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# Inversion of the Partition Function to Determine the Density of Energy States\*

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The density of energy states for a complex system may be deduced from thermodynamic functions when their dependence on temperature is specified. The method is general and depends for its accuracy on the closeness of approximation of the experimentally determined partition function by an appropriate equation. Accurate specific heat data are therefore essential. The degeneracy function is obtained by inverting the Laplace integral defining the sum-over-states; as illustrations, the energy states for an Einstein crystal, and for a modified Debye crystal without and with a transition are discussed. The author was not successful in finding a mathematical expression which fitted the last case sufficiently well to differentiate between transitions of first and higher order.

OF importance to any theory of molecular structure is a general procedure for locating the position and estimating the degeneracy of the characteristic energy states, applicable equally well to simple and complex molecules, crystals and liquids. As examples of recent interest, for which at the outset of any discussion, some form of the degeneracy function must be assumed, one may list the following two types. (a) Order-disorder transitions, often accompanied by  $\lambda$  phenomena; (b) transitions to the superconducting state, and the analogous phase change from liquid helium I to II. Since many investigators are concerned with these problems, it appeared worth while to study the possibilities of a very general method suggested previously by the author.<sup>1</sup> It is based on the use of thermodynamic functions, and is essentially the inverse of the current procedure of computing thermodynamic properties from spectral data.

The sum-over-states may be readily obtained as a function of the temperature from the experimentally determined entropy,

$$\frac{1}{N} \log Z(T) = \frac{1}{RT} \int_0^T S(T) dT + \frac{1}{N} \log G_0 e^{-E_0/kT} - \frac{9}{8} \frac{h\nu_m}{kT}.$$

The last two terms of the right member must be

\* This discussion was presented, in part, at the Baltimore meeting of the American Chemical Society.

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<sup>1</sup> S. H. Bauer, *J. Chem. Phys.* **6**, 403 (1938).

added to allow for the zero-point energy ( $-9h\nu_m/8kT$ , for a Debye crystal) and for the degeneracy of the basic state which is used as the reference level from which the energy spectrum is to be measured. On the other hand, a fundamental definition of quantum statistical mechanics relates the sum-over-states to the degeneracy function of the energy levels of the system as a whole,

$$Z(T) = \sum_m G(E_m) e^{-E_m/kT}. \quad (1)$$

The problem is then reduced to an inversion of (1) so that the density  $G(E_m)$  could be found once a  $Z(T)$  is given. If one does not restrict  $G(E)$  to the class of continuous functions, it is permissible to replace the summation by an integration even when discrete states are indicated. This will be illustrated by a discussion of the Einstein model for a crystal. The degeneracy function may then be obtained by inverting the Laplace integral equation, for a continuum of energy levels,

$$Y(x) \equiv Z(h\nu_m/kx) = h\nu_m \int_0^\infty G(E) e^{-xE} dE; \quad (2a)$$

or the Stieltjes integral equation, for a set of discrete states,

$$Y(x) = h\nu_m \int_0^\infty e^{-xE} dH(E);$$

deduced from (1) through the change of variable  $T = h\nu_m/kx$ , so that both  $E$  and  $x$  are dimensionless. Clearly, a rigorous solution is not feasible

since the partition function cannot be evaluated from experimental data for values of  $x$  approaching zero. The closeness of approximation will depend on how well the mathematical expression used for  $Y(x)$  represents the actual sum-over-states; here is the one limiting feature of the method. It is not only necessary to have a good fit over the known range but it is essential to use a function which approaches infinity at  $x=0$  and vanishes for  $x \rightarrow \infty$  in the correct manner. The uniqueness of the solution will depend on whether the representation is unique; in general that is not the case.

The restrictions which are imposed on the function  $G(E)$  to permit the Laplace inversion have been extensively discussed. They are sufficiently broad to include all cases which have physical reality insofar as partition functions are concerned. Thus, if (a) the real function  $g(E)$  and its first derivative are piecewise continuous; (b) at a point of discontinuity  $g(E) = \frac{1}{2} \times [g(E+0) + g(E-0)]$ ; and (c)

$$\int_0^\infty |g(E)| e^{-cE} dE$$

exists for  $c$  a real constant greater than zero, then  $g(E)$  may be represented by the complex integral

$$g(E) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{f(x)}{x} e^{xE} dx, \quad (3)$$

where

$$f(x) = x \int_0^\infty g(E) e^{-xE} dE, \quad (4)$$

and defines an analytic function in the half-plane.<sup>2</sup> We have then a solution for (4) in terms of the contour integral (3). Another form in terms of the derivatives of  $f(x)$  for large real positive values of  $x$  has been developed by Widder.<sup>3</sup> We shall use the results derived by either method as convenience dictates.

<sup>2</sup> For a discussion of the general case see H. Hamburger: *Math. Zeits.* **6**, 6 (1920).

<sup>3</sup> Restricting conditions and an inversion formula are given: D. V. Widder: *Trans. Am. Math. Soc.* **36**, 107 (1934). For the more general Laplace-Stieltjes integral,  $f(x)$  need not be analytic; it is necessary and sufficient that  $f(x)$  have derivatives of all orders and that integrals of the type  $\int_x^\infty \frac{u^k}{k!} |f^{(k+1)}(u)| du$  are bounded. See p. 151.

## DETAILS OF THE INVERSION

To facilitate the discussion of the solutions for (2a, b) let us consider several specific forms for  $Y(x)$ . Experience has shown that partition functions generally may be expressed as sums of terms involving  $e^{-ax}$  and  $e^{-ax}f(x)$  [where  $f(x)$  is restricted to forms of the types quoted below]. Hence the solutions  $G(E)$ ,  $H(E)$  may be compounded of solutions of (5) and (6), weighted by the corresponding coefficients of the expansion.

$$e^{-ax}f(x) = \int_0^\infty G(E) e^{-xE} dE; \quad (5)$$

$$e^{-ax} = \int_0^\infty dH(E) e^{-xE}. \quad (6)$$

The solution of the first of these is given by a general theorem of the Heaviside operational calculus,<sup>4</sup> viz., *If two functions,  $f(x)$  and  $g(E)$ , are so related [indicated by the symbol  $f(x) \doteq g(E)$ ] that they satisfy the equation*

$$f(x) = x \int_0^\infty g(E) e^{-xE} dE,$$

then

$$e^{-ax}f(x) \doteq \begin{cases} 0 & \text{for } E < a \\ g(E-a), & \text{for } E > a \end{cases} \quad \text{with } a > 0. \quad (7)$$

We now quote several transforms which will be useful for the applications suggested in this paper.

$$1 \doteq h(E) \quad \text{where } h(E) = \begin{cases} 1 & \text{for } E > 0, \\ 0 & \text{for } E < 0, \end{cases} \quad (8a)$$

$$x^{-n} \doteq E^n / \Gamma(n+1) \quad \text{for all } n \text{ except negative integers,} \quad (8b)$$

$$1/(x+\alpha) \doteq (1-e^{-\alpha E})/\alpha, \quad (8c)$$

$$x/(x+\alpha)^n \doteq e^{-\alpha E} E^{(n-1)} / (n-1)!,^5 \quad (8d)$$

$$x/(x+\alpha)(x+\beta) \doteq (e^{-\beta E} - e^{-\alpha E})/(\alpha - \beta). \quad (8e)$$

<sup>4</sup> The Heaviside operational calculus is almost exclusively based on the Laplace transform by means of the contour integral. A concise review by Louis A. Pipes appeared in the *J. App. Phys.* **10**, 172, 258, and 301 (1939). A long list of transforms is given from which the ones quoted in the text have been taken.

<sup>5</sup> Contrast (8d) with

$$\frac{wx}{w^2 + (x+\alpha)^2} \doteq e^{-\alpha E} \sin wE \quad \text{for } \begin{cases} n=2 \\ w^2 \ll 1. \end{cases}$$

The difference between the left members would hardly be noticeable experimentally, yet the forms of the two solutions are radically different. This demonstrates the lack of uniqueness mentioned above. For the applications suggested, the sinusoidal solution is not admissible.

Integrations by parts and successive differentiation of the Laplace integral equations corresponding to (8a-e) lead to more general transforms;<sup>6</sup> solutions for functions which are combinations of the left members also may be obtained. Thus,

If  $f_1(x) \doteq g_1(E)$  and  $f_2(x) \doteq g_2(E)$ , then

$$f_1 f_2 \doteq \frac{d}{dE} \int_0^E g_1(E-u) g_2(u) du; \quad (9)$$

so that

$$[f_1(x)]^2 \doteq \frac{d}{dE} \int_0^E g_1(E-u) g_1(u) du.$$

Generalization of these relations for the  $N$ th power of  $f_1(x)$  is obvious.

The contribution due to the discrete energy states is deduced in a straightforward manner from the more general Laplace-Stieltjes Eq. (6). The solution as given by Widder<sup>3</sup> expresses the function  $H(E)$  as the limit of

$$\begin{aligned} H(E) &= \lim_{k \rightarrow \infty} e^{-ak/E} \sum_{p=0}^k \frac{1}{(k-p)!} (ak/E)^{k-E} \\ &= \begin{cases} 0 & \text{for } 0 < E < a \\ \frac{1}{2} & E = a \\ 1 & a < E < \infty \end{cases}; \text{ Fig. 1.} \end{aligned} \quad (10)$$

To clarify the meaning of the Stieltjes integral and to demonstrate that the suggested procedure leads to the correct result, let us consider an Einstein crystal, for which

$$\begin{aligned} [Y(x)]^{1/N} &= \frac{e^{-3x/2}}{(1-e^{-x})^3} = \sum_{n=0}^{\infty} \binom{n+2}{n} e^{-(\frac{3}{2}+n)x} \\ &= h\nu_0 \int_0^{\infty} e^{-x\epsilon} d \left[ \sum_n \binom{n+2}{2} H_n(\epsilon) \right]; \end{aligned}$$

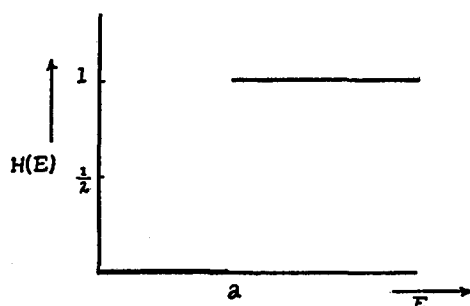


FIG. 1.

<sup>6</sup> Six theorems are discussed by Pipes. His exposition proved very helpful to the author, and sincere acknowledgment is here made.

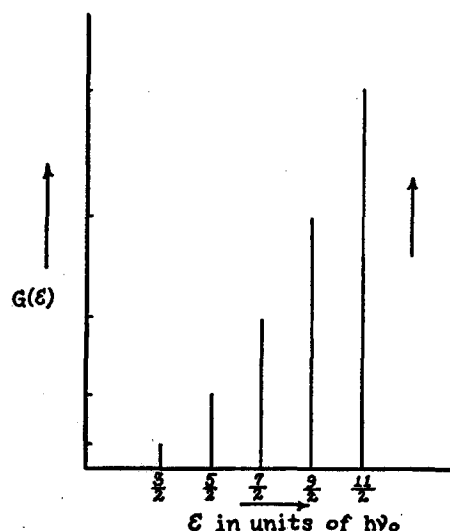


FIG. 2. The density of energy states for an Einstein crystal.

where  $x = h\nu_0/kT$ ,  $\nu_0$  denotes the characteristic frequency, and  $\epsilon_n$  the energy levels of a single oscillator. It is permissible to write the sum-over-states in terms of  $\epsilon_n$  rather than  $E_m$  (energy levels of the system as a whole) whenever the system is composed of  $N$  similar, weakly interacting elements which are permanently distinguishable; such is the case here. As is explicitly indicated, for each value of  $n$  there is a solution  $H_n(\epsilon)$  weighted by the corresponding binomial coefficient, and the degeneracy function is the sum of these. From (10),

$$H_n(\epsilon) = \begin{cases} 0 & 0 < \epsilon < (\frac{3}{2} + n) \\ \frac{1}{2} & \epsilon = (\frac{3}{2} + n) \\ 1 & (\frac{3}{2} + n) < \epsilon < \infty \end{cases}.$$

In contrast to Eq. (5), in which values of a function of  $E$  at particular values of the argument, are multiplied by increments of the argument and then summed as these increments are made to approach zero, the Stieltjes integral equation (6) requires that one multiply values of the function of  $\epsilon$  by increments in another function  $H(\epsilon)$  computed at the chosen points, and sum as  $\Delta H(\epsilon) \rightarrow 0$ . Hence, corresponding to the degeneracy function  $G(E)$ , is the limit

$$\lim_{\sigma \rightarrow 0} [H_n(\epsilon + \sigma) - H_n(\epsilon - \sigma)] = \begin{cases} 0 & \epsilon < (\frac{3}{2} + n), \\ 1 & \epsilon = (\frac{3}{2} + n), \\ 0 & \epsilon > (\frac{3}{2} + n). \end{cases}$$

This is clear from Fig. 1. The position of the energy levels is then given by  $\epsilon = (\frac{3}{2} + n)$ , and

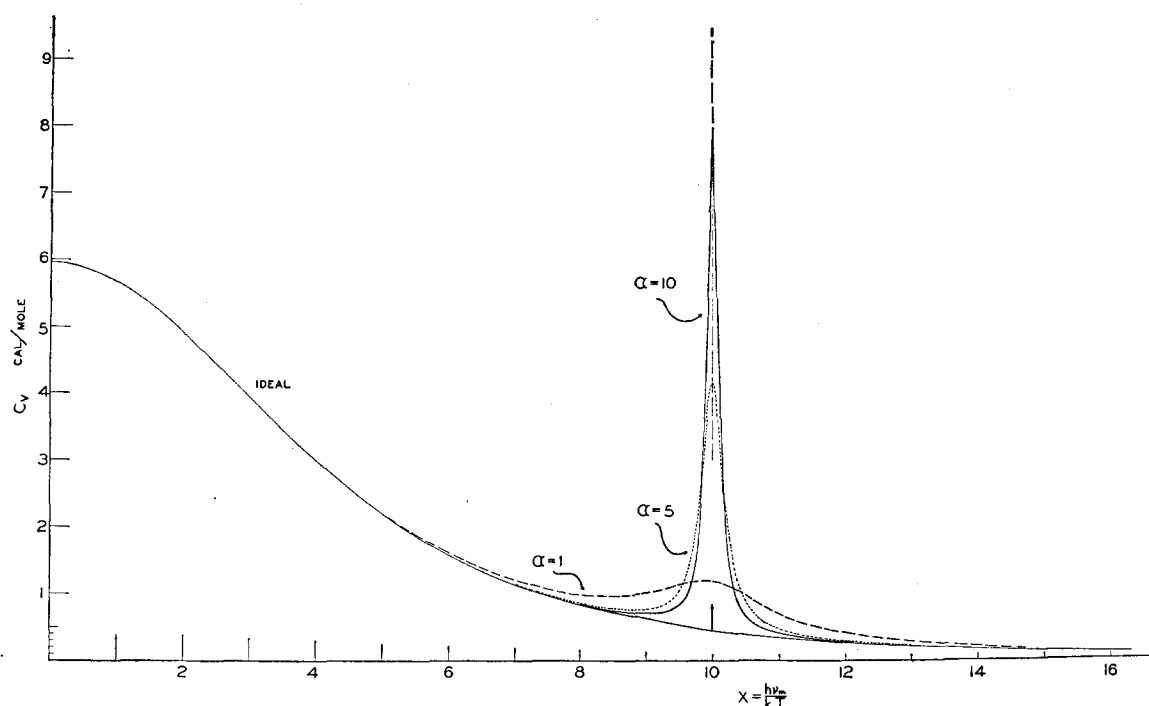


FIG. 3. Modified specific heat curves.

their degeneracy by  $\binom{n+2}{n}$ , which is the expected result;<sup>7</sup> Fig. 2.

That the representation of the experimentally determined partition function is not unique, even though the limiting conditions are satisfied has been indicated above. One must therefore rely on physical intuition as a guide to the acceptable forms.<sup>8</sup> For most systems, the sum-over-states may be represented to within the experimental error by sums of functions for which the transforms can be deduced through the application of the theorems given by Pipes<sup>4</sup> to (8a-e) and like terms.

#### SENSITIVITY OF THE METHOD

To gauge the sensitivity of the method, we studied the following model. To the specific heat

<sup>7</sup> The weight of the excited states of an Einstein crystal is given by the number of ways of placing  $n$  quanta into three groups; that is, the excitation of a three-dimensional harmonic oscillator:  $\frac{(3+n-1)!}{n!(3-1)!}$ .

<sup>8</sup> The types of equations suggested by G. M. Murphy (J. Chem. Phys. 5, 637 (1937)) and by J. W. Linnett and W. H. Avery (J. Chem. Phys. 6, 686 (1938)) cannot be used for the present purposes since they do not satisfy the necessary limiting conditions.

of a Debye crystal,

$$C_v(x) = \frac{36R}{x^3} \int_0^x \frac{z^3 dz}{e^{-z} - 1} - \frac{9Rx}{e^x - 1},$$

we added

$$C_t(x) = A/(1 + \alpha^2(x - x_0)^2); \quad (11)$$

a hump at  $x_0$ , rounded and of finite width, to simulate the type of maximum observed during a phase change of second order. The curves shown in Fig. 3 are of the modified specific heats as

TABLE I. Let  $W(x) = y(x)e^{-9x/8}$ .

$x$	$W(x)$ IDEAL*	$W(x)_r$ EQ. (13)	$W(x)_t$ IDEAL + TRANS. $\alpha = 1$	$\alpha = 10$	$\alpha = \infty$	$W(x)_{t,r}$ EQ. (14) $\alpha = \infty$
0.2	423.67	423.14	477.66	475.32	475.30	475.29
.4	65.824	66.431	73.818	73.699	73.624	74.335
.6	24.070	24.354	26.883	26.869	26.869	27.240
.8	12.453	12.557	13.859	13.874	13.874	14.073
1.0	7.7974	7.8133	8.6477	8.6616	8.6624	8.7500
1.5	3.6877	3.6911	4.0588	4.0718	4.0730	4.1035
2	2.4042	2.4085	2.6274	2.6388	2.6398	2.6396
5	1.1480	1.1458	1.2082	1.2162	1.2170	1.2168
6	1.0909	1.0873	1.1337	1.1400	1.1408	1.1412
9	1.0283	1.0266	1.0406	1.0403	1.0404	1.0458
10	1.0196	1.0194	1.0255	1.0210	1.0196	1.0334
11	1.0146	1.0146	1.0177	1.0150	1.0146	1.0248
15	1.0059	1.0058	1.0066	1.0060	1.0059	1.0088

\* These values were taken from the tables of F. H. MacDougall, *Thermodynamics and Chemistry* (Wiley and Sons, New York, 1926). The parameters of the Eqs. (13), and (14) were obtained by a method of successive approximations. Better fitting than the above is possible, but laborious.

functions of  $x$ , for  $x_0=10$  and  $\alpha=1, 5, 10$  and  $\infty$ , the latter representing a phase change of the usual type. For purposes of computation we have taken the area under  $C_t$  approximately equal to that under the Debye curve from infinity to  $x_0$ ; that is,

$$\frac{A\pi}{\alpha} = \frac{12\pi^4 R}{5} \int_{x_0}^{\infty} \frac{dx}{x^3} = 1.2\pi^4 \frac{R}{x_0^2}. \quad (12)$$

Further, we imposed the condition that as  $\alpha$  is made to approach infinity, the area is to remain

constant. Thus the limiting case of the specific heat curves typifying a transformation similar to that of second order is one with a sharp transition involving the same total heat effect. From these we deduced the entropy and the sum-over-states, and hoped to fit the  $Y(x)$  sufficiently well to distinguish these functions for various values of  $\alpha$ . It would thus be possible to determine the manner in which the density of energy states changes as  $\alpha$  approaches infinity.

It was only after investigating numerous func-

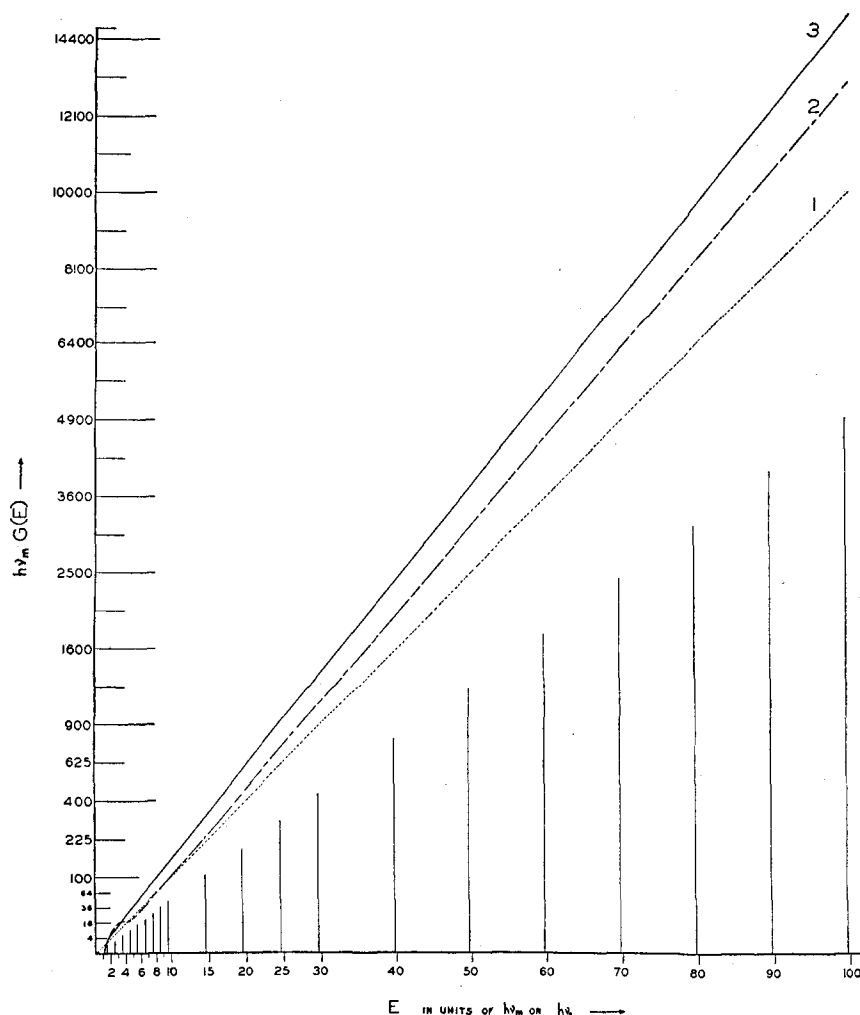


FIG. 4. The energy is plotted along the abscissa in units of  $h\nu_m$  for curves (2) and (3), or units of  $h\nu_0$  for the vertical lines. Note that the ordinate is a squared scale and gives, respectively,  $h\nu_m G(E)$  or  $h\nu_0 G(\epsilon)$ . For comparison, the dotted line (1) relates

$$\text{ordinate} = [\text{abscissa}]^2.$$

Curve (2) is the solution of the integral equation corresponding to (13) and specifies the density of energy states for the pseudo Debye crystal; Curve (3) corresponds to (14)—for the pseudo Debye crystal with a sharp transition at  $x=10$ . The vertical lines, most of which have been omitted, are the energy density spectrum for an Einstein crystal.

tions that a representation was found which had the proper limiting conditions and agreed with the known  $[Y(x)]^{1/N}$  values for the ideal crystal and for the superposed transition to within several tenths of a percent. The computations are relatively simple when the  $N$ th root of the partition function is dealt with, but become very cumbersome when the sum-over-states for the system as a whole has to be manipulated. To facilitate the computations for this test case, we arbitrarily replaced the Debye crystal by  $N$  similar but weakly interacting subsystems, and the degeneracy function was evaluated for the energy levels of the smaller units. Thus we have replaced  $[Y(x)]^{1/N}$  by  $y(x)$ , and considered the latter as the sum-over-states. Reference to Table I shows that the errors introduced using the equations given below are larger than the differences between the  $y(x)e^{9x/8}$  values for the various  $\alpha$ 's, although in absolute magnitude they are of the same order as those introduced by the specific heat measurements; values for a crystal without and with a transition are clearly distinguished. For the pseudo Debye crystal we assumed

$$y(x)_r = e^{-9x/8} \left( 1 + \frac{a(x)}{x^3} - b(x) \right),$$

where

$$\begin{aligned} a(x) &= 19.4818 - 16.7635(e^{-0.66x} \\ &\quad + e^{-0.73x} - e^{-1.237x}), \\ b(x) &= \frac{17.5x+1}{(x+1)^3} e^{-1.07x}. \end{aligned} \quad (13)$$

For this pseudo Debye crystal with a sharp transition at  $x=x_0$  ( $\alpha=\infty$ ), the same form for  $y(x)_r$  was assumed but

$$\begin{aligned} a(x) &= 19.4818 - 16.4264(e^{-0.66x} \\ &\quad + e^{-0.73x} - e^{-1.204x}), \\ b(x) &= \frac{7.2x+1}{(x+1)^3} e^{-0.25x} - \frac{26x}{(x+2.4)^3} e^{-0.2x}. \end{aligned} \quad (14)$$

To take the restrictions at  $x=0$  into consideration, for  $\alpha$  finite, the form of  $a(x)$  in (14) was modified;

$$a(x) = 19.4818 - (1.1241x^{-\epsilon} - 17.5505) \times (e^{-\rho x} + e^{-\sigma x} - e^{-\lambda x}),$$

where

$$\epsilon = \frac{1.2\pi^3}{x_0^2} \frac{\alpha}{1 + \alpha^2 x_0^2}.$$

Solutions for the integral equations corresponding to the above forms of  $y(x)_r$  follow from the application of (7) to (8b, c, d); the consequent degeneracy functions for this pseudo Debye crystal without and with a sharp transition are plotted in Fig. 4, in units of  $h\nu_m$ .

#### ACKNOWLEDGMENTS

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