Statistical Physics Computer Lab. #3
Einstein and Debye Solids

We study Einstein's model (1907) of a crystal. Start from the formula for the energy: $U=3Nh_{bar}\omega/2 + 3Nh_{bar}\omega/(\exp(h_{bar}\omega/kT) - 1)$. Then we determine the heat capacity: $C = dU/dT$ by using the symbolic processor of MATHCAD. The energy per atom u expressed in units of k_B. The Einstein temperature T_E stands for $h_{bar}\omega/k_B$.

$$u(T, T_E) := \frac{3 \cdot T_E}{2} + \frac{3 \cdot T_E}{e^{\frac{T_E}{T}} - 1}$$

Next we differentiate u with respect to T by using the symbolic processor.

$$\frac{d}{dT} u(T, T_E) \rightarrow 3 \cdot \frac{T_E^{\,2}}{\left[\left(\exp\left(\frac{T_E}{T}\right) - 1\right)^2 \cdot T^2\right]} \cdot \exp\left(\frac{T_E}{T}\right)$$

$$c(T, T_E) := 3 \cdot \frac{T_E^{\,2}}{\left[\left(\exp\left(\frac{T_E}{T}\right) - 1\right)^2 \cdot T^2\right]} \cdot \exp\left(\frac{T_E}{T}\right)$$

This is the heat capacity per atom in units of k_B.

The entropy can be obtained by symbolic integration starting from $c = Tds/dT$.

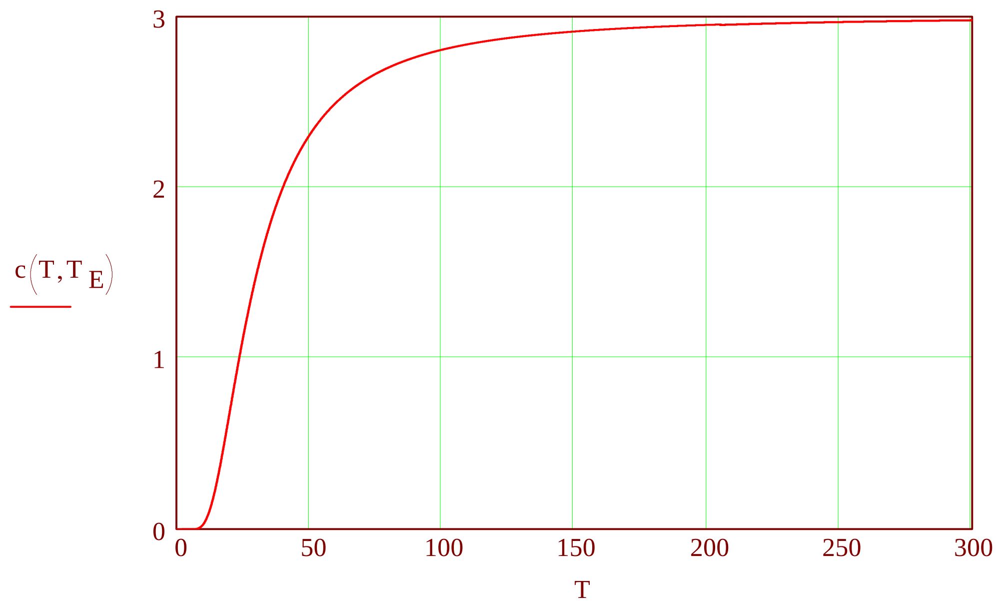
$$\int \frac{c(T, T_E)}{T}\, dT \rightarrow -3 \cdot \ln\left(\exp\left(\frac{T_E}{T}\right) - 1\right) + 3 \cdot \ln\left(\exp\left(\frac{T_E}{T}\right)\right) \cdot \frac{\exp\left(\frac{T_E}{T}\right)}{\left(\exp\left(\frac{T_E}{T}\right) - 1\right)}$$

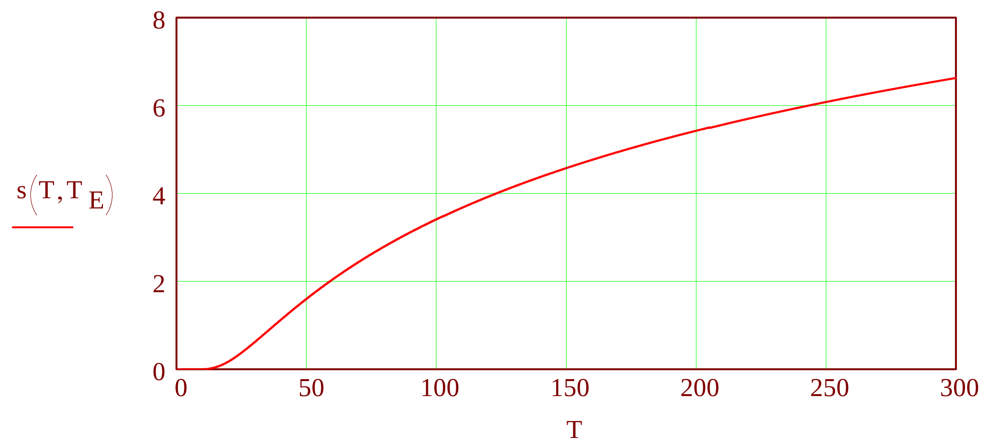
By invoking the third law of Thermodynamics, s = 0 at T = 0, we get the entropy, in units of k_B :

$$s(T, T_E) := -3\cdot\ln\left(\exp\left(\frac{T_E}{T}\right) - 1\right) + 3\cdot\ln\left(\exp\left(\frac{T_E}{T}\right)\right)\cdot\frac{\exp\left(\frac{T_E}{T}\right)}{\left(\exp\left(\frac{T_E}{T}\right) - 1\right)}$$

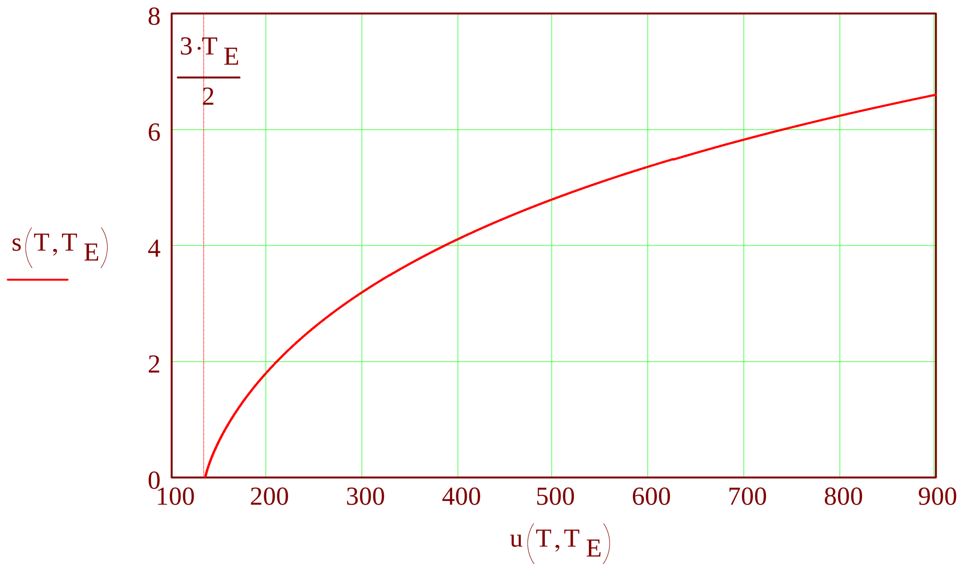
$T_E := 90$ **This the Einstein temperature for lead in kelvins.**

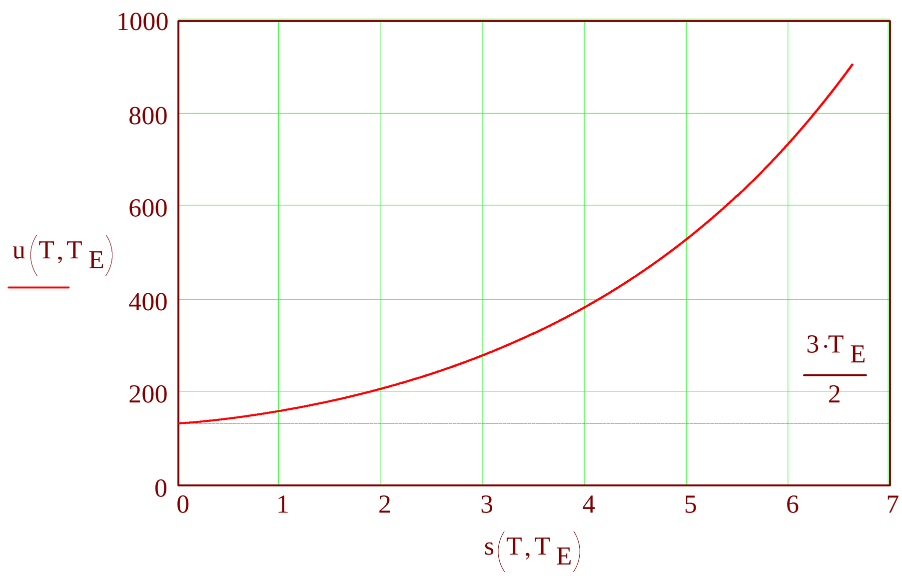
$T := .3, .35 .. 300$





Next we graph s vs. u . Note that s(u) is a concave function as required by thermodynamic stability (2'nd law). Equivantley, u is a convex function of s. Also note that the slope of the graph u vs s approaches zero as s approaches s. Explain this.

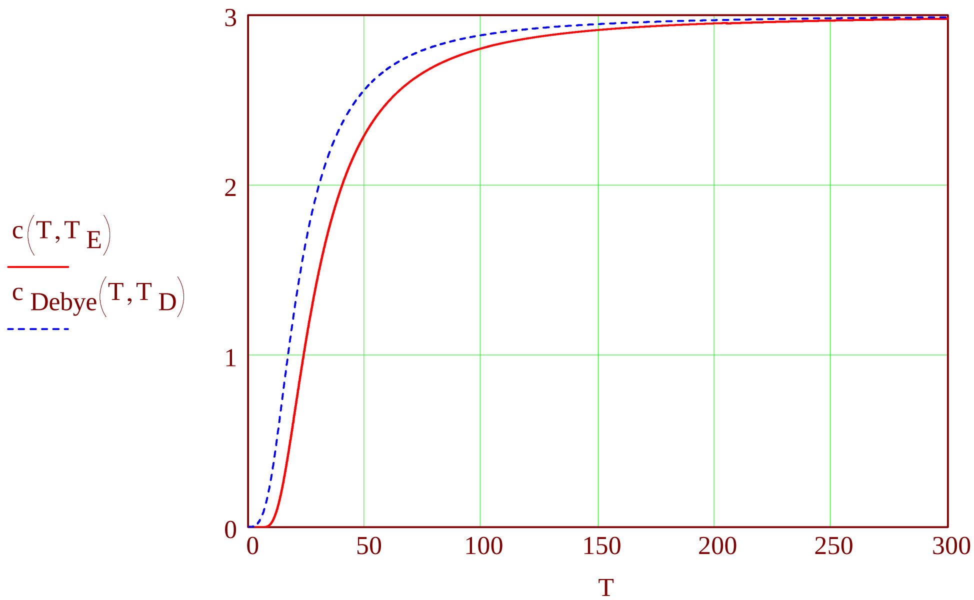




Although the Einstein model of a crystal gives general agreement with experiment, it is not in accord with very low temperature data. While the experimental data go to zero as T^3 the model predicts a faster, exponential dependence. A few years after Einstein's prediction, the Dutch chemist Peter Debye proposed a model treating a crystal as an elastic solid.

$T_D := 90$

$$c_{Debye}(T, T_D) := 9 \cdot \left(\frac{T}{T_D}\right)^3 \cdot \int_0^{\frac{T_D}{T}} y^4 \cdot \frac{e^y}{\left(e^y - 1\right)^2}\,dy$$



The Debye theory predicts the low-temperature T^3 behaviour. Indeed if $T << T_D$ we can take the upper limit of the integral to be infinity. We use Symbolics, Evaluate Floating point

$$\int_0^{\infty} y^4 \cdot \frac{e^y}{\left(e^y - 1\right)^2}\, dy$$

25.975757609067316596

We check that this value is $4\pi^4/15$:

$$\frac{4\cdot\pi^4}{15} = 25.9757576090673$$

In conclusion at low T: $C_V/Nk_B = 12\pi^4/5(T/T_D)^3$.

$$T := .1, .2 .. \frac{T_D}{10}$$