Ay126: Heating of Very Small Grains

S. R. Kulkarni

May 27, 2021

The computation of the grain temperature is straightforward. We equate the heating to the cooling. This classical approach is adequate for large grains. However, a remarkable development (as we learnt from IRAS, COBE, IRTS, IRTS, ISO, Spitzer, Herschel, Planck) observations) is that a comparable amount of emission from the dust results from very small grains, particularly PAHs. As the grain size decreases its store of internal energy decreases as well. Clearly, there is interesting physics when the energy of the optical/UV photon becomes comparable to that of the internal store. The physics of the latter is the topic of this note. All the material for this pedagogical note is from *Statistical Mechanics* by Pathria (a most excellent book).

1 Phonon Framework

Consider a solid. The ions are in some sort of quasi-regular arrangement. The nuclei, numbering N, can vibrate along the three spatial axis. The kinetic energy of the vibrating nuclei is

$$K = \frac{1}{2}m\sum_{i=1}^{3N}\dot{\xi}_i^2 \tag{1}$$

where $\xi_i = x_i - \bar{x}_i$ and the sum is over $3 \times N$ 3 one-dimensional vibrators. In addition, they are attracted to each other (otherwise the solid would not be formed) and so there is some sort of potential energy function, $\phi(x_1, x_2, ..., x_{3N})$. Since the solid is in equilibrium the mean force on each ion is zero. Thus

$$\frac{\partial\phi(x_i)}{\partial x_i} = 0 \tag{2}$$

where it is assumed that the derivative is evaluated with the nuclei at their equilibrium position, $\bar{x}_i$. With this simplification the potential can be Taylor expanded and, recognizing that the vibrational amplitudes are small compared to the ion-ion spacing, keep only the second derivatives (also evaluated at equilibrium positions). Thus the potential energy is

$$V = \phi_0 + \sum_{i,j}\alpha_{ij}\xi_i\xi_j \tag{3}$$

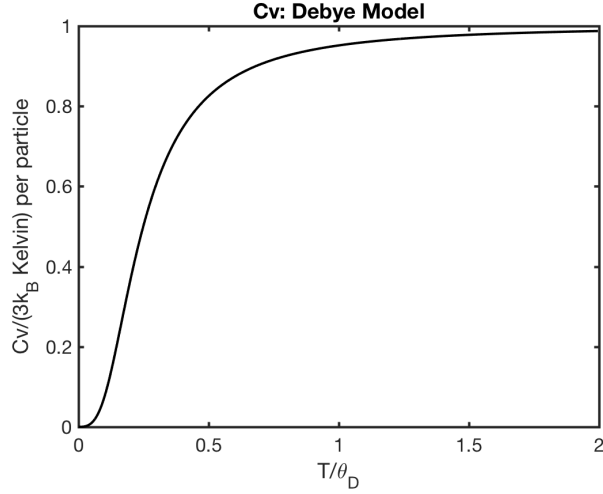$$\alpha_{ij} = \frac{1}{2}\left(\frac{\partial^2 \phi}{\partial x_i \partial x_j}\right). \tag{4}$$

Figure 1: Specific heat per particle, $c_v = C_V/(3k_B \text{ Kelvin})$, as a function of T/θ_D where T is the temperature and θ_D is the Debye temperature.

Seemingly it would appear that we would need to have $\approx (3N)^3$ coefficients in V. However, a transformation of the coordinates, $\xi_i \to q_i$, can always be found in which V can be recast in terms of $3N$ coefficients. The transformed coordinates are "normal" modes.[1] The Hamiltonian can thus be written as

$$H = \phi_0 + \sum_i^{3N} \frac{1}{2}m(\dot{q}_i^2 + \omega_i^2 q_i^2) \tag{5}$$

Here, ω_i are the characteristic frequencies of the normal modes. Thus the thermodynamics of a solid can be boiled down to a collection of oscillators, each with their own frequencies.

Einstein, following Planck, reasoned that phonons like photons are quantized. The modern QM eigenvalues for Equation 5 is

$$E\{n_i\} = \phi_0 + \sum_i (n_i + \frac{1}{2})\hbar\omega_i. \tag{6}$$

The internal energy is then

$$U(T) = \left\{\phi_0 + \sum_i \frac{1}{2}\hbar\omega_i\right\} + \sum_i N(\omega_i)\hbar\omega_i \tag{7}$$

---

[1]The standard example is that for a two coupled pendulums whose instantaneous positions are x_1 and x_2. The coordinates $q_1 = x_1 - x_2$ and $q_2 = x_1 + x_2$ are the normal coordinates for this system. With this transformation the Hamiltonian of q_i simplifies to that shown in Equation 5.

Clearly, the first term in curly brackets (the binding energy of the solid including the zero point oscillations) is negative and larger (in magnitude) than the sum of the energy in vibrations.

In Einstein's model all phonons had the same vibration frequency. Einstein postulated that the number density of phonons obeyed Boltzmann distribution. The number of phonons, unlike photons, were restricted by the highest vibration frequency that the lattice could bear. Thus, the internal energy of the crystal is

$$U = N\langle n\rangle \hbar\omega = \frac{N\hbar\omega}{\exp(\hbar\omega/(kBT)) - 1} \tag{8}$$

Then $C_V(T) = (\partial U \partial T)_V$. The model was a success at higher temperatures but failed to explain the low temperature behavior.

2 Debye Model: Internal Energy & Specific Heat

Debye's model improved upon Einstein's model by allowing for a range of frequencies (uniform in phase space). We now need to know the values of ω_i. If N is large enough we can replace the sum in Equation 7 with a density function, $g(\omega)$, for the distribution of ω. In the Debye model, the assumption is that

$$g(k) = 2 \cdot 4\pi k^2 dk \tag{9}$$

where $k = \omega/(2\pi c)$ is the wavenumber. This formulation – the Rayleigh assumption – assumes that the normal modes are uniformly distributed in wave numbers. However, unlike photons, there is a cap on ω, namely, the mode in which the displacement of each successive ion changes sign. Thus

$$\int_0^{\omega_D} g(\omega)d\omega = 3N \tag{10}$$

$g(\omega)d\omega$ is the number of normal modes of vibration whose frequency lies in the range $[\omega, \omega + \delta\omega]$. We are now all set[2] to compute the internal store, $U(T)$ and the specific heat[3] C_V:

$$C_V(T) = (\partial U/\partial T)_V = 3Nk_BD(x_0) \tag{11}$$

$$D(x_0) = \frac{3}{x_0^2}\int_0^{x_0}\frac{x^4\exp(x)dx}{(\exp(x)-1)^2} \tag{12}$$

---

[2]There are other complications that are being glossed over. There are two families of elastic waves in solids: longitudinal and transverse. waves etc.

[3]at constant volume – naturally for solids

where $x_0 = \theta_D/T$. The asymptotic limits are

$$
\begin{align}
D(x_0) &= 1 - \frac{x_0^2}{20} + ..., \qquad x_0 \ll 1 \tag{13} \\
D(x_0) &= \frac{4\pi^4}{5x_0^3} = \frac{4\pi^4}{5}\left(\frac{T}{\theta_D}\right)^3, \qquad x_0 \gg 1 \tag{14}
\end{align}
$$

Equation 14 is the much celebrated Debye relation. Plots of C_V and $U = \int_0^T C_V(T)dT$ as a function of T/θ_D can be found in Figures 1. and 2, respectively.
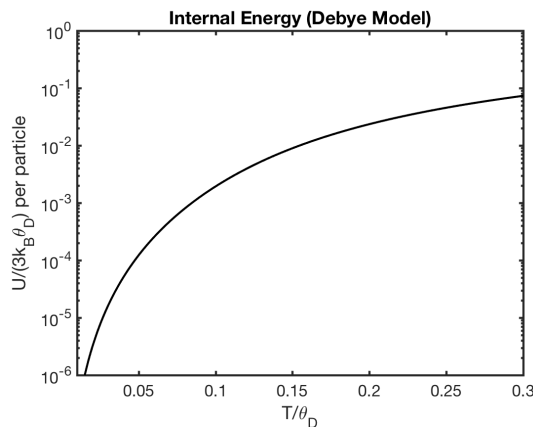

Figure 2: Internal energy per particle, $u = U/(3k_B\theta_D)$, in the Debye model as a function of T/θ_D where T is the temperature and θ_D is the Debye temperature.

3   Heat Capacity of Very Small Grains

Consider a grain whose density is ρ and is composed primarily of element with atomic number, A. The number of atomic nuclei in the grain of radius a is

$$
N = \frac{N_A}{A}\frac{4\pi a^3}{3}\rho \tag{15}
$$

and the heat content is

$$
U = 3k_B N\theta_D u \tag{16}
$$

where N_A is Avogadro's number and u is the ordinate in Figure 2.

Let us adopt, $T = 30\,\mathrm{K}$ and $\theta_D = 600\,K$ (see Figure 3). For these two choices, inspecting Figures 1 and 2 we $c_v = 1.2 \times 10^{-4}$ and $u \approx 1,2\times^{-6}$. Thus the store of internal energy of a a grain with radius $a = 50\,\text{Å}$ and $\rho = 3\,\mathrm{g\,cm}^{-3}$ is

$$
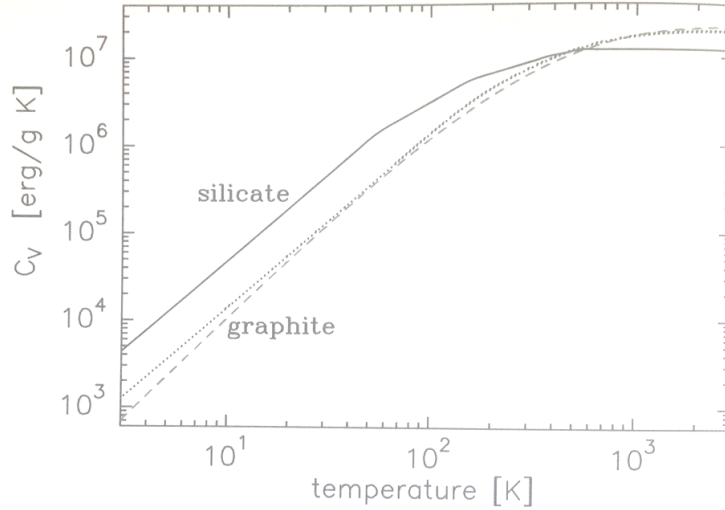U = 1.47\left(\frac{6}{A}\right)\left(\frac{\theta_D}{600\,\mathrm{K}}\right)\ \mathrm{eV}. \tag{17}
$$

4

Figure 3: The specific heat per gram of dust for silicate (full curve), graphite (broken curve) and PAHs without hydrogen atoms. Figure 8.9 of Krüger's book.

Clearly, the absorption of even a single photon of few eV is a "shock" to the grain. [Here, θ_D is typical of Silicates or Carbon dust.] The temperature of the dust grain rises dramatically and as a result the emission moves from LIR (larger dust grains) to the MIR.

3.1 PAH

PAHs and graphene are 2-D structure. The density of normal modes[4] is

$$g(\omega) = \frac{6N}{\omega_D^2}\omega \tag{18}$$

Note that the normalization has been correctly chosen so that $g(\omega)d\omega = 3N$. In any case, for such planar structure, $C_V \propto T^2$ in the low-temperature regime.

Separately, it is interesting to note that the lowest frequency of vibration depends on the size of the object (one wave across the grain). The minimum frequency is obtained by integrating $g(\omega)$ and setting to unity.

$$\int_0^{\omega_{\min}} g(\omega)d\omega = 1 \tag{19}$$

$$\frac{\hbar\omega}{k_B} = \frac{\theta_D}{\sqrt{3N}} \tag{20}$$

Say that you have a $10\,\text{Å}$ dust particle. With $A = 12$ we find $\hbar\omega_{\min}/k_B \approx \theta_D/44$. For

_____

[4] I am following Krügel's book, §8.4.6. I do not understand why it is $3N$ instead of $2N$.

PAH, $\theta_D = 950\,\mathrm{K}$ (out-of-plane bending) or $2500\,\mathrm{K}$ (in plane stretching). You can see that the minimum energy of the emitted photon is $250\,\mu\mathrm{m}$.