type* of distributions  $p_0(l)$  and  $\rho(\Delta\varepsilon)$ , and by the *values* of  $E_0$ ,  $\mathbb{N}$ , and the parameters  $\{a_{i,0}\}$ ,  $\{b_{i,0}\}$  that specify  $p_0(l)$  and  $\{c_i\}$  that specify  $\rho(\Delta\varepsilon)$ .

Using the same notation as for the semiclassical case,<sup>8</sup> the parameters  $\{a_{i,0}\}$  and  $\{b_{i,0}\}$  of the distribution  $p_0(l)$  are evaluated at  $\beta_0$  (indicated by the zero subscript), and hence are temperature independent. Equations (3) and (11) therefore directly yield the full temperature dependence of the excess free energy and derived thermodynamic functions. We could, on the other hand, make a similar derivation starting from Eq. (4). In that case we would need the distribution  $p(l)$ , the parameters of which are temperature dependent. The corresponding free energy expression is thus both explicitly and implicitly temperature dependent. To get the full explicit temperature dependence, we should first formulate and solve an ordinary differential equation in  $C_V$  and  $T$ , the thermodynamic master equation (TME),<sup>5,8,9</sup> providing in the end the same solution as Eqs. (3) and (11), where the TME is implicitly solved. For convenience we therefore used Eq. (3) instead of Eq. (4).

From Eq. (11) it follows that the free energy, energy, entropy, and heat capacity are given by

$$\begin{aligned} A(T) &= E_0 - TS_0 + (U_0 - E_0) \left( \frac{T}{T_0} \right) \\ &\quad - \mathbb{N} k T \int_0^\infty \ln\left\{ \sum_{l=0}^\infty e^{-\Delta\beta\Delta\varepsilon \cdot l} p_0(l) \right\} \rho(\Delta\varepsilon) d\Delta\varepsilon, \end{aligned} \quad (12)$$

$$\begin{aligned} U(T) &= E_0 - \mathbb{N} \int_0^\infty \frac{\partial}{\partial\beta} \\ &\quad \times \ln\left\{ \sum_{l=0}^\infty e^{-\Delta\beta\Delta\varepsilon \cdot l} p_0(l) \right\} \rho(\Delta\varepsilon) d\Delta\varepsilon, \end{aligned} \quad (13)$$

$$\begin{aligned} S(T) &= S_0 - \frac{(U_0 - E_0)}{T_0} \\ &\quad + \mathbb{N} k \int_0^\infty \ln\left\{ \sum_{l=0}^\infty e^{-\Delta\beta\Delta\varepsilon \cdot l} p_0(l) \right\} \rho(\Delta\varepsilon) d\Delta\varepsilon \\ &\quad - \frac{\mathbb{N}}{T} \int_0^\infty \frac{\partial}{\partial\beta} \ln\left\{ \sum_{l=0}^\infty e^{-\Delta\beta\Delta\varepsilon \cdot l} p_0(l) \right\} \rho(\Delta\varepsilon) d\Delta\varepsilon, \end{aligned} \quad (14)$$

$$\begin{aligned} C_V(T) &= \mathbb{N} k \beta^2 \int_0^\infty \frac{\partial^2}{\partial\beta^2} \\ &\quad \times \ln\left\{ \sum_{l=0}^\infty e^{-\Delta\beta\Delta\varepsilon \cdot l} p_0(l) \right\} \rho(\Delta\varepsilon) d\Delta\varepsilon, \end{aligned} \quad (15)$$

where  $U_0$  and  $S_0$  are the values of the energy and entropy at the reference temperature  $T_0 = 1/k\beta_0$ .

To obtain the numerical values of the parameters  $\{a_{i,0}\}$ ,  $\{b_{i,0}\}$ ,  $\{c_i\}$ ,  $E_0$ , and  $\mathbb{N}$ , we can use the “method of moments”,<sup>16</sup> i.e., equating the first few theoretical moments or cumulants of  $p_0(\varepsilon_L)$  [expressed in terms of the parameters of  $p_0(l)$  and  $\rho(\Delta\varepsilon)$ ] and the corresponding sample moments or cumulants of the energy  $\varepsilon_L$  (which, via statistical mechanics, are given by thermodynamic quantities like average energy, heat capacity etc.).

For a distribution with MGF  $G_x(t)$ , the cumulants  $\kappa_n[x]$  of order  $n$  are defined as<sup>16–18</sup>  $\kappa_n[x] = (\partial^n \ln G_x(t)/\partial t^n)_{t=0}$ . From Eq. (3) we see that  $t = -\Delta\beta$ , so  $t=0$  actually corresponds to  $\beta = \beta_0$ . To obtain  $r$  independent equations to solve the unknown parameters, we have to take derivatives up to the  $r$ th order on both the left- and right-hand side of Eq. (11), which slightly rewritten reads

$$\begin{aligned} -\Delta(\beta A) &= \ln G_{\varepsilon_L}^0(t) \\ &= E_0 t - \mathbb{N} \int_0^\infty \ln\left\{ \sum_{l=0}^\infty e^{t\Delta\varepsilon \cdot l} p_0(l; \{a_{i,0}\}, \{b_{i,0}\}) \right\} \\ &\quad \times \rho(\Delta\varepsilon; \{c_i\}) d\Delta\varepsilon, \end{aligned} \quad (16)$$

yielding the following set of equations:

$$\begin{aligned} \kappa_{1,\text{exp}}[\varepsilon_L] &= E_0 + \mathbb{N} \int_0^\infty \kappa_1[l](\Delta\varepsilon, \{a_{i,0}\}, \{b_{i,0}\}) \\ &\quad \times \Delta\varepsilon \rho(\Delta\varepsilon; \{c_i\}) d\Delta\varepsilon, \end{aligned} \quad (17)$$

$$\begin{aligned} \kappa_{2,\text{exp}}[\varepsilon_L] &= \mathbb{N} \int_0^\infty \kappa_2[l](\Delta\varepsilon, \{a_{i,0}\}, \{b_{i,0}\}) \\ &\quad \times \Delta\varepsilon^2 \rho(\Delta\varepsilon; \{c_i\}) d\Delta\varepsilon, \end{aligned} \quad (18)$$

...



$$\kappa_{n,\text{exp}}[\varepsilon_L] = \mathbb{N} \int_0^\infty \kappa_n[l](\Delta\varepsilon, \{a_{i,0}\}, \{b_{i,0}\}) \times \Delta\varepsilon^n \rho(\Delta\varepsilon; \{c_i\}) d\Delta\varepsilon, \quad n=2, \dots, r, \quad (19)$$

where the sample (“experimental”) cumulants are given by<sup>5,7,14,15</sup>

$$\kappa_{1,\text{exp}}[\varepsilon_L] = U_0, \quad (20)$$

$$\kappa_{2,\text{exp}}[\varepsilon_L] = (kT_0)[T_0 C_{V0}], \quad (21)$$

$$\kappa_{3,\text{exp}}[\varepsilon_L] = (kT_0)^2 \left[ T_0^2 \frac{\partial C_{V0}}{\partial T} + 2T_0 C_{V0} \right], \quad (22)$$

...

$$\kappa_{n,\text{exp}}[\varepsilon_L] = (-1)^{n+1} \left( \frac{\partial^n \beta A}{\partial \beta^n} \right)_{\beta_0}, \quad n=1, \dots, r. \quad (23)$$

In these equations,  $U_0$ ,  $C_{V0}$ , etc., are the values of the energy, heat capacity, etc., at the reference temperature  $T_0 = 1/k\beta_0$ , and  $\kappa_n[l](\Delta\varepsilon, \{a_{i,0}\}, \{b_{i,0}\})$  are the theoretical cumulants of  $p_0(l)$ , expressed in terms of the parameters.

Note that in the classical limit all energy gaps will tend to zero; hence  $\rho(\Delta\varepsilon)$  will tend to a Dirac delta function  $\delta(\Delta\varepsilon)$ , and the distribution  $p_0(l)$  transforms into a continuous probability density  $\rho(u)$  for the semiclassical continuous energy  $u$  of an elementary system.

### III. MODEL DISTRIBUTIONS

#### A. Model distributions for $\rho(\Delta\varepsilon)$

We can make the following assumptions for the model distribution of the energy gap  $\rho(\Delta\varepsilon)$ .

First, as already mentioned, the variable  $\Delta\varepsilon$  is approximately continuous; hence  $\rho(\Delta\varepsilon)$  is a continuous distribution function. Second, the domain of  $\Delta\varepsilon$  with nonzero probability is in general finite. However, the upper limit  $\Delta\varepsilon_m$  may be so large that we can approximate the distribution by one which is analytically defined up to infinity. In that case we should of course have  $\lim_{\Delta\varepsilon \rightarrow \infty} \rho(\Delta\varepsilon) = 0$ .

The restrictions on the possible distributions  $\rho(\Delta\varepsilon)$  are therefore (1) the distribution should be defined for values of  $\Delta\varepsilon \geq 0$ , (2) the upper limit may be finite ( $\Delta\varepsilon_m$ ) or infinite, and (3) for the free energy to converge for  $\beta > 0$ , the integral  $\int_0^\infty \ln \{g_l^0(-\beta\Delta\varepsilon)\} \rho(\Delta\varepsilon) d\Delta\varepsilon$  should converge for a specific choice of the distribution  $p_0(l)$  and corresponding MGF  $\tilde{g}_l^0(t)$ . In principle, we can use any system or family of distributions, for example, the Pearson system,<sup>19–21</sup> to obtain model curves with a sufficiently flexible shape.

The simplest possible distribution is the Dirac delta function,

$$\rho(\Delta\varepsilon; \Delta\varepsilon_E) = \delta(\Delta\varepsilon - \Delta\varepsilon_E), \quad \Delta\varepsilon_E \geq 0, \quad (24)$$

where it is assumed that there is only one unique energy gap  $\Delta\varepsilon_E$ .

One of the possible more complex curves with a fixed upper limit is the beta distribution,<sup>16,22</sup>

$$\rho(\Delta\varepsilon; a, b, \Delta\varepsilon_m) = \frac{1}{B(a, b)} \frac{1}{\Delta\varepsilon_m^{a+b-1}} \Delta\varepsilon^{a-1} \times (\Delta\varepsilon_m - \Delta\varepsilon)^{b-1}, \quad \Delta\varepsilon_m > 0, \quad a > 0, \quad b > 0, \quad (25)$$

where  $0 \leq \Delta\varepsilon \leq \Delta\varepsilon_m$  and  $B(a, b) = \Gamma(a)\Gamma(b)/\Gamma(a+b)$  is the Euler beta function and  $\Gamma(a)$  the Gamma function.<sup>23</sup> Note that for  $a$  integer,  $\Gamma(a) = (a-1)!$ . Equation (25) represents a distribution with a very flexible shape; for example, with  $b=1$  we obtain the power function,<sup>16</sup>

$$\rho(\Delta\varepsilon; a, \Delta\varepsilon_m) = \frac{a}{\Delta\varepsilon_m^a} \Delta\varepsilon^{a-1}, \quad \Delta\varepsilon_m > 0, \quad a > 0. \quad (26)$$

Note that for  $a=3$  we obtain a parabola and for  $a=1$  the uniform distribution.

Finally, a simple and often used distribution with no finite upper limit for  $\Delta\varepsilon$  is the gamma distribution,<sup>16,21</sup>

$$\rho(\Delta\varepsilon; a, \tau) = \frac{\tau^a}{\Gamma(a)} \Delta\varepsilon^{a-1} e^{-\tau\Delta\varepsilon}, \quad a > 0, \quad \tau > 0, \quad (27)$$

where  $\Delta\varepsilon \geq 0$ .

Note that for each distribution we can define a corresponding characteristic temperature (see also Sec. IV). For the Dirac delta function we define  $\Theta_E = \Delta\varepsilon_E/k$ , for the power function with parameter  $a$  we define  $\Theta_{Da} = \Delta\varepsilon_m/k$ , for the beta distribution with parameters  $a$  and  $b$  we define  $\Theta_{Ba,b} = \Delta\varepsilon_m/k$ , and, finally, for the gamma distribution with parameter  $a$  we define  $\Theta_{\Gamma a} = 1/(k\tau)$ . By equating the average energy gap ( $\Delta\varepsilon$ ) for the various distributions,<sup>24,25</sup> we obtain approximate relationships between the different characteristic temperatures,

$$\Theta_E \approx \frac{a}{a+1} \Theta_{Da} \approx \frac{a}{a+b} \Theta_{Ba,b} \approx a \Theta_{\Gamma a}. \quad (28)$$

#### B. Model distributions for $p_0(l)$

For the model distribution  $p_0(l)$  we can formulate several physical–mathematical restrictions.

First, for physical reasons, the domain of  $l$  is  $0, 1, 2, \dots$ . Second, we see from Eq. (3) that the MGF  $G_{\varepsilon_L}^0(-\beta)$  diverges for  $\beta \rightarrow 0$ . Hence, to guarantee for any finite upper limit of  $\Delta\varepsilon$  the correct behavior of  $G_{\varepsilon_L}^0(-\beta)$ , from Eq. (11) it follows that also the MGF  $\tilde{g}_l^0(t) = \tilde{g}_l^0(-\beta\Delta\varepsilon)$  must diverge for  $\beta \rightarrow 0$ , i.e., for some specific finite value of  $t \rightarrow t_d = \beta_0 \Delta\varepsilon$ . Hence the MGF of any appropriate model distribution must be finite for  $t < t_d$  and diverge at some finite value of  $t$ , i.e., at  $t_d$ .

One of the possible and very convenient families or systems of discrete distributions, the generalized hypergeometric probability (GHP) family, is a generalization of a discrete version of the Pearson system,<sup>19</sup> set up by Katz<sup>7,26</sup> and Ord.<sup>19</sup> The Katz system, the simplest discrete analog of the Pearson system, was generalized by Kemp to the family of GHP distributions.<sup>17,27,28</sup> The corresponding difference equation for  $p_0(l)$  is

$$\frac{p_0(l+1) - p_0(l)}{p_0(l)} = \frac{(a_{1,0}+l) \cdots (a_{p,0}+l)\lambda - (b_{1,0}+l) \cdots (b_{q,0}+l)(1+l)}{(b_{1,0}+l) \cdots (b_{q,0}+l)(1+l)}, \quad (29)$$

with MGF

$$\tilde{g}_l^0(t) = \frac{{}_pF_q[a_{1,0}, \dots, a_{p,0}; b_{1,0}, \dots, b_{q,0}; \lambda e^t]}{{}_pF_q[a_{1,0}, \dots, a_{p,0}; b_{1,0}, \dots, b_{q,0}; \lambda]}, \quad (30)$$

where  $\lambda > 0$ ;  ${}_pF_q[a_{1,0}, \dots, a_{p,0}; b_{1,0}, \dots, b_{q,0}; x]$  is the generalized hypergeometric function,<sup>17,23</sup> with  $\{a_{i,0}\}$  and  $\{b_{j,0}\}$  the parameters of the distribution ( $i = 1, \dots, p$ ,  $j = 1, \dots, q$ ). For a given order  $p$  and  $q$  the distribution follows from solving Eq. (29) or inverting the MGF, Eq. (30). From the second physical-mathematical restriction (the divergence of the MGF), combined with general properties of the generalized hypergeometric functions, we obtain that for any acceptable distribution within the GHP family, the orders  $p$  and  $q$  in Eqs. (29) and (30) must be given by

$$p = q + 1, \quad (31)$$

with  $a_i$  ( $i = 1, \dots, p$ ) not a negative integer. In those conditions the MGF converges when

$$\lambda e^t < 1, \quad (32)$$

and diverges elsewhere. From this follows that

$$\lambda = e^{-t_d} = e^{-\beta_0 \Delta \varepsilon}, \quad (33)$$

eliminating thus one of the parameters. Note that for  $\lim_{\Delta \varepsilon \rightarrow \infty} \lambda \rightarrow 0$  and the MGF  $\tilde{g}_l^0(t)$  is still converging for any  $\beta > 0$ . It is therefore possible to combine members of this family with distributions  $\rho(\Delta \varepsilon)$  that are defined up to infinity.

The simplest case of Eqs. (29) and (30) is  $\{p = 1, q = 0\}$ , which corresponds to the Katz family of distributions (binomial, Poisson, and negative binomial). The Poisson distribution is actually a limiting case and corresponds to  $\{p = 0, q = 0\}$  and, since its MGF is therefore always converging,<sup>17</sup> it is physically not acceptable. In this respect the Poisson distribution plays the same role as the Gaussian distribution in the continuous Pearson system.<sup>5</sup> For the binomial distribution  $a_{1,0} = -n$  is a negative integer, so the MGF also never diverges.

Hence the only physically acceptable distribution within the Katz family is the diverging negative binomial distribution,

$$p_0(l; n, \lambda) = \binom{n+l-1}{n-1} \lambda^n (1-\lambda)^n \quad l = 0, 1, \dots, \quad (34)$$

where  $a_{1,0} = n > 0$  is not necessarily an integer. The corresponding MGF is given by

$$\tilde{g}_l^0(t) = \frac{{}_1F_0[n; \lambda e^t]}{{}_1F_0[n; \lambda]} = \left( \frac{1-\lambda}{1-\lambda e^t} \right)^n, \quad (35)$$

with  $\lambda$  given by Eq. (33).

#### IV. STATISTICAL STATES

Since for solid systems the most interesting thermodynamic property is the heat capacity, we will only give explicit expressions for  $C_V(T)$ . Other thermodynamic properties can be easily derived, using Eqs. (12)–(14).

For the assessment and parametrization of the various model distributions and corresponding statistical states, we will use the following experimental facts.

- (1) At low temperature, for isotropic crystals the heat capacity increases as<sup>15,29</sup>  $C_V(T) \approx c_{3,\text{exp}} T^3$ . However, for anisotropic crystals the heat capacity may increase over a considerable temperature range in a different way. In the case of layer lattices like graphite,<sup>30</sup> gallium, and black phosphorus,<sup>29</sup> it is found that  $C_V(T) \approx c_{2,\text{exp}} T^2$ . For solids which are supposed to consist of polymeric chains, like selenium and tellurium,<sup>29</sup> the heat capacity increases as  $C_V(T) \approx c_{1,\text{exp}} T$ . In general, we can say that the heat capacity at low temperature for different crystal classes behaves as  $C_V(T) \approx c_{s,\text{exp}} T^s$ , i.e., a  $T^s$ -law, with  $s = 1, 2$ , or 3. Note, however, that very close to zero Kelvin, the heat capacity even of very anisotropic crystals will behave like  $T^3$ , although over a very small temperature range (typically a few Kelvin).
- (2) At high (“infinite”) temperature, the heat capacity converges to the classical Dulong and Petit value  $C_{V\infty}$  (i.e.,  $3Nk$  for monatomic solids consisting of  $N$  atoms, for example).

For the discrete distribution  $p_0(l)$  we start with the simplest physically acceptable member of Kemp’s GHP family of distributions, the diverging negative binomial (dNB). According to Eqs. (33)–(35), this distribution is given by

$$p_0(l; n, \Delta \varepsilon) = \binom{n+l-1}{n-1} e^{-\beta_0 \Delta \varepsilon \cdot l} (1 - e^{-\beta_0 \Delta \varepsilon})^n, \quad (36)$$

$$\tilde{g}_l^0(-\Delta \beta \Delta \varepsilon) = \left( \frac{1 - e^{-\beta_0 \Delta \varepsilon}}{1 - e^{-\beta \Delta \varepsilon}} \right)^n, \quad (37)$$

whence from Eq. (11), the heat capacity is given by

$$C_V(T) = Nnk \int_0^\infty \frac{(\beta \Delta \varepsilon)^2 e^{-\beta \Delta \varepsilon}}{(1 - e^{-\beta \Delta \varepsilon})^2} \rho(\Delta \varepsilon) d\Delta \varepsilon. \quad (38)$$

First, we can eliminate the parameters  $N$  and  $n$ , irrespective of the particular distribution  $\rho(\Delta \varepsilon)$ , by evaluating the high temperature limit of Eq. (38), and equating this to the Dulong and Petit value  $C_{V\infty}$ ,

$$\begin{aligned} \lim_{\beta \rightarrow 0} C_V(T) &\equiv C_{V\infty} = \lim_{\beta \rightarrow 0} Nnk \int_0^\infty \frac{(\beta \Delta \varepsilon)^2 (1 - \beta \Delta \varepsilon + \dots)}{(1 - 1 + \beta \Delta \varepsilon - \dots)^2} \\ &\quad \times \rho(\Delta \varepsilon) d\Delta \varepsilon \\ &= Nnk \int_0^\infty \rho(\Delta \varepsilon) d\Delta \varepsilon \\ &= Nnk. \end{aligned} \quad (39)$$

For  $\rho(\Delta \varepsilon)$  we can use either one of the distributions of Sec. III A [Eqs. (24)–(27)]. A combination of the diverging

negative binomial  $p_0(l; n, \lambda(\Delta\epsilon))$ , Eq. (36), with, e.g., a beta distribution  $\rho(\Delta\epsilon; a, b, \Delta\epsilon_m)$ , Eq. (25), will be referred to as “beta-dNB state.”

### A. Delta-dNB state

The “delta-dNB state,” with  $\rho(\Delta\epsilon)$  the delta function given by Eq. (24), yields the following expression for the heat capacity, Eq. (38):

$$C_V(T) = C_{V\infty} \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{-\Theta_E/T}}{(1 - e^{-\Theta_E/T})^2}, \quad (40)$$

where we defined the characteristic temperature  $\Theta_E = \Delta\epsilon_E/k$ .

Obviously, this is the well-known Einstein model,<sup>2,15,31</sup> which has the right qualitative behavior. The low temperature behavior of the heat capacity, however, does not match any of the experimental  $T^s$ -laws, since

$$C_V(T) \xrightarrow{T \rightarrow 0} C_{V\infty} \left( \frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T}, \quad (41)$$

which goes to zero too rapidly.

### B. Power-dNB state

The “power-dNB state,” uses for  $\rho(\Delta\epsilon)$  the power distribution, Eq. (26). The heat capacity is given by

$$C_V(T) = C_{V\infty} a \left( \frac{T}{\Theta_{Da}} \right)^a \int_0^{\Theta_{Da}/T} \frac{x^{a+1} e^{-x}}{(1 - e^{-x})^2} dx, \quad (42)$$

where we defined  $\Theta_{Da} = \Delta\epsilon_m/k$ .

Obviously, for  $a = 1, 2$ , and  $3$  this corresponds to the one-, two-, and three-dimensional Debye models.<sup>3,4,15,31</sup> In the low temperature limit, the upper limit of the integral goes to infinity, and hence integrating Eq. (42) by parts and using  $e^{-x}/(1 - e^{-x}) = \sum_{n=1}^{\infty} e^{-nx}$ , we see that  $C_V(T)$  behaves at low temperature as<sup>24</sup>

$$\begin{aligned} C_V(T) &\xrightarrow{T \rightarrow 0} C_{V\infty} a \left( \frac{T}{\Theta_{Da}} \right)^a \int_0^{\infty} \frac{x^{a+1} e^{-x}}{(1 - e^{-x})^2} dx \\ &= C_{V\infty} a \Gamma(a+2) \zeta(a+1) \left( \frac{T}{\Theta_{Da}} \right)^a \quad (a \geq 1), \end{aligned} \quad (43)$$

with  $\zeta(x) = \sum_{n=1}^{\infty} n^{-x}$  the Riemann zeta function<sup>23</sup> which rapidly goes to one for increasing  $x > 1$ . Special values are  $\zeta(2) = \pi^2/6$  and  $\zeta(4) = \pi^4/90$ ;  $\zeta(3) \approx 1.20206$ . If we want our model to reproduce a  $T^s$ -law at low temperature, it follows from Eq. (43) that  $a = s$ . Moreover, if we measure the proportionality constant  $c_{s,\text{exp}}$  at low temperature, we can hence estimate  $\Theta_{Ds}$  in the “elastic” limit as

$$\Theta_{Ds,\text{el}} = \left( \frac{s \Gamma(s+2) \zeta(s+1) C_{V\infty}}{c_{s,\text{exp}}} \right)^{1/s}. \quad (44)$$

Otherwise, we can use experimental heat capacity data to obtain  $\Theta_{Ds}$ .

### C. Beta-dNB state

The “beta-dNB state,” employs for  $\rho(\Delta\epsilon)$  the beta distribution, given by Eq. (25). The heat capacity is given by

$$\begin{aligned} C_V(T) &= C_{V\infty} \frac{1}{B(a,b)} \left( \frac{T}{\Theta_{Ba,b}} \right)^{a+b-1} \\ &\times \int_0^{\Theta_{Ba,b}/T} x^{a+1} \left( \frac{\Theta_{Ba,b}}{T} - x \right)^{b-1} \frac{e^{-x}}{(1 - e^{-x})^2} dx \end{aligned} \quad (45)$$

$$\begin{aligned} &= C_{V\infty} \frac{1}{B(a,b)} \left( \frac{\Theta_{Ba,b}}{T} \right)^2 \int_0^1 y^{a+1} \\ &\times (1-y)^{b-1} \frac{e^{-(\Theta_{Ba,b}/T)y}}{(1 - e^{-(\Theta_{Ba,b}/T)y})^2} dy, \end{aligned} \quad (46)$$

where  $\Theta_{Ba,b} = \Delta\epsilon_m/k$ . For  $b = 1$ , using the fact that  $B(a,1) = 1/a$ , these expressions become the  $a$ -dimensional Debye model, Eq. (42). For the low temperature behavior we define  $\alpha = \Theta_{Ba,b}/T$ , and integrating Eq. (46) by parts and using the same kind of substitution as in Eq. (43), i.e.,  $e^{-\alpha y}/(1 - e^{-\alpha y}) = \sum_{n=1}^{\infty} e^{-n\alpha y}$ , we have

$$\begin{aligned} C_V(T) &= \frac{C_{V\infty}}{B(a,b)} \alpha^2 \int_0^1 y^{a+1} (1-y)^{b-1} \frac{e^{-\alpha y}}{(1 - e^{-\alpha y})^2} dy \\ &= \frac{C_{V\infty}}{B(a,b)} \alpha \left[ (a+1) \int_0^1 y^a (1-y)^{b-1} \frac{e^{-\alpha y}}{1 - e^{-\alpha y}} dy \right. \\ &\quad \left. - (b-1) \int_0^1 y^a (1-y)^{b-2} \frac{e^{-\alpha y}}{1 - e^{-\alpha y}} dy \right] \\ &= \frac{C_{V\infty}}{B(a,b)} \alpha \left[ (a+1) \sum_{n=1}^{\infty} \int_0^1 y^a (1-y)^{b-1} e^{-n\alpha y} dy \right. \\ &\quad \left. - (b-1) \sum_{n=1}^{\infty} \int_0^1 y^a (1-y)^{b-2} e^{-n\alpha y} dy \right] \\ &= \frac{C_{V\infty}}{B(a,b)} \alpha \left[ (a+1) B(a+1, b) \sum_{n=1}^{\infty} {}_1F_1(a+1, \right. \\ &\quad \left. a+b+1; -n\alpha) - (b-1) B(a+2, b-1) \right. \\ &\quad \left. \times \sum_{n=1}^{\infty} {}_1F_1(a+2, a+b+1; -n\alpha) \right] \\ &\xrightarrow{\alpha \rightarrow \infty} \frac{C_{V\infty}}{B(a,b)} \alpha \left[ (a+1) B(a+1, b) \frac{\Gamma(a+b+1)}{\Gamma(b)} \right. \\ &\quad \left. \times \sum_{n=1}^{\infty} (n\alpha)^{-(a+1)} - (b-1) B(a+2, b-1) \right. \\ &\quad \left. \times \frac{\Gamma(a+b+1)}{\Gamma(b-1)} \sum_{n=1}^{\infty} (n\alpha)^{-(a+2)} \right] \\ &= C_{V\infty} \frac{\Gamma(a+2)}{B(a,b)} \left[ \zeta(a+1) \left( \frac{T}{\Theta_{Ba,b}} \right)^a \right. \\ &\quad \left. + (1-b) \zeta(a+2) \left( \frac{T}{\Theta_{Ba,b}} \right)^{a+1} \right] \\ &= C_{V\infty} \frac{\Gamma(a+2)}{B(a,b)} \zeta(a+1) \left( \frac{T}{\Theta_{Ba,b}} \right)^a, \end{aligned} \quad (47)$$

where in the fourth step we used a limit property of the Kummer confluent hypergeometric function  ${}_1F_1(a, b; x)$ , see Ref. 23. To obtain a  $T^s$ -law, we see that also in this case  $a = s$ , and hence from very low temperature data we can estimate  $\Theta_{Bs, b, el}$  via

$$\Theta_{Bs, b, el} = \left( \frac{\Gamma(s+2)\zeta(s+1)C_{V\infty}}{B(s, b)c_{s, exp}} \right)^{1/s} \quad (48)$$

or obtain  $\Theta_{Bs, b}$  using other experimental heat capacity data.

### D. Gamma-dNB state

Finally, the ‘‘gamma-dNB state’’ state, with the gamma distribution for  $\rho(\Delta\epsilon)$  given by Eq. (27), yields for the heat capacity

$$C_V(T) = C_{V\infty} \frac{1}{\Gamma(a)} \left( \frac{T}{\Theta_{\Gamma a}} \right)^a \int_0^\infty \frac{x^{a+1} e^{-(1+T/\Theta_{\Gamma a})x}}{(1-e^{-x})^2} dx, \quad (49)$$

where we defined the characteristic temperature  $\Theta_{\Gamma a} = 1/k\tau$ . For the low temperature behavior, we can integrate Eq. (49) by parts, substitute  $e^{-x}/(1-e^{-x}) = \sum_{n=1}^\infty e^{-nx}$  and  $z = (n+T/\Theta_{\Gamma a})x$ , and use the Taylor series of the generalized Riemann zeta function<sup>17,23</sup>  $\zeta(x, k) \equiv \sum_{n=1}^\infty (n+k)^{-x} = \sum_{r=0}^\infty (-1)^r (s)_r \zeta(x+r) k^r / r!$ , with  $(s)_r = s(s+1)\cdots(s+r-1)$  Pochhammer’s symbol.<sup>17</sup> The low temperature behavior is therefore

$$\begin{aligned} C_V(T) &= \frac{C_{V\infty}}{\Gamma(a)} \left( \frac{T}{\Theta_{\Gamma a}} \right)^a \int_0^\infty x^{a+1} e^{-(T/\Theta_{\Gamma a})x} \frac{e^{-x}}{(1-e^{-x})^2} dx \\ &= \frac{C_{V\infty}}{\Gamma(a)} \left( \frac{T}{\Theta_{\Gamma a}} \right)^a \left[ (a+1) \int_0^\infty x^a e^{-(T/\Theta_{\Gamma a})x} \frac{e^{-x}}{1-e^{-x}} dx \right. \\ &\quad \left. - \left( \frac{T}{\Theta_{\Gamma a}} \right) \int_0^\infty x^{a+1} e^{-(T/\Theta_{\Gamma a})x} \frac{e^{-x}}{1-e^{-x}} dx \right] \\ &= \frac{C_{V\infty}}{\Gamma(a)} \left( \frac{T}{\Theta_{\Gamma a}} \right)^a \left[ (a+1) \sum_{n=1}^\infty \left( n + \frac{T}{\Theta_{\Gamma a}} \right)^{-(a+1)} \right. \\ &\quad \times \int_0^\infty z^a e^{-z} dz - \left( \frac{T}{\Theta_{\Gamma a}} \right) \sum_{n=1}^\infty \left( n + \frac{T}{\Theta_{\Gamma a}} \right)^{-(a+2)} \\ &\quad \times \int_0^\infty z^{a+1} e^{-z} dz \Big] \\ &= C_{V\infty} \frac{\Gamma(a+2)}{\Gamma(a)} \left( \frac{T}{\Theta_{\Gamma a}} \right)^a \left[ \zeta(a+1, T/\Theta_{\Gamma a}) \right. \\ &\quad \left. - \zeta(a+2, T/\Theta_{\Gamma a}) \left( \frac{T}{\Theta_{\Gamma a}} \right) \right] \\ &= C_{V\infty} \frac{\Gamma(a+2)}{\Gamma(a)} \zeta(a+1) \left( \frac{T}{\Theta_{\Gamma a}} \right)^a \left[ 1 + \sum_{r=1}^\infty (-1)^r \right. \\ &\quad \times \frac{(a+1)_r}{r!} \frac{(a+r+1)\zeta(a+r+1)}{(a+1)\zeta(a+1)} \left( \frac{T}{\Theta_{\Gamma a}} \right)^r \Big] \\ &\xrightarrow{T \rightarrow 0} C_{V\infty} a(a+1)\zeta(a+1) \left( \frac{T}{\Theta_{\Gamma a}} \right)^a. \quad (50) \end{aligned}$$

We see that when  $a = s$  we get approximately a  $T^s$ -behavior, and so we can obtain the ‘‘elastic’’  $\Theta_{\Gamma s}$  from

$$\Theta_{\Gamma s, el} = \left( \frac{s(s+1)\zeta(s+1)C_{V\infty}}{c_{s, exp}} \right)^{1/s}. \quad (51)$$

Note that also for this statistical state the heat capacity converges to the Dulong and Petit value, even though the distribution  $\rho(\Delta\epsilon)$  has no finite maximum energy gap  $\Delta\epsilon_m$ .

### E. Classical limit

Obviously, in the classical limit all energy gaps will tend to zero, and hence  $\rho(\Delta\epsilon)$  will tend to a Dirac delta function [Eq. (24)], i.e., with  $\Delta\epsilon_E \rightarrow 0$ . Therefore the parameter  $\lambda = e^{-\beta_0 \Delta\epsilon_E}$  of the dNB distribution  $p_0(l)$  tends to one. It is interesting to note that Pessin<sup>32</sup> has proved that as  $\lambda \rightarrow 1$  with  $n$  constant, the negative binomial distribution tends to a gamma; in this case a diverging negative binomial tending to a diverging gamma distribution. Hence all the described statistical states will transform in the classical limit to a diverging gamma state<sup>8</sup> with

$$\lim_{\Delta\epsilon \rightarrow 0} C_V(T) = C_{V\infty} = C_{V0}. \quad (52)$$

As already observed, the delta-dNB and power-dNB states correspond to the Einstein and Debye models, since the energy and index distribution of a single quantum harmonic oscillator (QHO) is given by a (diverging) geometric distribution,<sup>17</sup> and that of a set of independent QHOs by a (diverging) negative binomial distribution (being the convolution of geometric distributions). Hence we see that in the classical limit the dNB states, corresponding to a QHO Hamiltonian, convert into a diverging gamma state of  $N$  classical harmonic oscillators, with  $C_V(T) = C_{V0} = 3Nk$  according to the equipartition principle, see also Ref. 5.

### V. APPLICATIONS TO Cu, $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, AND GRAPHITE

We applied the various statistical states to solid Cu,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $\alpha$ -alumina or sapphire), and graphite. Experimental  $C_V$  heat capacity data were taken from Castanet *et al.*<sup>33</sup> and for graphite we used  $C_p$  data from DeSorbo and Tyler<sup>30</sup> ( $10 < T < 300$  K) and Butland and Maddison<sup>34</sup> ( $300 < T < 3000$  K). In the latter case  $C_V$  was calculated using the Nernst–Lindemann approximation.<sup>4,35</sup>

An analysis of the low temperature data ( $10 < T < 25$  K) on log–log scale showed that  $a = 3.11$  for Cu,  $a = 3.07$  for  $\alpha$ -alumina, and  $a = 2.00$  for graphite; hence for the former two we set  $a = s = 3$ , for graphite  $a = s = 2$ . Note that  $C_V$  of graphite behaves like  $T^3$  only below 1 K (see Refs. 36 and 37). Taking  $C_{V\infty} = 3R$  for copper and graphite and  $15R$  for alumina, we used the Mathematica<sup>38</sup> routine ‘‘FindMinimum’’ to obtain the best least-square values of the different characteristic temperatures, as well as  $b$  for the beta-dNB state. For copper we used experimental heat capacity data within the range  $10 < T < 1000$  K, for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>



TABLE I. Characteristic temperatures and parameters of Cu for various statistical states.

Method	$C_{V\infty}/R$	$a=s$	$\Theta_E$ (K)	$\Theta_{Da}$ (K)	$\Theta_{Ba,b}$ (K)	$b$	$\Theta_{\Gamma a}$ (K)	$c_{s,\text{exp}}$ (J/mol K $^{s+1}$ )
$C_V$ fit	3	3	228	313	316	1.035	86.7	
Literature	3	3	225 <sup>a</sup>	313 <sup>a</sup>	315 <sup>b,c,d</sup>			
Elastic limit	3	3	...	345	352	1.035	190	$4.755 \cdot 10^{-5b}$
Literature	3	3	...	345 <sup>e</sup>				

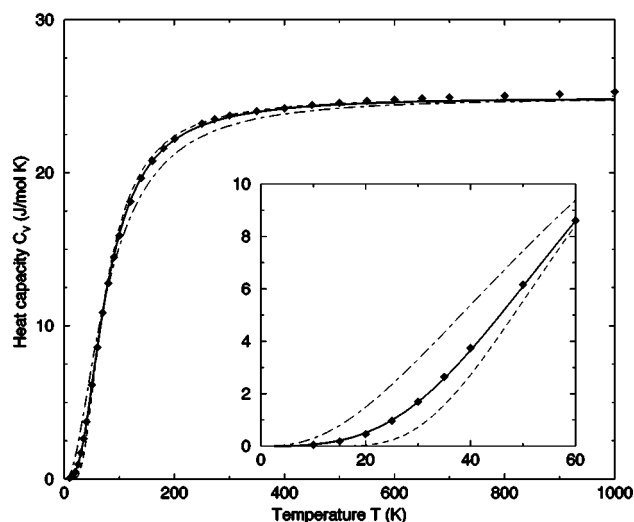
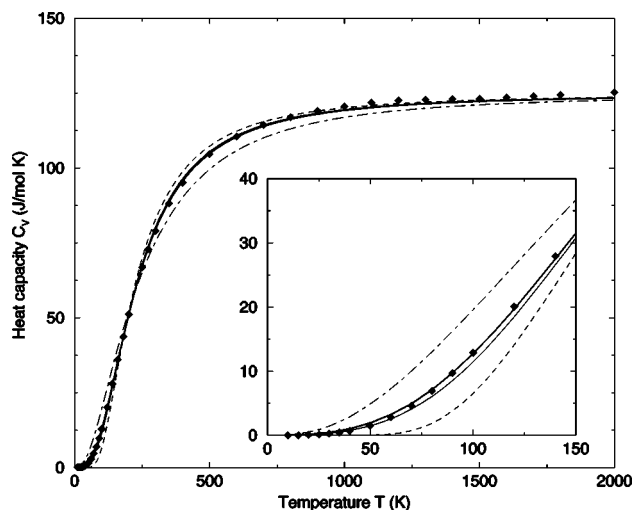
<sup>a</sup>Reference 43.<sup>b</sup>Reference 33.<sup>c</sup>Reference 24.<sup>d</sup>Reference 15.<sup>e</sup>Reference 31.TABLE II. Characteristic temperatures and parameters of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for various statistical states.

Method	$C_{V\infty}/R$	$a=s$	$\Theta_E$ (K)	$\Theta_{Da}$ (K)	$\Theta_{Ba,b}$ (K)	$b$	$\Theta_{\Gamma a}$ (K)	$c_{s,\text{exp}}$ (J/mol K $^{s+1}$ )
$C_V$ fit	15	3	678	933	1059	1.482	263	
Literature	15	3						
Elastic limit	15	3	...	1034			568.9	$8.8 \cdot 10^{-6a}$
Literature	15	3	...	1035 <sup>a</sup>				

<sup>a</sup>Reference 33.

TABLE III. Characteristic temperatures and parameters of graphite for various statistical states.

Method	$C_{V\infty}/R$	$a=s$	$\Theta_E$ (K)	$\Theta_{Da}$ (K)	$\Theta_{Ba,b}$ (K)	$b$	$\Theta_{\Gamma a}$ (K)	$c_{s,\text{exp}}$ (J/mol K $^{s+1}$ )
$C_V$ fit	3	2	1094	1820	3575	3.32	761	
Literature	3	2		~1878 <sup>a</sup>				
Elastic limit	3	2	...	1322			935	$2.06 \cdot 10^{-4b}$
Literature	3	2	...	1370 <sup>c</sup>				

<sup>a</sup>Reference 4, using a Tarasov equation.<sup>b</sup>Reference 30.<sup>c</sup>Reference 44.FIG. 1. Heat capacity of Cu: experimental data ( $\blacklozenge$ ), delta-dNB state, Eq. (40) (---), power-dNB state, Eq. (42) (—), beta-dNB state, Eq. (45) (---), and gamma-dNB state, Eq. (49) (-·-·-). Parameters are listed in Table I.FIG. 2. Heat capacity of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>: experimental data ( $\blacklozenge$ ), delta-dNB state, Eq. (40) (---), power-dNB state, Eq. (42) (—), beta-dNB state, Eq. (45) (---), and gamma-dNB state, Eq. (49) (-·-·-). Parameters are listed in Table II.

within the range  $10 < T < 2000$  K, and for graphite within the range  $10 < T < 3000$  K. We also evaluated the “elastic” characteristic temperatures from the low temperature  $T^s$  behavior,<sup>30,33</sup> using Eqs. (44), (48), and (51). Parameters are given in Tables I–III and the resulting heat capacity curves using the parameters obtained by least-square fit are given in Figs. 1–3. Root-mean-square deviations from the experimental  $C_V$  data are presented in Table IV.

For copper (Table I, Fig. 1), which is an example of a simple isotropic monatomic crystal, we see that as expected the power-dNB state (three-dimensional Debye model) provides a good description, both at low and high temperature, indicated by the fact that the least-square and “elastic” values of  $\Theta$  are in fair agreement. For the beta-dNB state, which may be regarded as a generalization of the Debye model, we find that  $b = 1.035$ , very close to the Debye value  $b = 1$ . It hence gives almost indistinguishable results from the power-

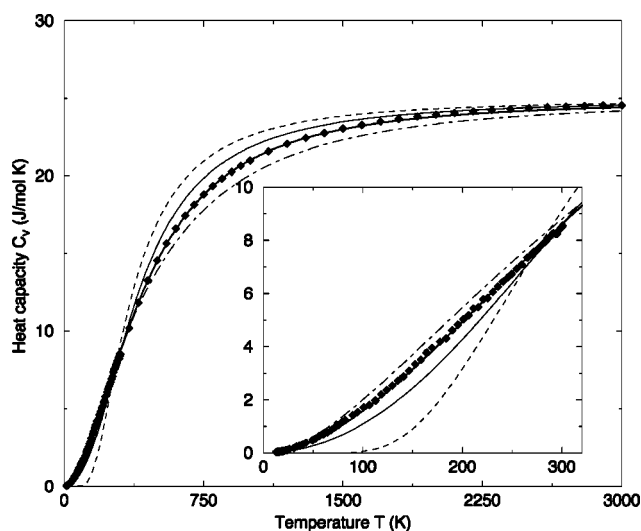
FIG. 3. Heat capacity of graphite: experimental data ( $\blacklozenge$ ), delta-dNB state, Eq. (40) (---), power-dNB state, Eq. (42) (—), beta-dNB state, Eq. (45) (---), and gamma-dNB state, Eq. (49) (-·-·-). Parameters are listed in Table III.

TABLE IV. Root-mean-square deviations of the heat capacity (J/mol K) for different statistical states, using the parameters obtained by least-square fit, see Tables I–III.

System	$T$ -range (K)	$N_{\text{data}}$	Delta-dNB	Power-dNB	Beta-dNB	Gamma-dNB
Cu	10–1000	32	0.44	0.15	0.15	0.86
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	10–2000	38	2.69	0.96	0.78	3.73
Graphite	10–3000	108	1.28	0.52	0.08	0.49

dNB state. Both the delta-dNB (Einstein) and gamma-dNB reproduce the qualitative behavior, but deviate especially at low temperature; the delta-dNB state tending to zero too fast, the gamma-dNB state too slow.

Alumina (Table II, Fig. 2) is somewhat less isotropic than copper, but still the power-dNB state (Debye model) agrees very well with the experimental data. For the beta-dNB state we find a value  $b \approx 1.5$  which deviates more from unity and results in a somewhat better description than the Debye model. Again, the delta-dNB and gamma-dNB states are comparable to each other and less accurate than the other two states.

Finally, graphite (Table III, Fig. 3) is an anisotropic crystal consisting of weakly bound layers<sup>37</sup> with a different low-temperature behavior up to about 100 K: a  $T^2$ -law.<sup>30</sup> In this case we see that the simple delta-dNB state (Einstein model) deviates more than for isotropic crystals. Also the two-dimensional Debye model (power-dNB state) is less accurate, and now comparable to the gamma-dNB state. The beta-dNB state, however, with a large  $b$  value (3.22), gives a very accurate description over the whole temperature range, also indicated by the fact that the least-square and “elastic”  $\Theta$  values are very close.

Around 1950, Tarasov<sup>39–41</sup> derived a model to describe the heat capacity of anisotropic crystals. Using quantum harmonic oscillators, he furthermore assumed that the frequency spectrum at low frequency (up to  $\nu_3$ ) could be described by a three-dimensional continuum model, from  $\nu_3$  to  $\nu_2$  by a two-dimensional, and from  $\nu_2$  to  $\nu_1$  by a one-dimensional continuum model. Defining  $\Delta\epsilon_a = h\nu_a$ , the “Tarasov” distribution  $\rho(\Delta\epsilon)$  is given by

$$\rho(\Delta\epsilon) = \begin{cases} 3 \frac{\Delta\epsilon^2}{\Delta\epsilon_1 \Delta\epsilon_2 \Delta\epsilon_3}, & 0 < \Delta\epsilon < \Delta\epsilon_3 \\ 2 \frac{\Delta\epsilon}{\Delta\epsilon_1 \Delta\epsilon_2}, & \Delta\epsilon_3 < \Delta\epsilon < \Delta\epsilon_2 \\ \frac{1}{\Delta\epsilon_1}, & \Delta\epsilon_2 < \Delta\epsilon < \Delta\epsilon_1 \end{cases} \quad (53)$$

This yields for the heat capacity<sup>4,37</sup>

$$C_V(T) = C_{V\infty} \left[ D_1\left(\frac{\Theta_1}{T}\right) - \frac{\Theta_2}{\Theta_1} \left\{ D_1\left(\frac{\Theta_2}{T}\right) - D_2\left(\frac{\Theta_2}{T}\right) \right\} - \frac{\Theta_3^2}{\Theta_1 \Theta_2} \left\{ D_2\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right) \right\} \right], \quad (54)$$

where

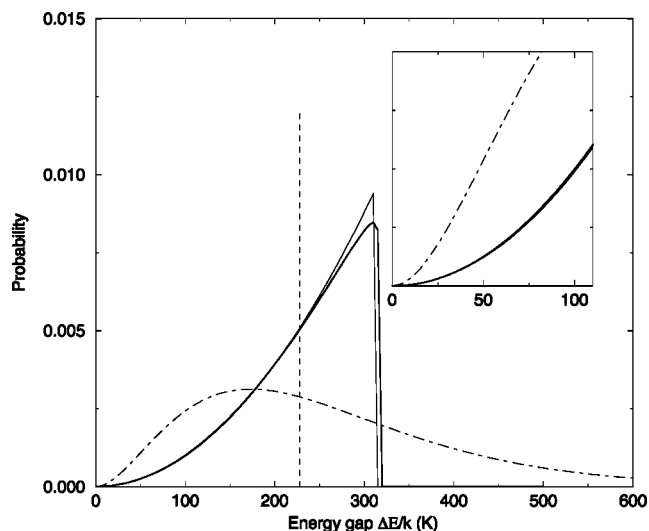


FIG. 4. Energy gap distributions  $\rho(\Delta\epsilon)$  of Cu: delta function, Eq. (24) (---), power function, Eq. (26) (—), beta distribution, Eq. (25) (—), and gamma distribution, Eq. (27) (.....).

$$D_a\left(\frac{\Theta_a}{T}\right) = a \left(\frac{T}{\Theta_a}\right)^a \int_0^{\Theta_a/T} \frac{x^{a+1} e^{-x}}{(1 - e^{-x})^2} dx \quad (55)$$

is the  $a$ -dimensional Debye function [cf. Eq. (42)], and  $\Theta_a = h\nu_a/k$  the corresponding characteristic temperature. At very low temperature Eq. (54) converges to a three-dimensional Debye model [Eq. (42),  $a=3$ ] with  $\Theta_{D3} = \sqrt[3]{\Theta_1 \Theta_2 \Theta_3}$ . Pyda *et al.*<sup>4</sup> analyzed graphite data<sup>37</sup> from 0.5 to 1500 K using this equation, obtaining  $\Theta_1 = 2571$ ,  $\Theta_2 = 932$ , and  $\Theta_3 = 6.0$  K. The corresponding heat capacity is, on the scale of Fig. 3, coinciding with the beta-dNB results, and corresponds very well with the experimental data: the root-mean-square deviation is 0.12 J/mol K, which is similar to that of the beta-dNB state (0.08, see Table IV). Note that both the beta-dNB state and the Tarasov equation have three parameters ( $\Theta_{Ba,b}$ ,  $a$ ,  $b$ , and  $\Theta_1$ ,  $\Theta_2$ ,  $\Theta_3$ ).

In Figs. 4–6 we show the corresponding energy gap distributions. Note that the low temperature behavior of the heat capacity is especially sensitive to the left tail of  $\rho(\Delta\epsilon)$ , which is enlarged in the insets. For copper the power and beta distributions are virtually identical, and behave very differently from the gamma distribution at small  $\Delta\epsilon$ . For alumina, the power and beta distribution are more distinct, even at the left tails. Finally, for graphite the beta distribution now more or less resembles the gamma distribution. It is interesting to note that when the value of the maximum energy gap  $\Delta\epsilon_m$  increases (and hence also the characteristic temperatures  $\Theta_D$  and  $\Theta_B$ ), the accuracy of the gamma distribution and corresponding gamma-dNB state improves; compare, e.g., Cu ( $\Theta_B \sim 300$  K) and graphite ( $\Theta_B \sim 3600$  K). It is also evident that the behavior of  $C_V$  is less sensitive to the right tail of  $\rho(\Delta\epsilon)$ . For graphite, compare, e.g., the power and gamma results, which are of comparable accuracy, but have a completely different right tail of the energy gap distribution; also the beta and Tarasov distribution, which have comparable accuracy in  $C_V$ , are rather different on the right tail.

This clearly shows the known difficulty of “inverting” the heat capacity to the frequency distribution<sup>37</sup> [or  $\rho(\Delta\epsilon)$  in

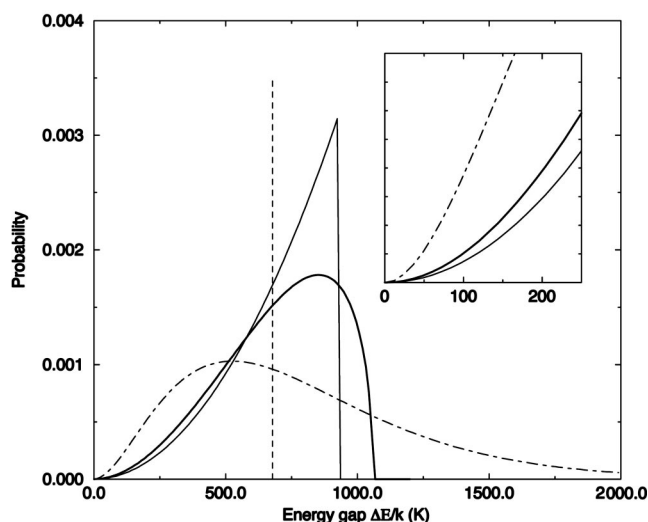


FIG. 5. Energy gap distributions  $\rho(\Delta\epsilon)$  of  $\alpha$ - $\text{Al}_2\text{O}_3$ : delta function, Eq. (24) (---), power function, Eq. (26) (—), beta distribution, Eq. (25) (—), and gamma distribution, Eq. (27) (----).

our terms]. From our “macroscopic” treatment, starting from the energy fluctuations of the whole system, it cannot be expected that the model distribution for  $\rho(\Delta\epsilon)$  matches in a precise way the distribution, which arises from an analysis of experimental data using atomic details and a model Hamiltonian (see, e.g., Young and Koppel<sup>42</sup> for the frequency distribution of graphite); however, the thermodynamic functions of the system, which are macroscopic observables, are reproduced very well using, for example, a simple beta distribution.

## VI. DISCUSSION AND CONCLUSIONS

In this article we described how to derive the temperature dependence of thermodynamic functions of pure quantum systems using the quasi-Gaussian entropy theory (QGE),

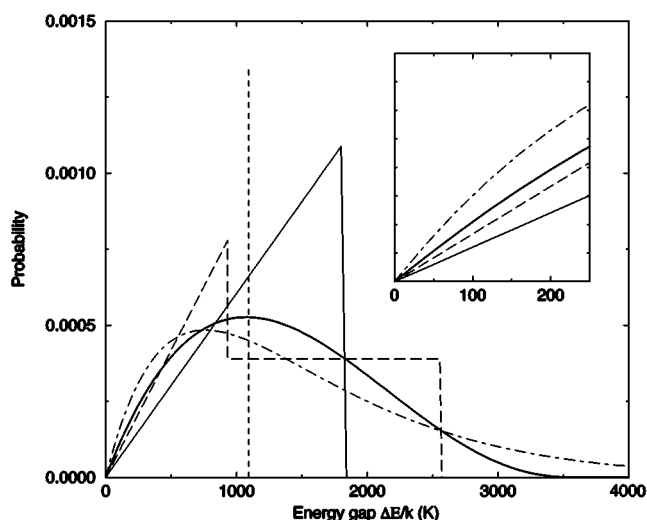


FIG. 6. Energy gap distributions  $\rho(\Delta\epsilon)$  of graphite: delta function, Eq. (24) (---), power function, Eq. (26) (—), beta distribution, Eq. (25) (—), gamma distribution, Eq. (27) (----) and Tarasov distribution, Eq. (53) (— — —).

i.e., by expressing the excess Helmholtz free energy in terms of the moment generating function (MGF) of the (discrete) energy distribution of the system, and modeling the latter as a quasi-Gaussian distribution. Using only a few very reasonable assumptions, this complicated MGF can be decomposed into “subelementary” MGFs, which are specified by the discrete (lattice) distribution of the energy level index  $l$ , and the continuous distribution of the energy gap  $\Delta\epsilon$ . In the classical limit the energy gap distribution tends to a Dirac delta function located at zero, and hence the complicated overall discrete energy distribution transforms into a continuous distribution, as described in previous articles.<sup>8</sup>

We derived restrictions on possible model distributions for the index and energy gap distributions, and presented some examples of statistical states, i.e., the thermodynamics of a combination of a specific index and energy gap distribution. We combined the simplest physically acceptable index distribution, a diverging negative binomial (dNB) with several energy gap distributions: the delta function, power function, beta and gamma distributions. It is very interesting to note that among these various statistical states are some which are thermodynamically equivalent to well-known models, like the Einstein model (equivalent to the delta-dNB state) and the one-, two-, and three-dimensional Debye models (equivalent to the power-dNB states). This is a consequence of the fact that the dNB distribution is the exact index distribution of a set of quantum harmonic oscillators. Interestingly, within the QGE scheme these models can therefore also be derived without an explicit Hamiltonian model, only using a basic set of physical requirements and assumptions. The beta-dNB state can be regarded as a generalization of the Debye models, to which it reduces for  $b=1$ . All these states reduce in the classical limit to the diverging gamma state,<sup>5,8</sup> which is the exact statistical state of a set of classical harmonic oscillators.

The different statistical states were applied to copper,  $\alpha$ -alumina, and graphite, showing that in all cases the beta-dNB state provides an accurate thermodynamic description of these crystals, both at low and high temperature. For an anisotropic crystal like graphite, which consists of weakly bound layers, the beta energy gap distribution differs greatly from the one corresponding to the Debye model, but they become identical for the simple isotropic monatomic copper crystal. For graphite, the accuracy of the beta-dNB state is comparable to that of the general Tarasov equation, having the same number of parameters.

Finally, the complexity of the statistical states may be enlarged in a rather systematic way, either by using more complicated energy gap distributions and/or by employing more complicated discrete index distributions, for example arising from the GHP family.

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