Specific Heat of a Metallic Solid

It is an experimental observation that for a solid the specific heat is

\[ c(T) = \gamma T + \alpha T^3 \]

This is usually emphasized graphically by plotting \( \frac{c(T)}{T} \) vs. \( T^2 \)

\[ \frac{c(T)}{T} = \gamma + \alpha T^2 \]

Our goal is to understand the \( \alpha T^3 \) contribution.

We will come back to \( \gamma T \) after discussing electron motion in a metal.
Specific heat definition

\[ C = \frac{d\langle E \rangle}{dT} \]

Increase \( T \)
eg particles more
fast, more KE

Alternate view \[ d\langle E \rangle = C \, dT \]

\( \Delta \) how much
\( \Delta \) does energy
\( \Delta \) change in temperature?

\( \Delta \) charge

Physics is full of response functions

\[ \chi = \frac{d\langle M \rangle}{dB} \] magnetoe susceptibility

\[ d\langle M \rangle = \chi \, dB \]

\[ dI = \Sigma dV \quad (\text{Conductivity } \Sigma = \frac{1}{R}) \]

\[ d\Phi = \Sigma dV \]

At a phase transition the response function often diverges.

If a system is about to become a spontaneous magnet

(\( M \neq 0 \) even for \( B = 0 \)) then \( \chi \) is enormous
Specific heat of ideal gas?

\[ \langle E \rangle = \frac{3}{2} N k_B T \]

\[ C = \frac{3}{2} N k_B \quad A - T \text{ independent constant} \]

Basic principle/rule of Statistical Mechanics (Boltzmann)
Brief Introduction to Statistical Mechanics

0. Purpose: These notes are intended to provide a very quick introduction to Statistical Mechanics. The field is of course far more vast than could be contained in these few pages. However, what is described here are some of the basic equations and examples of the field that everyone should know.

1. Introduction: In classical mechanics the goal is to compute the trajectory of a particle, that is, the position as a function of time $x(t)$. This is accomplished by determining the forces acting on the particle $F(x)$ and solving Newton’s equation

$$F(x) = ma = m\frac{d^2x}{dt^2}$$

For example, for a constant force $F_0$ one gets uniformly accelerated motion,

$$x(t) = x_0 + v_0 t + \frac{F_0 t^2}{2m}.$$ 

For the simple harmonic oscillator $F(x) = -kx = -m\omega^2x$ (with $\omega$ defined as $\omega = \sqrt{k/m}$) one gets,

$$x(t) = x_0 \cos(\omega t) + \left(\frac{v_0}{\omega}\right) \sin(\omega t).$$

Here $x_0$ and $v_0$ are the initial position and velocity of the particle. Much of classical mechanics boils down to solving a differential equation (Newton’s 2nd law $F = ma$).

Because of the uncertainty principle, quantum mechanics is forced to take a different approach. We cannot compute the position $x(t)$ of a particle. Instead the best we can do is compute the “wave function” $\Psi(x,t)$ from which we can determine the probability $|\Psi(x,t)|^2$ that the particle will be between $x$ and $x + dx$ at time $t$. The wave function is obtained by solving a partial differential equation, the Schroedinger equation. From the probability we can compute average quantities, like the average position, $\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi(x,t)|^2 dx$.

Statistical mechanics is like quantum mechanics in that we abandon the idea of computing the trajectory $x(t)$. This is not because the uncertainty principle forbids us from doing it, but instead because with many particles present, it would be very hard. In addition, we do not really want to know the individual trajectories of the $10^{23}$ oxygen molecules inside a container. We want to know things like pressure, which are averaged properties ($P$ is obtained as an average of all the collisions of the molecules with the side of the container.)

2. Boltzmann’s Rule: Consider a system that can be in different states $s$ with energies $E(s)$. Boltzmann stated a simple rule for the probability the system chooses to be in state $s$:

$$P(s) = \frac{1}{Z} e^{-E(s)/k_B T}.$$ 

Here $k_B = 1.38 \times 10^{-23} J/\circ K$ is Boltzmann’s constant. The partition function $Z$ is chosen so that the probabilities all add up to one, similar to the normalization rule in quantum mechanics that requires $\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$. 

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state. On the contrary, high temperature means all states are equally likely. This can be seen mathematically by noting that if $T = \infty$ then $E(s)/k_B T = 0$ for all the states $s$. Thus $P(s)$ doesn’t depend on $s$.

We will come back to this example later.

3b. Example Two- A particle moving on the $x$ axis with no potential energy: The state $s$ of the system is described by the position $x$ and momentum $p$. To emphasize this, I write $s = x, p$. We will assume there are walls at $x = 0$ and $x = L$ so that the particle moves just in the interval $0 < x < L$. The momentum obeys $-\infty < p < +\infty$.

If there is no potential energy, $E(s) = p^2/2m$ (only the kinetic energy exists). $E(s)$ does not depend on $x$. According to Boltzmann,

$$P(s) = P(x, p) = \frac{1}{Z} e^{-\beta p^2/2m}.$$

To determine $Z$ we again insist that the sum of $P(s)$ over all states $s$ equals one. In this case, because $x, p$ are continuous variables, what we mean by ‘sum’ is actually ‘integral’.

$$1 = \int_0^L dx \int_{-\infty}^{\infty} dp \frac{1}{Z} e^{-\beta p^2/2m} \quad \text{or} \quad Z = \int_0^L dx \int_{-\infty}^{\infty} dp e^{-\beta p^2/2m}$$

You should memorize the following integrals because they are used all the time in physics:

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad \text{and} \quad \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}.$$

Using these integrals we see that

$$Z = L \sqrt{\frac{2\pi m}{\beta}} = L \sqrt{2\pi mk_B T} \quad \text{and} \quad P(x, p) = \frac{1}{L \sqrt{2\pi mk_B T}} e^{-\beta p^2/2m}.$$

There is a slight complication concerning units which we must mention. Probabilities are dimensionless, so $p$ and $Z$ should have no units. Yet $Z$ has units of $ML^2/T$ from the integrals over $x$ and $p$. Interestingly, this is the same units as Planck’s constant $\hbar$. (Recall the uncertainty relation which tells us $\hbar$ has units of $x$ times $p$.) It turns out that the correct expressions for $Z$ and $p$ have a factor of $\hbar$ to make the units right.

4. Average Energy, Free Energy, and Entropy: The most fundamental quantity we can compute is the average energy of the system, $\langle E \rangle = \sum_s E(s) P(s)$. If the states $s$ are described by a continuous variable the sum is understood to be an integral. A very useful identity is $\langle E \rangle = -\partial \ln Z / \partial \beta$. See Exercise 1.

The specific heat is defined as $C = d\langle E \rangle / dT$.

The free energy $F$ is less familiar. Its definition is $F = k_B T \ln Z$. One useful thing about $F$ is that from $F$ and $\langle E \rangle$ we can get the entropy $S$. The formula is $S = (\langle E \rangle - F)/T$. 

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6. Some Exercises:

[1.] Prove $\langle E \rangle = -\partial \ln Z / \partial \beta$.

[2.] This is a variant of example one. Compute and plot (as functions of temperature), the quantities $P(1), P(2), P(3), \langle E \rangle, C,$ and $S$ for a three state system with $E(1) = 1, E(2) = 3,$ and $E(3) = 4$. Again, set $k_B = 1$. Comment on the physics of the plots, especially what happens to the various quantities at low and high temperature.

[3.] This is a variant of example two. Consider a particle moving in a three dimensional box $0 < x, y, z < L$ with no potential energy. Its state $s$ is labeled by its position $x, y, z$ and momentum $p_x, p_y, p_z$ and the energy is purely kinetic. $E(s) = E(x, y, z, p_x, p_y, p_z) = (p_x^2 + p_y^2 + p_z^2) / 2m$. Compute $Z, \langle E \rangle$, and $C$ as functions of temperature.

[4.] Do problem [3] for a collection of $N$ particles in the box. Assume they are an ‘ideal gas’, that is they do not interact with each other (no potential energy). You might want to start with $N = 2$ particles and see how the algebra compares with $N = 1$.

[5.] Like the entropy $S$, the pressure $P$ can also be obtained from the free energy $F$. The formula is $P = -\partial F / \partial V$. Use this, and the result of Exercise 4, to prove the ideal gas law $PV = Nk_BT$.

[6.] Redo problem [2] assuming there is gravitational potential energy so that $E(s) = E(x, y, z, p_x, p_y, p_z) = (p_x^2 + p_y^2 + p_z^2) / 2m + mgz$. 
Quantum Oscillator

Classical: $E(x,p) = \frac{1}{2} k x^2 + p^2/2m$


$$Z = \int dx \int dp \ e^{-\beta E}$$

$$= \int dx \int dp \ e^{-\frac{1}{2} k \beta x^2 - \frac{p^2}{2m} \beta}$$

$$= \left(\frac{2\pi \hbar}{k \beta}\right)^\frac{1}{2} \left(\frac{2\pi m}{\hbar \beta}\right)^{\frac{3}{2}} \sim \beta^{-1}$$

$$\frac{\partial Z}{\partial \beta} \ln Z = \frac{1}{\beta} = k_B T$$

$$C = k_B$$

$$E_n = (n + \frac{1}{2}) \hbar \omega$$

Amazingly, Quantum Stat Mech same procedure as classical

stat mech! Except extra initial step: solve Schrod eq $n = 0 \rightarrow E_n$

$$Z = \sum_n e^{-\beta E_n} = e^{\frac{-p^2}{2m\hbar^2}} \sum_0 (e^{-\beta \hbar \omega})^n$$

$$\sum_0 x^n = \frac{1}{1-x}$$

DIVOGA
\[ Z = e^{-\beta \frac{1}{2} k_B T} \left( 1 - e^{-\beta k_B T} \right)^{-1} \]

\[ \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \left[ -\beta \frac{1}{2} k_B T - \ln \left( 1 - e^{-\beta k_B T} \right) \right] \]

\[ = \frac{\langle \mathcal{N} \rangle}{k_B T \xi} - \frac{1}{1 - e^{-\beta k_B T}} \xi \]

\[ = \frac{\langle \mathcal{N} \rangle}{k_B T \xi} + \frac{1}{2} \]

\[ \langle E \rangle = k_B T \left[ \langle \mathcal{N} \rangle + \frac{1}{2} \right] \]

\[ \text{Bose-Einstein distribution} \]

Consider high \( T \) (\( \beta \) small) \((k_B T \gg k_B \xi)\)

\[ e^{\beta k_B T} \approx 1 + \beta k_B T \]

\[ \langle E \rangle \approx k_B T \left[ \frac{1}{\beta k_B T} + \frac{1}{2} \right] \]

\[ = \frac{1}{\beta} + \frac{1}{2} \xi k_B T \]

\[ = k_B T \frac{1}{\beta} \]

\[ \Rightarrow k_B T \xi \]

\[ \text{Recover classical limit at high } T \]
We expect quantum → classical
large systems
quantum → classical
\( \hbar \to 0 \)

Did we expect quantum → classical at high \( T \)?

One assumed \( T \beta \) enters so \( T \to 0 \) as \( \beta \to 0 \)
equivalent to \( \hbar \to 0 \)

Another way: Path integral \( e^{-\beta (\hat{A} + \hat{B})} \)

\[ e^{-\beta (\hat{A} + \hat{B})} \neq e^{-\beta \hat{A}} e^{-\beta \hat{B}} \quad \text{if} \quad [\hat{A}, \hat{B}] \neq 0 \]

But if \( \beta \to 0 \) it's a good approximation!

\[ 1 - \beta (\hat{A} + \hat{B}) + \frac{\beta^2}{2} (\hat{A} + \hat{B})^2 \]

\[ 1 - \beta \hat{A} + \frac{\beta^2}{2} \hat{A}^2 \quad 1 - \beta \hat{B} + \frac{\beta^2}{2} \hat{B}^2 \]

Difference?
Move on path integral

\[ e^{\beta H} = e^{-\beta H} \]

\[ \beta = L \epsilon \]

\[ P \xrightarrow{\text{small}} \text{large} \]

\[ \sum = e^{-\epsilon H} e^{-\epsilon H} \ldots e^{-\epsilon H} \]

exact!

\[ \approx e^{\hat{A}} e^{\hat{B}} e^{-\hat{A}} e^{-\hat{B}} \ldots e^{-\hat{A}} e^{-\hat{B}} \]

\[ [\hat{H}, \hat{H}] = 0 \]

\[ \text{if } \hat{H} = \hat{A} + \hat{B} \]

good approximation if \( \epsilon \to 0 \) (large \( L \))

(like Riemann sum \( \sim \) to integral)
So far considered a single harmonic oscillator with frequency $\omega$, but we know we have whole family of oscillators $\omega(q) = \frac{2k}{m}[1 - \cos q]$ in 1 d.

Debye model $\omega(q) = \nu q$ (phonons) $\nu q$

Q: Why might that be reasonable at low $T$?

A: only small $q$ occupied.

$$E \sim \int_0^\infty \frac{q^2 dq}{e^{\frac{q^2}{\nu^2}} - 1} \sim \int_0^\infty \frac{q^3 dq}{e^{\beta\nu q} - 1}$$

3D

Change variables $x = \beta\nu q$, $q = \frac{xT\nu}{k}$

$$E \sim T^4 \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

$$E \sim T^4$$

$[c \sim T^3]$ Key CM physics result phonons contribute $T^3$ to specific heat of solid.

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Time independent Schrödinger Eqn:

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi(x) + V(x) \psi(x) = E \psi(x) \]

Laplace/Poisson Eqn:

\[ -\nabla^2 \phi(x) = \frac{p(x)}{\varepsilon_0} \]

Diffusion Eqn:

\[ \frac{\partial p(x,t)}{\partial t} = \nabla^2 p(x,t) \]

So, \( \nabla^2 \) ubiquitous in QM, EM, CM

\[ \frac{df}{dx} = \frac{f(x+\Delta x) - f(x)}{\Delta x} \]

\[ \frac{d^2f}{dx^2} = \frac{f(x+\Delta x) - 2f(x) + f(x-\Delta x)}{(\Delta x)^2} \]

\[ \frac{d^2f}{dx^2} \rightarrow \begin{bmatrix} -1 & 2 & -1 \\ -1 & 2 & -1 \\ -1 & 2 & -1 \end{bmatrix} \begin{bmatrix} f(\text{n-1}\Delta x) \\ f(n\Delta x) \\ f(\text{n+1}\Delta x) \end{bmatrix} \]
Why specific heat?

1. A familiar example

\[ \frac{C}{N} = \frac{5}{2} k_B \] diatomic ideal gas

\[ \frac{C}{N} = \frac{3}{2} k_B \] monatomic ideal gas

So you can tell gases apart.

2. Less familiar: Superconductivity

\[ C(T) \]

\[ \text{usual electronic } \bar{C}T \]

Prediction of BCS

Height of peak is 2\(\gamma\) times

Value just before peak confirmed in exp +

\[ I_C \]

\[ C(T) \sim e^{-\Delta/k_B T} \]

gives energy gap \(\Delta\), a crucial quantity

\[ \Delta = \text{energy to break Cooper pair} \]

\(\Delta = kT_c \text{ electron pair}\)
Even crucial to high $T_c$ SC

$\Delta_k$: energy to break \textit{K}\textsubscript{F} \textit{d}\textsubscript{1} bound state

Conventional is $\Delta_k$ is $k$ independent $\Delta_0$

High $T_c$ $\Delta_k$ does depend on $k$ and can vanish for certain momenta

$\Delta_k = \Delta_0 \cos k_x \cos k_y$ "d-wave"

Consequence

$T_\beta$ instead of $e^{-\Delta/k_BT}$

A key $\text{expt}$ to prove d-wave symmetry

DivoGA Inexplicably about high $T_c$. 