# Debye Crystal

The Debye Crystal (*1*) is a direct application of the vibrational partition function for the calculation of thermodynamic properties for the solid state. Contrary to gases and liquids, atoms and molecules in a solid phase have very restricted motion. Translation takes place as a whole group, and the particles have no translation movement of their own. Rotations are also hindered or inexistent. Vibrational motion also takes place in groups of many atoms or molecules, constituting what in physics is known as a phonon. Phonons originate from the quantum mechanical description of vibrational motion, in which a group (lattice) of particles uniformly oscillates at a given frequency. The Debye model for lattice vibrations constitutes a semi-classical model that describes properties of crystals.

For this, consider a one-dimensional crystal lattice, composed by a single chemical species with an equilibrium interparticle distance of $a$. Since particles in the solid are not still but rather move, we may define the vector $x_i$, which gives the instantaneous displacement in the particle's coordinates with respect to the equilibrium position due to vibrational motion (for a one-dimensional crystal $x_i$ is a scalar). In principle, a particle in this lattice will feel a potential resulting from the interaction with all other particles in the crystal. For simplicity however, one considers that only interactions with the immediate neighbours are significant, namely interactions up to a distance $2a$. The potential energy between any two particles in the lattice is given by $u(r)$, where $r$ defines the interparticle distance. Since the particles in the lattice are all the same, then there is only one potential function to define.

We furthermore consider that the crystal is composed by $N$ particles. $N$ is in principle a very large number, in the order of magnitude of the Avogadro constant. Due to its dimension, end- or edge effects on the crystal are negligible. From these definitions we may furthermore give $L = Na$ as the total length of the crystal.

Using the displacement vectors, the instantaneous distance between two consecutive particles in the crystal is given by

$$\Delta x = a + x_{i+1} - x_i \tag{1}$$

Since we are neglecting end-effects and interactions further than $2a$ apart, then the total potential energy for the system is given by

$$U(x) = \sum\nolimits_{i=1}^{N} [u(a + x_{i+1} - x_i) + u(2a + x_{i+2} - x_i)] \tag{2}$$

Note that each interaction has to be counted only once, therefore we only count the interactions for particles $i+1$ and $i+2$. Equivalently we could have accounted for the interactions with particles $i-1$ and $i-2$.

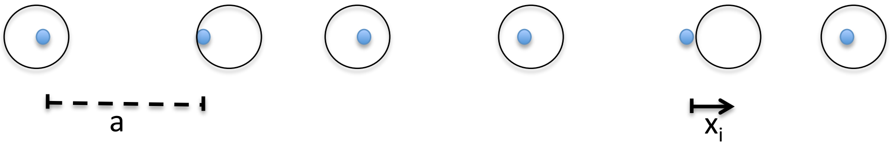

Figure 1: Scheme of a one-dimensional monoatomic crystal lattice to describe the Debye model for lattice vibrations. The blue points represent the equilibrium positions of the atomic centers at zero Kelvin. $a$ is the distance between two particles at equilibrium. The circles show the position of atoms at a given time. This displacement, represented by the vector $x_i$, is due to vibrational motion.

If all particles are at their equilibrium position, *i.e.* if all $x_i = 0$, then

$$U(0) = \sum_{i=1}^{N} [u(a) + u(2a)] = N\,[u(a) + u(2a)] \tag{3}$$

The total kinetic energy for the particles in the crystal is given by

$$T = \sum_{i=1}^{N} \frac{1}{2} m \dot{x}_i^2 \tag{4}$$

This contribution to the Hamiltonian is separable into the sum of many single particle components, contrary to the potential energy contribution as it was presented above. To proceed further and still have a system of equations with manageable dimensions, we have thus to decouple the potential energy into single particle contributions. To do so, we start by defining

$$\delta = x_{j+1} - x_j \tag{5}$$

$$\eta = x_{j+2} - x_j \tag{6}$$

which allows one to write

$$U(x) = \sum_{i=1}^{N} [u(a+\delta) + u(2a+\eta)] \tag{7}$$

If we then apply a Taylor expansion,

$$U(x) = \sum_{i=1}^{N} \left[ u(a) + u'(a)\delta + \frac{1}{2}u''(a)\delta^2 + ... + u(2a) + u'(2a)\eta + \frac{1}{2}u''(2a)\eta^2 + ... \right] \tag{8}$$

In the limit of small vibrations, we may restrict the above series to quadratic terms. Furthermore, since the Taylor expansion goes around the equilibrium position (a minimum in the potential energy surface), then the first derivative zeroes and we are left with

$$\begin{aligned} U(x) &= \sum\nolimits_{i=1}^{N}\left[u(a)+\frac{1}{2}u''(a)\delta^2+u(2a)+\frac{1}{2}u''(2a)\eta^2\right] \\ &= U(0)+\frac{1}{2}\sum\nolimits_{i=1}^{N}\left[u''(a)\delta^2+u''(2a)\eta^2\right] \end{aligned} \tag{9}$$

Putting everything together, then in the limit of short vibrational motion the total Hamiltonian for the crystal is given by

$$H = T + U(x) = \sum\nolimits_{i=1}^{N}\frac{1}{2}m\dot{x}_i^2 + U(0) + \frac{1}{2}\sum\nolimits_{i=1}^{N}\left[u''(a)\delta^2+u''(2a)\eta^2\right] \tag{10}$$

Just as before, the total Hamiltonian is not separable, meaning that the motion of a given particle is not independent from the motion of other particles. Fortunately, we know that there exists always a linear combination of the variables that will diagonalize the total Hamiltonian (*2*), even if one cannot find such transformation. This means that there is always a set of variables $\xi_i$ that are linear combinations of the atomic coordinates, such that in the new coordinate system the Hamiltonian is a diagonal matrix.

$$H = \sum\nolimits_{i=1}^{N}H_i = \sum\nolimits_{i=1}^{N}\left(\frac{U(0)}{N}+\frac{1}{2}f_i\xi_i^2+\frac{1}{2}M_i\xi_i^2\right) \tag{11}$$

In the new system of coordinates, $M_i$ are effective masses, whereas $f_i$ are effective force constants. We note furthermore, that in the limit of small vibrations, the single particle Hamiltonian is the harmonic oscillator, for which the solutions are well known. The eigenvalues to this Hamiltonian are given by

$$\varepsilon_{in} = \left(n+\frac{1}{2}\right)h\nu_i \tag{12}$$

with

$$\nu_i = \frac{1}{2\pi}\sqrt{\frac{f_i}{M_i}} \tag{13}$$

Therefore, via their dependence on $f_i$ and $M_i$, the characteristic vibrational frequencies are functions of the thermodynamic variable $a = \frac{L}{N}$. Before proceeding to write the partition function for this system we would like to point out the fact that since the Hamiltonian is separable for one dimension, one may likewise proceed similarly to obtain solutions to the three-dimensional quantum harmonic oscillator under the same approximations. The differences are that the characteristic vibrational frequencies should be functions of the volume (and not length) and that summations go over three dimensional particles, thus over $3N - 6$. For the rest of the derivation we will consider that the solid is three- and no longer one-dimensional.

To build the partition function we note that unlike gases or liquids, particles in solids have fixed positions. These are thus distinguishable. This means that the total partition function does not require the $N!$ term that accounts for particle indistinguishability. Thus the crystal's partition function is given by

$$Z = e^{\frac{U(0)}{k_B T}} \prod\nolimits_{i=1}^{3N-6} q\left(\theta_i\right) \tag{14}$$

with

$$q\left(\theta_i\right) = \frac{exp\left(-\frac{\theta_i}{2T}\right)}{1 - exp\left(-\frac{\theta_i}{T}\right)} \tag{15}$$

$$\theta_i = \frac{h\nu_i}{k_B} \tag{16}$$

The exponential factor with $U(0)$ in the partition function corresponds to a zero point energy, in which all particles are at rest. From this analysis we conclude that small vibrations in a crystal can be decomposed rigorously into independent normal modes of vibration, being the crystal system a combination of those many subsystems. However, the quantity we are interested in is the natural logarithm of the partition function, so that we may apply the machinery of statistical mechanics:

$$log(Z) = log\left(\prod\nolimits_{i=1}^{3N-6} q(\theta_i)\right) - \frac{U(0)}{k_B T} \approx log\left(\prod\nolimits_{i=1}^{3N} q(\theta_i)\right) - \frac{U(0)}{k_B T}$$

$$= \sum\nolimits_{i=1}^{3N} log q(\theta_i) - \frac{U(0)}{k_B} = \sum\nolimits_{i=1}^{3N} log \frac{exp\left(-\frac{\theta_i}{2T}\right)}{1 - exp\left(-\frac{\theta_i}{T}\right)} - \frac{U(0)}{k_B T}$$

$$log(Z) = -\sum\nolimits_{i=1}^{3N} \frac{\theta_i}{2T} - \sum\nolimits_{i=1}^{3N} log\left(1 - exp\left(-\frac{\theta_i}{T}\right)\right) - \frac{U(0)}{k_B T} \tag{17}$$

Using now the virial theorem annd the equations of motion for the particles, we know that

$$m \frac{\partial^2}{\partial t^2} x_j = u'(a - x_j) + u'(2a - x_j) - u'(a - x_j) - u'(2a + x_j) = -\frac{d\phi(x_j)}{dx_j}$$

which yields, after integration

$$\phi(x_j) = u(a - x_j) + u(2a - x_j) + u(a - x_j) + u(2a + x_j) \tag{18}$$

At zero displacement,

$$\phi(0) = 2u(a) + 2u(2a) \tag{19}$$

comparing this with the previous equations, we conclude that

$$U(0) = \frac{N\phi(0)}{2} \tag{20}$$

Whereas $U(0)$ is the total potential energy when all particles are at rest, $\phi(0)$ measures the interaction of a given particle (they are all the same though) with all other particles at rest at their lattice points. The partition function can thus be written as

$$log(Z) = -\sum_{i=1}^{3N} \frac{\theta_i}{2T} - \sum_{i=1}^{3N} log\left(1 - exp\left(-\frac{\theta_i}{T}\right)\right) - \frac{N\phi(0)}{2k_B T} \tag{21}$$

Since we take our solid to be composed by $N$ particles, where $N$ is on the order of magnitude of the Avogadro constant, then the total number of vibrational modes is almost three-times larger. It is therefore legitimate to assume that there is a continuous distribution of vibrational frequencies $g(\nu)$. With this assumption we go from the realm of quantum mechanics to the world of classical physics, meaning that we may replace the summations by the respective integrals. For that purpose we require $g(\nu)d\nu$, the number of vibrational modes with frequencies between $\nu$ and $\nu + d\nu$. The total number of vibrational frequencies is obtained by integration

$$\int_0^{+\infty} g(\nu)d\nu = 3N \tag{22}$$

The partition function then becomes

$$log(Z) = -\int_0^{+\infty} \frac{\theta}{2T} g(\nu)d\nu - \int_0^{+\infty} log\left(1 - exp\left(-\frac{\theta}{T}\right)\right) g(\nu)d\nu - \frac{N\phi(0)}{2k_B T} \tag{23}$$

From this description one sees that in this semi-classical approach, knowing the frequency distribution function $g(\nu)$ is all we need to completely characterize the system thermodynamically. We may now use our statistical mechanics toolkit to derive expressions for some thermodynamic quantities:

$$\begin{aligned} A &= -k_B T log Z \\ &= k_B T \int_0^{+\infty} \frac{\theta}{2T} g(\nu)d\nu + k_B T \int_0^{+\infty} log\left(1 - exp\left(-\frac{\theta}{T}\right)\right) g(\nu)d\nu + \frac{N\phi(0)}{2} \end{aligned} \tag{24}$$

$$\begin{aligned} U &= -k_B T^2 \left(\frac{\partial log Z}{\partial T}\right)_{V,N} \\ &= \frac{N\phi(0)}{2} + k_B \int_0^{+\infty} \frac{\theta}{2} g(\nu)d\nu + k_B \int_0^{+\infty} \frac{\theta exp\left(-\frac{\theta}{T}\right)}{1 - exp\left(-\frac{\theta}{T}\right)} g(\nu)d\nu \end{aligned} \tag{25}$$

$$C_V = \frac{\partial U}{\partial T} = k_B \int_0^{+\infty} \left(\frac{\theta}{T}\right)^2 \frac{exp(\frac{\theta}{T})}{\left(exp(\frac{\theta}{T}) - 1\right)^2} g(\nu) d\nu \tag{26}$$

$$S = \frac{U-A}{T} = k_B \int_0^{+\infty} \frac{\frac{\theta}{T} exp(-\frac{\theta}{T})}{1 - exp(-\frac{\theta}{T})} g(\nu) d\nu - k_B \int_0^{+\infty} log\left(1 - exp\left(-\frac{\theta}{T}\right)\right) g(\nu) d\nu \tag{27}$$

For other thermodynamic properties like pressure, enthalpy or Gibbs energy, one must know how the vibrational frequencies depend on the system's volume, which requires knowing the change of variable applied when diagonalizing the Hamiltonian.

The task is now the estimation of the frequency distribution, which is where the Debye approximation first comes in. Phonons in solids are typically partitioned in two classes: acoustic phonons with larger wavelength; optical phonons with smaller wavelength. Acoustic phonons cannot "see" the crystal structure, and therefore the crystal behaves as if it were a continuous medium for the vibrations. Taking the crystal to be an elastic continuum, the asymptotic behaviour of $g(\nu)$ for small $\nu$ can be deduced. The Debye approximation consists in taking this behaviour for the whole frequency spectrum.

For a three-dimensional continuum medium, in the limit of low vibrational frequencies,

$$g(\nu) = \alpha\nu^2 = \frac{12\pi V}{{v_s}^3}\nu^2 \tag{28}$$

where $V$ is the volume and $v_s$ is the speed of sound in the medium. As this function tends to infinity for large enough vibrational frequencies, using this distribution function for all vibrational frequencies requires a cutoff value, thus

$$g(\nu) = \begin{cases} \frac{12\pi V}{{v_s}^3}\nu^2, & \text{if } \nu < \nu_m \\ 0, & \text{otherwise} \end{cases} \tag{29}$$

using the limiting condition for the distribution function, equation 22,

$$\int_0^{+\infty} g(\nu) d\nu = \frac{\alpha\nu_m^3}{3} = 3N \tag{30}$$

then

$$\nu_m = \left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}} v_s \tag{31}$$

By plugging the frequency distribution function estimated by Debye we can then obtain explicit formulas for thermodynamic quantities.

$$
\begin{aligned}
A = \frac{N\phi(0)}{2} + \frac{12\pi V}{v_s^3}\frac{(k_BT)^3}{h^2}\int_0^{\nu_m} log\left[1 - exp\left(-\frac{h\nu}{k_BT}\right)\right]\left(\frac{h\nu}{k_BT}\right)^2 d\nu \\
+\frac{12\pi V}{v_s^3}\frac{(k_BT)^3}{h^2}\int_0^{\nu_m}\frac{1}{2}\left(\frac{h\nu}{k_BT}\right)^3 d\nu \\
= \frac{N\phi(0)}{2} + \frac{9R\theta_D}{8} + \frac{9RT^4}{\theta_D^3}\int_0^{\frac{\theta_D}{T}} x^2 log\left(1 - e^{-x}\right)dx
\end{aligned}
\tag{32}
$$

where the Debye temperature $\theta_D$ is given by

$$
\theta_D = \frac{hv_s}{k_B}\left(\frac{3N_A\rho}{4\pi M}\right)^{\frac{1}{3}} \tag{33}
$$

$M$ is the mass per mole of the particle composing the crystal (atomic or molecular weight) and $\rho$ the density of the crystal. Proceeding similarly for other quantities one obtains,

$$
U = \frac{N\phi(0)}{2} + \frac{9RT^4}{\theta_D^3}\left(\int_0^{\frac{\theta_D}{T}} x^3\frac{e^{-x}}{1 - e^{-x}}dx + 2\left[\frac{\theta_D}{2T}\right]^4\right) \tag{34}
$$

$$
S = \frac{9RT^3}{\theta_D^3}\left(\int_0^{\frac{\theta_D}{T}} x^3\frac{e^{-x}}{1 - e^{-x}}dx - \int_0^{\frac{\theta_D}{T}} x^2 log\left(1 - e^{-x}\right)dx\right) \tag{35}
$$

and

$$
C_V = \frac{9RT^3}{\theta_D^3}\int_0^{\frac{\theta_D}{T}} x^4\frac{e^x}{(1 - e^x)^2}dx \tag{36}
$$

One may furthermore calculate the chemical potential for the solid phase since

$$
\mu = \frac{A + p_0V}{N}
$$

where $p_0V$ is related to the solid, meaning that it is like a Poynting correction factor. If we consider that in the conditions at which the Debye model apply $p_0V << A$ it results in

$$
\mu = \frac{\phi(0)}{2} + \frac{9k_B\theta_D}{8} + \frac{9k_BT^4}{\theta_D^3}\int_0^{\frac{\theta_D}{T}} x^2 log\left(1 - e^{-x}\right)dx \tag{37}
$$

Despite being neglected in the calculation of the chemical potential for the crystal, if we know the chemical potential of a gas phase we may then estimate the vapour pressure associated with it. Using the theoretical expression we derived for the chemical potential of an ideal gas we can make

$$\begin{aligned}\mu_{crystal} = \mu_{gas} = -\frac{3}{2}k_B T log\left(\frac{2\pi m}{h^2}\right) - 4k_B T log(k_B T) + k_B T log P_0 + k_B T log\sigma \\ +\frac{k_B}{2}\sum\nolimits_{i=1}^{3N_n-6}\theta_i + k_B T\sum\nolimits_{i=1}^{3N_n-6} log\left(1-e^{-\frac{\theta_i}{T}}\right) - \frac{k_B T}{2} log\pi - \frac{k_B T}{2}\sum\nolimits_{j=1}^{3} log\left(\frac{8\pi^2 I_j}{h^2}\right)\end{aligned} \tag{38}$$

We recall that in the expression above $m$ is the single particle mass (atomic or molecular weight divided by $N_A$), $\theta_i$ are the vibrational frequencies of the single molecule in the gas phase and the respective sums (index $i$) run over all the vibrational modes ($3n-6$ for a non-linear $n$-atomic molecule or $3n-5$ if the molecule is linear). Finally, $\sigma$ is the symmetry factor in the rotational partition function and the $I_j$ are the eigenvalues of the inertia matrix. Note that for both the gas and crystal phases we neglected the contribution from the electronic partition function. Combining both chemical potentials we obtain the logarithm of the vapour pressure as

$$\begin{aligned}log P_{vap} = \frac{\mu_{crystal}}{k_B T} + 4log(k_B T) + \frac{3}{2}log\left(\frac{2\pi m}{h^2}\right) - \frac{1}{2}\sum\nolimits_{i=1}^{3N_n-6}\frac{\theta_i}{T} \\ -\sum\nolimits_{i=1}^{3N_n-6} log\left(1-e^{-\frac{\theta_i}{T}}\right) + \frac{1}{2}log\pi - log\sigma + \frac{1}{2}\sum\nolimits_{j=1}^{3} log\left(\frac{8\pi^2 I_j}{h^2}\right)\end{aligned} \tag{39}$$

If we now subtract to equation 39 the vapour pressure of the crystal at standard conditions $P_0$ and $T_0$ one gets

$$\begin{aligned}log\frac{P_{vap}}{P_0} = \frac{\phi_0}{2k_B}\left(\frac{1}{T}-\frac{1}{T_0}\right) + \frac{9\theta_D}{8}\left(\frac{1}{T}-\frac{1}{T_0}\right) + 4log\frac{T}{T_0} \\ +\left(\frac{3}{\theta_D}\right)^3\left[T^3\int_0^{\frac{\theta_D}{T}} x^2 log(1-e^{-x})dx - T_0^3\int_0^{\frac{\theta_D}{T_0}} x^2 log(1-e^{-x})dx\right] \\ -\frac{1}{2}\left(\frac{1}{T}-\frac{1}{T_0}\right)\sum\nolimits_{i=1}^{3N_n-6}\theta_i - \sum\nolimits_{i=1}^{3N_n-6} log\left[\frac{1-exp\left(-\frac{\theta_i}{T}\right)}{1-exp\left(-\frac{\theta_i}{T_0}\right)}\right] \Leftrightarrow \\ \Leftrightarrow log\frac{P_{vap}}{P_0} = \frac{\phi_0}{2k_B}\left(\frac{1}{T}-\frac{1}{T_0}\right) + \frac{9\theta_D}{8}\left(\frac{1}{T}-\frac{1}{T_0}\right) + 4log\frac{T}{T_0} \\ +\left(\frac{3}{\theta_D}\right)^3\left[T^3\int_0^{\infty} x^2 log(1-e^{-x})dx - T_0^3\int_0^{\infty} x^2 log(1-e^{-x})dx\right] \\ -\left(\frac{3}{\theta_D}\right)^3\left[T^3\left(\frac{\theta_D}{T}\right)^3\int_1^{\infty} x^2 log\left(1-e^{-\frac{\theta_D x}{T}}\right)dx - T_0^3\left(\frac{\theta_D}{T_0}\right)^3\int_1^{\infty} x^2 log\left(1-e^{-\frac{\theta_D x}{T_0}}\right)dx\right] \\ -\frac{1}{2}\left(\frac{1}{T}-\frac{1}{T_0}\right)\sum\nolimits_{i=1}^{3N_n-6}\theta_i - \sum\nolimits_{i=1}^{3N_n-6} log\left[\frac{1-exp\left(-\frac{\theta_i}{T}\right)}{1-exp\left(-\frac{\theta_i}{T_0}\right)}\right]\end{aligned}$$

If we now replace the first set of integrals with the corresponding values,

$$log\frac{P_{vap}}{P_0}=\frac{\phi_0}{2k_B}\left(\frac{1}{T}-\frac{1}{T_0}\right)+\frac{9\theta_D}{8}\left(\frac{1}{T}-\frac{1}{T_0}\right)+4log\frac{T}{T_0}$$
$$+\left(\frac{3}{\theta_D}\right)^3\left[T_0^3\sum_{n=1}^{+\infty}\frac{2}{n^4}-T^3\sum_{n=1}^{+\infty}\frac{2}{n^4}\right]+27\left[\int_1^{\infty}x^2log\left(\frac{1-e^{-\frac{\theta_D x}{T_0}}}{1-e^{-\frac{\theta_D x}{T}}}\right)dx\right]$$
$$-\frac{1}{2}\left(\frac{1}{T}-\frac{1}{T_0}\right)\sum_{i=1}^{3N_n-6}\theta_i-\sum_{i=1}^{3N_n-6}log\left[\frac{1-exp\left(-\frac{\theta_i}{T}\right)}{1-exp\left(-\frac{\theta_i}{T_0}\right)}\right]$$

The series $\sum_{n=1}^{+\infty}\frac{1}{n^4}$ is a particular value for the Riemmann $\zeta$ function, whose value is also known. By making such replacement, we finally reach

$$\begin{aligned}log\frac{P_{vap}}{P_0}&=\frac{\phi_0}{2k_B}\left(\frac{1}{T}-\frac{1}{T_0}\right)+\frac{9\theta_D}{8}\left(\frac{1}{T}-\frac{1}{T_0}\right)+4log\frac{T}{T_0}\\&+\frac{3\pi^4}{5\theta_D^3}\left[T_0^3-T^3\right]+27\left[\int_1^{\infty}x^2log\left(\frac{1-e^{-\frac{\theta_D x}{T_0}}}{1-e^{-\frac{\theta_D x}{T}}}\right)dx\right]\\&-\frac{1}{2}\left(\frac{1}{T}-\frac{1}{T_0}\right)\sum_{i=1}^{3N_n-6}\theta_i-\sum_{i=1}^{3N_n-6}log\left[\frac{1-exp\left(-\frac{\theta_i}{T}\right)}{1-exp\left(-\frac{\theta_i}{T_0}\right)}\right]\end{aligned}\tag{40}$$

If we now take as approximation $\frac{T}{T_0}\approx 1$ and $\frac{1-exp\left(-\frac{a}{T}\right)}{1-exp\left(-\frac{a}{T_0}\right)}\approx 1$ where $a$ is any constant, then we obtain

$$log\frac{P_{vap}}{P_0}=\frac{1}{2}\left(\frac{\phi_0}{k_B}+\frac{9\theta_D}{4}-\sum_{i=1}^{3N_n-6}\theta_i\right)\left(\frac{1}{T}-\frac{1}{T_0}\right)+\frac{3\pi^4}{5\theta_D^3}\left[T_0^3-T^3\right]$$

The last term on the right-hand-side deserves further analysis. If both temperatures are close enough, then this term will have a negligible contribution. This can always be ensured by careful selection of the reference temperature $T_0$. However, carefully choosing the reference temperature is not strictly necessary if we consider low enough temperatures, such that the last term in the last equation will have a negligible contribution. This restriction to low temperatures is necessary for $p_0V << A$. Therefore, we can write

$$log\frac{P_{vap}}{P_0}=\frac{1}{2}\left(\frac{\phi_0}{k_B}+\frac{9\theta_D}{4}-\sum_{i=1}^{3N_n-6}\theta_i\right)\left(\frac{1}{T}-\frac{1}{T_0}\right)\tag{41}$$

Direct comparison of this expression with the Clausius-Clapeyron equation yields the enthalpy of sublimation for our solid:

$$\Delta_{sub}h=\frac{1}{2}\left(R\sum_{i=1}^{3N_n-6}\theta_i-N_A\phi_0-\frac{9R\theta_D}{4}\right)\tag{42}$$

Note that this expression is only valid for low enough temperatures.

Alternatively, we can derive a temperature dependent heat of sublimation by direct calculation of the derivative of the logarithm of the vapour pressure with respect to temperature. Then

$$\frac{dlogP_{vap}}{dT} = \frac{d}{dT}\left[\frac{\phi_0}{2k_BT} + \frac{9\theta_D}{8T} + 9\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} x^2 log\left(1-e^{-x}\right)dx + 4log(k_BT)\right]$$

$$+\frac{d}{dT}\left[\frac{3}{2}log\left(\frac{2\pi m}{h^2}\right) - \frac{1}{2}\sum_{i=1}^{3N_n-6}\frac{\theta_i}{T} - \sum_{i=1}^{3N_n-6} log\left(1-exp\left[-\frac{\theta_i}{T}\right]\right) + \frac{1}{2}log\pi\right]$$

$$+\frac{d}{dT}\left[-log\sigma + \frac{1}{2}\sum_{i=1}^{3} log\left(\frac{8\pi^2 I_j}{h^2}\right)\right] \Leftrightarrow$$

$$\Leftrightarrow \frac{dlogP_{vap}}{dT} = -\frac{1}{T^2}\left[\frac{1}{2}\left(-\sum_{i=1}^{3N_n-6}\theta_i + \frac{\phi_0}{k_B} + \frac{9\theta_D}{4}\right)\right] + \frac{4}{T} + \sum_{i=1}^{3N_n-6}\frac{\theta_i}{T^2}\frac{1}{exp\left(\frac{\theta_i}{T}\right)-1}$$

$$+\frac{27T^2}{\theta_D^3}\left[\int_0^{+\infty} x^2 log\left(1-e^{-x}\right)dx - \int_{\frac{\theta_D}{T}}^{+\infty} x^2 log\left(1-e^{-x}\right)dx\right]$$

$$+\frac{9T^3}{\theta_D^3}\frac{d}{dT}\left[\int_0^{+\infty} x^2 log\left(1-e^{-x}\right)dx - \int_{\frac{\theta_D}{T}}^{+\infty} x^2 log\left(1-e^{-x}\right)dx\right] \Leftrightarrow$$

$$\Leftrightarrow \frac{dlogP_{vap}}{dT} = \frac{1}{T^2}\left[\frac{1}{2}\left(\sum_{i=1}^{3N_n-6}\theta_i - \frac{\phi_0}{k_B} - \frac{9\theta_D}{4}\right) + 4T + \sum_{i=1}^{3N_n-6}\frac{\theta_i}{exp\left(\frac{\theta_i}{T}\right)-1}\right]$$

$$+\frac{27T^2}{\theta_D^3}\left[-2\zeta(4) - \left(\frac{\theta_D}{T}\right)^3 \int_1^{+\infty} x^2 log\left(1-e^{-\frac{\theta_D x}{T}}\right)dx\right]$$

$$-9T^3\frac{d}{dT}T^{-3}\int_1^{+\infty} x^2 log\left(1-e^{-\frac{\theta_D x}{T}}\right)dx \Leftrightarrow$$

$$\Leftrightarrow \frac{dlogP_{vap}}{dT} = \frac{1}{T^2}\left[\frac{1}{2}\left(\sum_{i=1}^{3N_n-6}\theta_i - \frac{\phi_0}{k_B} - \frac{9\theta_D}{4}\right) + 4T + \sum_{i=1}^{3N_n-6}\frac{\theta_i}{exp\left(\frac{\theta_i}{T}\right)-1}\right]$$

$$-\frac{27T^2}{\theta_D^3}\left[\frac{\pi^4}{45} + \left(\frac{\theta_D}{T}\right)^3 \int_1^{+\infty} x^2 log\left(1-e^{-\frac{\theta_D x}{T}}\right)dx\right]$$

$$+\frac{27}{T}\int_1^{+\infty} x^2 log\left(1-e^{-\frac{\theta_D x}{T}}\right)dx - 9\frac{d}{dT}\int_1^{+\infty} x^2 log\left(1-e^{-\frac{\theta_D x}{T}}\right)dx \Leftrightarrow$$

$$\Leftrightarrow \frac{dlogP_{vap}}{dT} = \frac{1}{T^2}\left[\frac{1}{2}\left(\sum_{i=1}^{3N_n-6}\theta_i - \frac{\phi_0}{k_B} - \frac{9\theta_D}{4}\right) + 4T + \sum_{i=1}^{3N_n-6}\frac{\theta_i}{exp\left(\frac{\theta_i}{T}\right)-1}\right]$$

$$-\frac{27\pi^4 T^2}{45\theta_D^3} + 9\int_1^{+\infty} x^3 \frac{\theta_D}{T^2}\frac{e^{-\frac{\theta_D x}{T}}}{1-e^{-\frac{\theta_D x}{T}}}dx$$

If we now transform back the integral

$$\frac{dlogP_{vap}}{dT} = \frac{1}{T^2}\left[\frac{1}{2}\left(\sum_{i=1}^{3N_n-6}\theta_i - \frac{\phi_0}{k_B} - \frac{9\theta_D}{4}\right) + 4T + \sum_{i=1}^{3N_n-6}\frac{\theta_i}{exp\left(\frac{\theta_i}{T}\right)-1}\right] \\ -\frac{27\pi^4T^2}{45\theta_D^3} + 9\frac{T^2}{\theta_D^3}\int_{\frac{\theta_D}{T}}^{+\infty} x^3\frac{e^{-x}}{1-e^{-x}}dx \Leftrightarrow$$

$$\Leftrightarrow \frac{dlogP_{vap}}{dT} = \frac{1}{T^2}\left[\frac{1}{2}\left(\sum_{i=1}^{3N_n-6}\theta_i - \frac{\phi_0}{k_B} - \frac{9\theta_D}{4}\right) + 4T + \sum_{i=1}^{3N_n-6}\frac{\theta_i}{exp\left(\frac{\theta_i}{T}\right)-1}\right] \\ -9\frac{T^2}{\theta_D^3}\int_0^{\frac{\theta_D}{T}} x^3\frac{e^{-x}}{1-e^{-x}}dx$$

Comparing the latter expression with Clausius-Clapeyron's

$$\frac{d}{dT}logP_{vap} = \frac{\Delta_{sub}h}{RT^2} \tag{43}$$

We obtain

$$\Delta_{sub}h = \frac{R}{2}\sum_{i=1}^{3N_n-6}\theta_i - \frac{\phi_0 N_A}{2} - \frac{9R\theta_D}{8} + 4RT + R\sum_{i=1}^{3N_n-6}\frac{\theta_i}{exp\left(\frac{\theta_i}{T}\right)-1} \\ -\frac{9RT^4}{\theta_D^3}\int_0^{\frac{\theta_D}{T}} x^3\frac{e^{-x}}{1-e^{-x}}dx \tag{44}$$

This expression is more general than the previous one, as it includes now three temperature dependent terms.

As might be seen, many of the thermodynamic quantities can be obtained once some non-trivial integrals are solved. The integrals involved in the calculation of the heat capacity and internal energy are commonly known as Debye integrals. Their solution was unknown for many years and therefore only approximated solutions were used. Now-a-days it is known that these integrals are solved analytically by polylogarithm functions (*3*). For the heat capacity integral we have

$$\int_0^t x^{k+1}\frac{e^x}{(1-e^x)^2}dx = (k+1)!\zeta(k+1) - \sum_{m=0}^{k+1}\frac{(k+1)!}{m!}x^m Li_{k-m+1}(e^{-t}) \tag{45}$$

where $Li_s$ is the polylogarithm function and $\zeta$ is the Riemann zeta-function (previously mentioned). Since both $\theta_D$ and $T$ are temperatures, these values are always positive. Therefore, the arguments to the polylogarithm are always positive, which means that the argument to the polylogarithm involved in the calculation of heat capacities is a positive number smaller than one. We therefore expect no problem in the calculation of heat capacities. For the other Debye integral,

$$\int_0^t x^k \frac{e^{-x}}{1-e^{-x}} dx = (-1)^k k! \zeta(k+1) - \sum\nolimits_{m=0}^{k} \left[ (-1)^{k-m+1} \frac{k!}{m!} x^m Li_{k-m+1}(e^t) - \frac{t^{k+1}}{k+1} \right] \tag{46}$$

the argument to the polylogarithm can be problematic, since $Li_s(x)$ is complex for $x > 1$. To overcome this difficulty, we approximate the integral by its low temperature value:

$$lim_{T \to 0} \int_0^{\frac{\theta_D}{T}} x^3 \frac{e^{-x}}{1-e^{-x}} dx = \int_0^{+\infty} x^3 \frac{e^{-x}}{1-e^{-x}} dx = \frac{\pi^4}{15} \tag{47}$$

Finally, there is still the integral involved in the calculation of the Helmoltz energy. This integral can be calculated using integrals involved in the calculation of the overlap matrix in electronic structure calculations. Using the series representation of the logarithm

$$log(1-x) = -\sum\nolimits_{n=1}^{+\infty} \frac{x^n}{n} \tag{48}$$

then

$$x^m log(1-e^{-x}) = -\sum\nolimits_{n=1}^{+\infty} \frac{x^m e^{-nx}}{n} \tag{49}$$

and the integral we want to solve becomes

$$\int_0^t x^m log(1-e^{-x}) dx = -\sum\nolimits_{n=1}^{+\infty} \frac{1}{n} \int_0^t x^m e^{-nx} dx \tag{50}$$

From the Atomic Orbital (AO)-integrals we know that

$$\int_0^{+\infty} x^m e^{-nx} dx = \frac{m!}{n^{m+1}} \tag{51}$$

$$\int_1^{+\infty} x^m e^{-nx} dx = A_m(n) \tag{52}$$

and

$$\int_a^{+\infty} f(x) dx = a \int_1^{+\infty} f(ax) dx \tag{53}$$

Placing all results together yields finally

$$\int_0^t x^m log(1-e^{-x}) dx = \sum\nolimits_{n=1}^{+\infty} \frac{1}{n} \left[ t^{m+1} A_m(nt) - \frac{m!}{n^{m+1}} \right] \tag{54}$$

With the integrals specified, we have all quantities required for the calculation of thermodynamic properties of crystals.

# Bibliography

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