# MATH327: Statistical Physics, Spring 2022

Tutorial comments — Einstein solid

The heat capacity for a solid of non-interacting spins is

$$c_v = \frac{\partial E}{\partial T} = -\beta^2 \frac{\partial}{\partial \beta}\left[-NH\tanh(\beta H)\right] = \frac{N\beta^2 H^2}{\cosh^2(\beta H)},$$

which is non-negative, as required. Clearly when $H = 0$ the heat capacity vanishes exactly, but even with $H > 0$ this prediction is qualitatively different than the experimental data. For low temperatures $\beta \to \infty$ our result vanishes exponentially rapidly. While the experimental heat capacities also vanish as $T \to 0$ (this is sometimes called the **third law of thermodynamics**), we will see that this happens polynomially rather than exponentially. The big problem appears at high temperatures, $\beta \to 0$, where $\cosh(\beta H) \to 1$ and $c_v \propto \beta^2$ vanishes quadratically in the inverse temperature, rather than approaching the roughly constant value measured experimentally. The full behaviour vs. T/H is shown below.
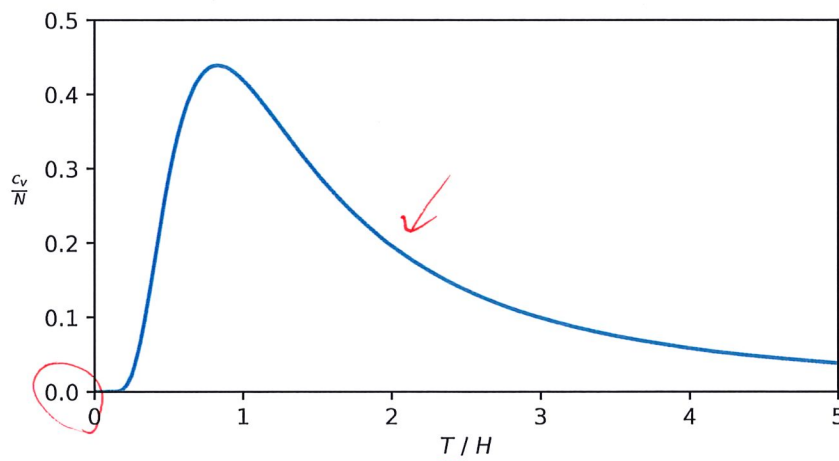
Moving on to the Einstein solid, there is an elegant way of computing the total number of micro-states, by viewing the K units of energy as indistinguishable balls to be divided among N *distinguishable* boxes representing the oscillators that can be identified by their location in the solid. We can represent each unique division of balls into boxes by drawing a sequence of K dots separated by $N - 1$ walls between the boxes. For example, $\bullet\bullet\bullet|\bullet||\bullet|\bullet\bullet\bullet\bullet\bullet|\bullet$ corresponds to $N = 6$ boxes with $k = (3, 1, 0, 1, 5, 1)$ units of energy. The number of different sequences is given by the possible ways of choosing K of these $K + N - 1$ symbols to be balls, which fixes the remaining $N - 1$ walls. In other words,

$$M = \binom{K + N - 1}{K} = \frac{(K + N - 1)!}{K!\,(N - 1)!}.$$

For a minimal system with $N = 3$ oscillators, we can explicitly list all possible micro-states $k = (k_1, k_2, k_3)$ when $K = \sum_i k_i$ is reasonably small. For $K = 0$, there

is only $\binom{2}{0} = 1$ possibility, $k = (0,0,0)$. $K = 1$ is equally easy,

$$k = (1,0,0) \qquad\qquad (0,1,0) \qquad\qquad (0,0,1)$$

with $M = 3$ matching the $\binom{3}{1}$ from our computation above. With $K = 2$ we finally get behaviour distinct from the spin system,

$$
\begin{aligned}
k = (2,0,0) & \qquad (0,2,0) & \qquad (0,0,2) \\
(1,1,0) & \qquad (1,0,1) & \qquad (0,1,1)
\end{aligned}
$$

with $M = 6 = \binom{4}{2} = \frac{4!}{2^2}$. Finally, when $K = 3$ we have

$$
\begin{aligned}
k = (3,0,0) & \quad (0,3,0) & \quad (0,0,3) & & & (1,1,1) \\
(2,1,0) & \quad (2,0,1) & \quad (0,2,1) & \quad (1,2,0) & \quad (1,0,2) & \quad (0,1,2)
\end{aligned}
$$

and $M = 10 = \binom{5}{3} = \frac{5!}{3 \cdot 2}$.

Returning to our usual domain $K \gg 1$ and $N \gg 1$, we can approximate

$$M = \frac{(K+N-1)!}{K!\,(N-1)!} \approx \frac{(K+N)!}{K!\,N!}$$

with entropy

$$S = \log M \approx (K+N)\log(K+N) - K\log K - N\log N,$$

where the linear terms from $\log n \approx n\log n - n$ all cancel out.

To determine the temperature we need to consider the derivative with respect to the energy $E = K\hbar\omega$,

$$
\begin{aligned}
\frac{1}{T} = \frac{\partial S}{\partial E} &= \frac{1}{\hbar\omega}\frac{\partial}{\partial K}\left[(K+N)\log(K+N) - K\log K - N\log N\right] \\
&= \frac{1}{\hbar\omega}\left[\log(K+N) + 1 - \log K - 1\right] = \frac{1}{\hbar\omega}\log\left(1 + \frac{N}{K}\right)
\end{aligned}
$$

Rearranging, the temperature is

$$T = \frac{\hbar\omega}{\log\left(1 + \frac{N}{K}\right)} = \frac{\hbar\omega}{\log\left(1 + \frac{N\hbar\omega}{E}\right)} \geq 0$$

Because both N and K are large positive numbers, $\log\left(1 + \frac{N}{K}\right) > \log(1) = 0$ and we find a 'natural' positive temperature. This reflects the fact that larger amounts of energy 'open up' a larger number of micro-states for the Einstein solid, in contrast to the spin system we considered in Section 2.3.

It is now straightforward to invert the result above to express the energy as a function of the temperature,

$$\log\left(1 + \frac{N\hbar\omega}{E}\right) = \frac{\hbar\omega}{T} = \beta\hbar\omega \quad\Longrightarrow\quad \frac{N\hbar\omega}{E} = e^{\beta\hbar\omega} - 1 \quad\Longrightarrow\quad E = \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}.$$

Taking the derivative, we obtain the heat capacity

$$c_v = \frac{\partial E}{\partial T} = -\beta^2 \frac{\partial}{\partial \beta} \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1} = \beta^2 \frac{N\hbar\omega}{\left(e^{\beta\hbar\omega} - 1\right)^2} \hbar\omega e^{\beta\hbar\omega} = \frac{Nx^2 e^x}{\left(e^x - 1\right)^2}, \qquad (1)$$

changing variables to $x = \beta\hbar\omega = \hbar\omega/T$.

To compare this with the experimental data, we should again consider the low- and high-temperature limits, just as we did for the simpler spin system above. As $T \to 0$ and $x \to \infty$, we again find a vanishing heat capacity, as required by the third law of thermodynamics:

$$\frac{c_v}{N} = \frac{x^2 e^x}{\left(e^x - 1\right)^2} \approx \frac{x^2 e^x}{e^{2x}} = \frac{x^2}{e^x} \to 0.$$

As $T \to \infty$ and $x \to 0$, we can expand the exponentials,

$$\frac{c_v}{N} = \frac{x^2 e^x}{\left(e^x - 1\right)^2} \to \frac{x^2(1)}{(x)^2} = 1.$$

Rather than vanishing, the heat capacity for the Einstein solid approaches a constant at high temperatures, in much better agreement with experiments compared to the spin system considered above.

Although the asymptotic limits above reveal that the Einstein solid heat capacity vanishes exponentially quickly at low temperatures, some more work is needed to see how it approaches that high-temperature constant. We need to expand the exponentials to higher orders, making sure to retain all terms that appears with a given power of x *in the full expression, not just in the denominator*:

$$\frac{c_v}{N} = \frac{x^2 \left[1 + x + \frac{1}{2}x^2 + \cdots\right]}{\left(x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \cdots\right)^2} = \frac{1 + x + \frac{1}{2}x^2 + \cdots}{\left(1 + \frac{1}{2}x + \frac{1}{6}x^2 + \cdots\right)^2}$$

$$= \frac{1 + x + \frac{1}{2}x^2 + \cdots}{1 + \left[x + \left(\frac{1}{4} + \frac{2}{6}\right)x^2 + \cdots\right]}$$

$$= \left(1 + x + \frac{x^2}{2}\right)\left[1 - \left(x + \frac{7x^2}{12}\right) + \left(x + \frac{7x^2}{12}\right)^2\right] + \mathcal{O}\left(x^3\right)$$

$$= 1 + x(1 - 1) + x^2\left(\frac{1}{2} - 1 - \frac{7}{12} + 1\right) + \mathcal{O}\left(x^3\right)$$

$$= 1 - \frac{1}{12}\frac{\hbar^2\omega^2}{T^2} + \mathcal{O}\left(\frac{\hbar^3\omega^3}{T^3}\right)$$

So we find that deviations from the high-temperature limit vanish $\propto 1/T^2$ at leading order. The figure on the next page shows the full result vs. $T/(\hbar\omega)$, which at least qualitatively resembles the experimental data that motivated this work. (To quote Murray Gell-Mann, "In our field it is customary to put theory and experiment on the same piece of paper", but I will leave that as an exercise.)

$\sim 1/T^2$
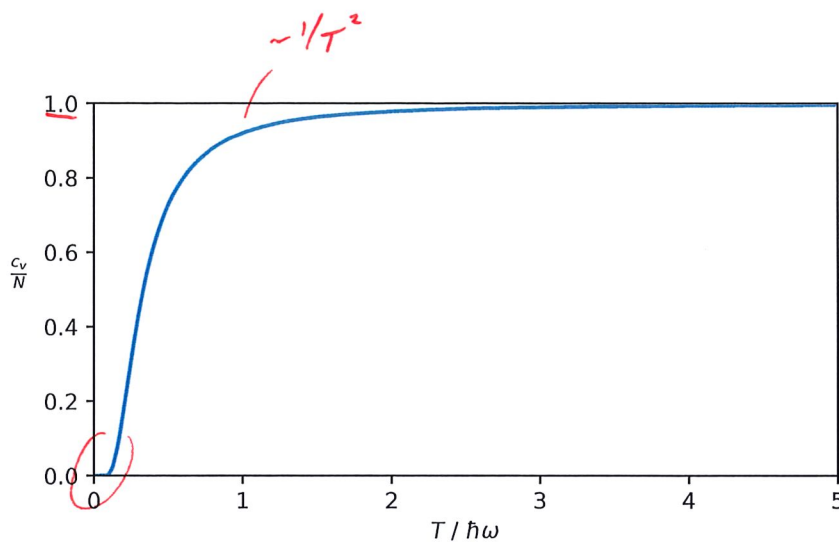
However, there is still room for improvement. As mentioned above, heat capacities for real materials vanish polynomially in T, as opposed to the exponential dependence we have now derived for both the spin system and the Einstein solid. This is demonstrated by the figure below, which shows c_v/T varying linearly with T^2 at low temperatures $T \lesssim 4$ K, and (for these three metals) approaching a non-zero constant value at absolute zero:

$$\frac{c_v}{T} = \alpha + \gamma T^2 \qquad \Longrightarrow \qquad c_v = \alpha T + \gamma T^3.$$
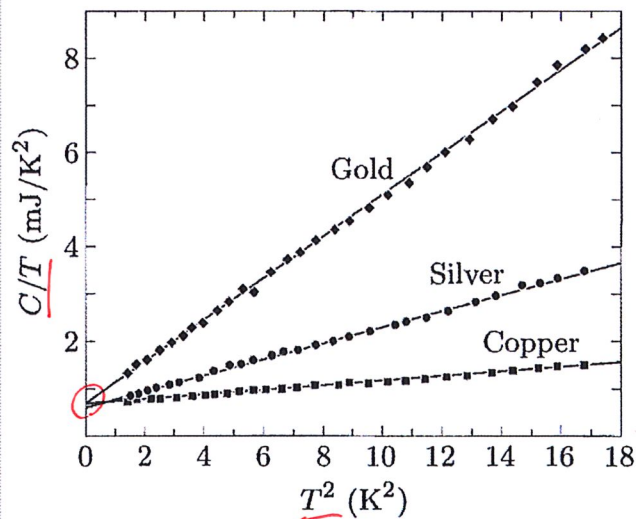

We have actually already derived the linear piece in the supplemental Section 8.8 — this comes from the (fermionic) electrons in these metals, treated as a low-temperature ideal quantum gas. Our calculations identify $\alpha = N\pi^2/(2E_F)$, providing a means to measure the Fermi energy of this electron gas.

The cubic dependence on T is also related to work we have done, though less directly. The main problem with the Einstein solid as a model of real materials

is that it ignores interactions between different oscillators. Recall that each oscillator is attached to two atoms, and assigned with holding those atoms in place in the solid. If one of these atoms starts to move out of position, the oscillator exerts a force to restore it. This in turn requires an equal and opposite force to be exerted on the oscillator, which is passed along to the other atom on the other side of the oscillator — and then on to the other oscillators that hold that second atom in place.

Remarkably, it is still possible to model the collective motion of atoms in a solid in terms of non-interacting degrees of freedom — this produces the **Debye** theory of solids (named after Peter Debye), which provides an important foundation for modern solid-state physics. As illustrated by the figure below (from Section 7.5 of Schroeder's *Introduction to Thermal Physics*, which discusses this approach in detail), this motion can be described in terms of propagating waves — called **phonons** — that are similar in some ways to photons. However, there are some differences in the details, the most important of which is that phonons have a maximum frequency (i.e., minimum wavelength) proportional to $\sqrt[3]{N}$ where N is now the number of atoms in the solid, corresponding to $3N$ oscillators in three dimensions.
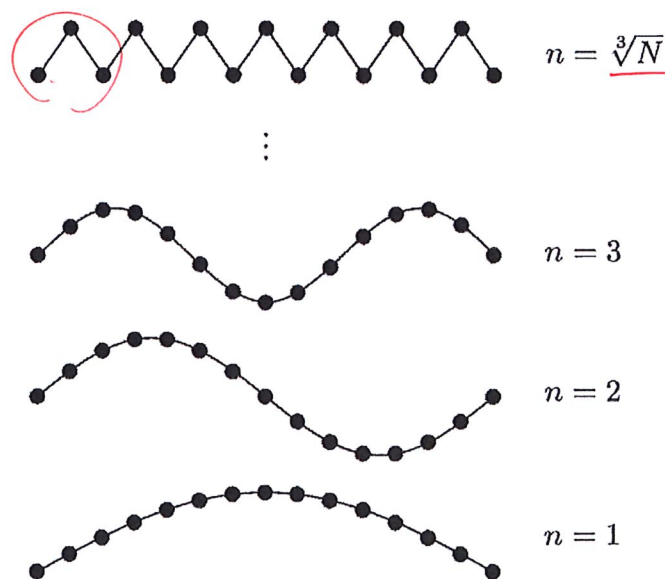
If we adapt our computation of the photon gas energy density (from the start of Section 8.3) to the case of phonons, we end up with an integral of the same functional form, but now with a high-frequency cutoff:

$$\frac{\langle E \rangle_D}{V} \propto \int_0^{\omega_{\text{max}}} \frac{\omega^3}{e^{\beta \hbar \omega} - 1} \, d\omega \propto T^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} \, dx,$$

making the same substitution $x = \beta \hbar \omega = \hbar \omega / T$. Here the constant $T_D \propto \sqrt[3]{N/V}$ is known as the Debye temperature.

At temperatures high relative to T_D, the upper bound is $T_D/T \ll 1$ and x is very small throughout the entire range of the integral. Therefore we can approximate

$$\langle E \rangle_D \propto VT^4 \int_0^{T_D/T} \frac{x^3}{x} \, dx \propto VT^4 \left(\frac{T_D}{T} \right)^3 \propto (VT_D^3)T \propto NT \qquad \text{for} \quad T \gg T_D,$$

producing a constant heat capacity, just as we found for the Einstein solid. (In fact, if we were to compute all the constant factors, we would derive exactly the same result $c_v/(3N) = 1$.)

At low temperatures, $T \ll T_D$, the Debye model succeeds where Einstein's fails. With $T_D/T \gg 1$, we can approximate the integral as the full $I_4 = \Gamma(4)\zeta(4) = \pi^4/15$ from page 111. This is just another constant factor, leaving

$$\langle E \rangle_D \propto VT^4 \qquad \Longrightarrow \qquad c_v \propto T^3 \qquad \text{for} \quad T \ll T_D,$$

correctly reproducing experimental data.