

## EINSTEIN SOLID - ANALYTIC SOLUTION FOR HEAT CAPACITY

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The properties of an Einstein solid can be investigated analytically. The multiplicity of a solid with  $N$  oscillators and  $q$  energy quanta is

$$\Omega = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \quad (1)$$

For large  $q$  and  $N$ , we can approximate this by

$$\Omega \approx \sqrt{\frac{N}{2\pi q(q+N)}} \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \quad (2)$$

For very large systems, the square root factor can be neglected compared to the two power terms as it is merely “large” compared to the “very large” power terms. We thus get

$$\Omega \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \quad (3)$$

From this we can get the entropy

$$S = k \ln \Omega \quad (4)$$

$$= k(q+N) \ln(q+N) - kq \ln q - kN \ln N \quad (5)$$

The total energy of the system is

$$U = q\epsilon \quad (6)$$

where  $\epsilon$  is the energy of a single quantum, so we can get the temperature as defined from the entropy

$$\frac{1}{T} = \frac{\partial S}{\partial U} \quad (7)$$

$$= \frac{1}{\epsilon} \frac{\partial S}{\partial q} \quad (8)$$

$$= \frac{k}{\epsilon} [\ln(q + N) + 1 - \ln q - 1] \quad (9)$$

$$= \frac{k}{\epsilon} \ln \frac{q + N}{q} \quad (10)$$

$$= \frac{k}{\epsilon} \ln \frac{U + N\epsilon}{U} \quad (11)$$

$$T = \frac{\epsilon}{k \ln \frac{U + N\epsilon}{U}} \quad (12)$$

We can invert this to obtain  $U(T)$ :

$$e^{\epsilon/kT} = \frac{U + \epsilon N}{U} \quad (13)$$

$$U = \frac{\epsilon N}{e^{\epsilon/kT} - 1} \quad (14)$$

Finally, the heat capacity is obtained from

$$C = \frac{\partial U}{\partial T} \quad (15)$$

$$= - \frac{\epsilon N e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2} \left( - \frac{\epsilon}{kT^2} \right) \quad (16)$$

$$= \frac{\epsilon^2 N e^{\epsilon/kT}}{kT^2 (e^{\epsilon/kT} - 1)^2} \quad (17)$$

A plot of the dimensionless quantities  $C/Nk$  versus  $kT/\epsilon$  is in Fig. 1.

To compare this with Schroeder's Figure 1.14, we need to insert some actual numbers so we can plot  $C$  versus  $T$ . Figure 1.14 is for one mole of atoms, but an Einstein solid treats  $N$  oscillators, where each oscillator is a one-dimensional simple harmonic oscillator. Each atom in a real solid can vibrate in three directions, so one mole of atoms in a real solid contains three moles of oscillators in an Einstein solid. Thus to compare the plots for one mole of "real" atoms, we should use  $N = 3 \times 6.02 \times 10^{23}$ .

Using  $k = 8.62 \times 10^{-5} \text{ eV K}^{-1}$  and multiplying the result of  $C$  by  $1.602 \times 10^{-19}$  to convert the result from  $\text{eV K}^{-1}$  to  $\text{J K}^{-1}$  (which are the units used

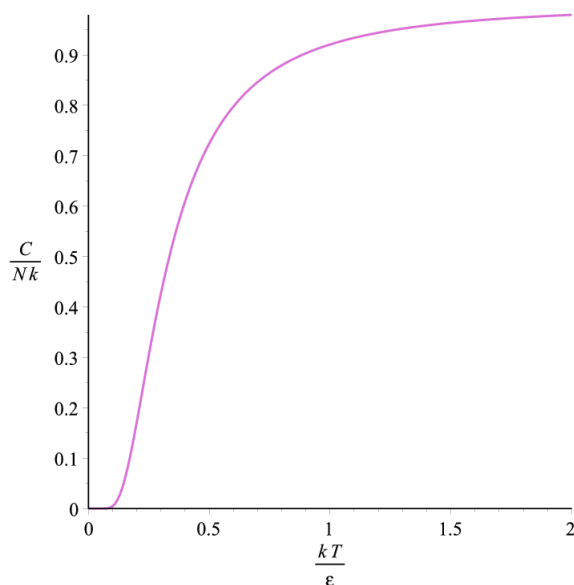


FIGURE 1. Heat capacity for Einstein solid.

in Figure 1.14), we then need to choose some values for  $\epsilon$  to get the curves for lead, aluminum and diamond.

As a starting point, I used the values from the numerical solution done earlier. The values for lead and aluminum turned out (surprisingly, considering the numerical solution was worked out for very small systems) to work quite well, but the value for diamond needed to be adjusted a bit. The final values were

$$\epsilon_{Pb} = 0.00862 \text{ eV} \quad (18)$$

$$\epsilon_{Al} = 0.0259 \text{ eV} \quad (19)$$

$$\epsilon_{Dia} = 0.12 \text{ eV} \quad (20)$$

The resulting plots are in Fig. 2.

The curves are lead (red), aluminum (green) and diamond (blue). They are a good match to the curves shown in Figure 1.14.

We can get an expression for the heat capacity in the limit of high temperatures by expanding the exponential. As a first approximation we'll use

$$e^{\epsilon/kT} \approx 1 + \frac{\epsilon}{kT} \quad (21)$$

Then from 17

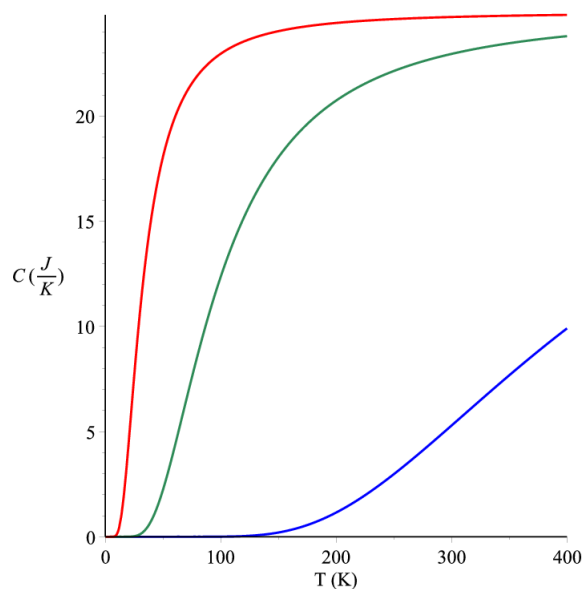


FIGURE 2. Heat capacities for lead (red), aluminum (green) and diamond (blue).

$$C \approx \frac{\epsilon^2 N}{k} \frac{(1 + \epsilon/kT)}{T^2 (\epsilon^2/k^2 T^2)} = Nk \left(1 + \frac{\epsilon}{kT}\right) \approx Nk \quad (22)$$

This is the expected result from the equipartition theorem, since the heat capacity for a system whose thermal energy is entirely in the form of quadratic degrees of freedom is

$$C = \frac{1}{2} N f k \quad (23)$$

where  $f$  is the number of degrees of freedom. For a harmonic oscillator,  $f = 2$  (one from the kinetic energy term and one from the potential energy), so we'd expect  $C = Nk$ .

To get a more accurate approximation, we can expand the exponential out to a few more terms using the Taylor expansion for small  $x \equiv \epsilon/kT$ :

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \quad (24)$$

To get the next term in the expansion beyond 22, we need to expand out to  $x^3$ , so we get

$$\frac{C}{Nk} = x^2 \frac{e^x}{(e^x - 1)^2} \quad (25)$$

$$\approx x^2 \frac{1 + x + \frac{x^2}{2} + \frac{x^3}{6}}{\left(x + \frac{x^2}{2} + \frac{x^3}{6}\right)^2} \quad (26)$$

$$= \frac{1 + x + \frac{x^2}{2} + \frac{x^3}{6}}{\left(1 + \frac{x}{2} + \frac{x^2}{6}\right)^2} \quad (27)$$

The denominator can now be expanded again using a Taylor series. This gets quite tedious so I used Maple to do the expansion (you're welcome to try it by hand by calculating the derivatives) with the result

$$\frac{C}{Nk} \approx \left(1 + x + \frac{x^2}{2} + \frac{x^3}{6}\right) \left(1 - x + \frac{5}{12}x^2\right) \quad (28)$$

$$= 1 - \frac{x^2}{12} + \mathcal{O}(x^3) \quad (29)$$

$$C \approx Nk \left(1 - \frac{1}{12} \left(\frac{\epsilon}{kT}\right)^2\right) \quad (30)$$