1. How to get from A to B?

\[ \begin{align*}
A & \leftarrow x \rightarrow B \\
\end{align*} \]

1. Classical mechanics. Constant force \( F \) gives rise to acceleration. Imagine falling with negligible air resistance.

\[ \begin{align*}
\text{acceleration} &= \text{constant} = \frac{\Delta x}{\Delta t^2} \\
x &= x + \frac{1}{2} a \cdot t^2 + c \\
\end{align*} \]

2. Most things are damped. Aristotelian law then applies: force \( \propto \) velocity.

\[ \begin{align*}
\text{velocity} &= \text{constant} = \frac{\Delta v}{\Delta t} \\
x &= x + \Delta v \cdot t + c \\
\end{align*} \]

g Penny dropped from tall building.
3. Many things do not know which way to go. Random walk.

One-dimensional random walk.
\[ X(t+1) = X(t) + S(t) \]
where \( S(t) = \text{step at time } t \).

Let's say \( S(t) = \pm 1 \), randomly.

Probability (5)

\[
\begin{align*}
\text{Probability (5)} &= 1. \\
X(t) &= X(t-1) + S(t-1) \\
X(t+1) &= X(t-2) + S(t-2)
\end{align*}
\]
etc.

so \( X(t) = \sum_{2=1}^{t-1} S(2) \), with \( X(1) = 0 \), say.

\[ \langle X(t) \rangle = \text{average value of } X = \sum_2 S(2) \]

But \( S = \pm 1 \) randomly, so \( \langle S \rangle = 0 \), and

\[ \langle X(t) \rangle = 0. \]
Interesting quantity is root-mean-square of \( R \). That is
\[
R \leq \sqrt{2} \quad \text{Dimensions of length.}
\]
which is not zero.
\[
\langle x^2(t) \rangle = \sum_{t=1}^{t-1} \sum_{t'=1}^{t-1} \langle S(t) S(t') \rangle
\]
Assume \( t \gg 1 \) to make this a little easier.
\[
\langle x^2(t) \rangle = \sum_{t=0}^{t} \langle S(t) S(t') \rangle
\]
\[
= \sum_{t=0}^{t} \langle S^2(t) \rangle + \sum_{t=0}^{t} \langle S(t) S(t') \rangle
\]
\[
= \sum_{t=2}^{t} \langle S^2(t) \rangle + \sum_{t=2}^{t} \langle S(t) S(t') \rangle
\]
But the step at different times is random, and does not know about previous steps.

Hence \( \langle S(t) S(t') \rangle = \langle S(t) \rangle \langle S(t') \rangle = 0 \) if \( t \neq t' \)
Also \( S = \pm 1 \), so \( S^2 = 1 \). Hence
\[
\langle S^2(t) \rangle = 1.
\]
So we have
\[ \langle x^2(t) \rangle = \sum_{t=0}^{t} 1 = t \]
and
\[ \langle x_{\text{RMS}}^2 \rangle = \langle x^2(t) \rangle^{1/2} = t^{1/2} \]

Actual path:

length scale \( \sim t^{1/3} \)

Characteristic of random walks and diffusion. Microscopic mechanism related to Brownian motion by Einstein.

Intriguing to note that path is "self-
similar to parts of the path look like the whole path. Common emergent behavior associated with scaling and fractals.

Possible to do more easily and more generalizable in continuous limit.

\[ \frac{dx}{dt} = y \]

where \( y \) is a noise. By the central limit theorem (which we will quickly show later), \( y \) has only two nontrivial "moments"\( \langle y \rangle = 0 \), \( \langle y(t)y(t') \rangle = D \delta(t - t') \)

where \( \delta(t) \) is the Dirac delta function. It has the property

\[ \int dt \delta(t - t') f(t) = f(t') \]

\[ \delta(t - t_0) \]

\( t \) \( \rightarrow \) \( t_0 \) \( \rightarrow \) \( t \)

Handy form: \( \delta(t) = \int_{-\infty}^{\infty} dw e^{-iwt} \cdot e^{-i\omega t} \)

from Fourier theorem.
Back to original equation.

\[ \frac{dx}{dt} = \eta \]

So \[ x(t) = \int_0^t dt' \eta(t') \]

assuming \[ x(0) = 0 \].

Then, immediately \[ \langle x(t) \rangle = 0 \] and

\[ \langle x(t)^2 \rangle = \int_0^t dt' \int_0^t dt'' \langle \eta(t') \eta(t'') \rangle \]

\[ = D \int_0^t dt' \]

\[ \langle x^2(t) \rangle = D t \]

\[ x_{\text{rms}} = \langle x^2(t) \rangle^{1/2} = \sqrt{D t} \]

Note that if this is a two-dimensional or three-dimensional random walk

\[ \frac{dx}{dt} = \eta \]

and one easily gets again

\[ x_{\text{rms}} = \langle x^2 \rangle^{1/2} = \sigma \sqrt{t} \]
A single example to show relevance of this.

Rip a piece of paper in half. A constant tension (constant force) gives rise to a constant velocity of the tear.

Note one can "hear" the velocity. Faster velocities give higher frequencies.

What is making the noise?

\[ v \approx 1 \text{ mm/sec} \]
\[ f \approx 1000 \text{ Hz} \]

Length scale is \( \frac{v}{f} = \) microns

Paper rips at weak part separated by about 1 micron. Ripping is like random walk because y axis becomes time axis as v is constant, time = y/v.

Rip sound is "buzz" not pure frequency. Many structure within structure.
Total region involved in interface

\[ y \times \delta^2 = \gamma \]

\[ \delta = \frac{y}{\gamma^2} \]

Von Koch snowflake

For \( n \) steps,

\[ P_\infty = 4^n \ell, \quad L_\infty = 3^n \ell \]

\[ \ln \frac{P_\infty}{\ell} = n \ln 4, \quad \ln \frac{L_\infty}{\ell} = n \ln 3 \]

\[ \frac{P}{\ell} = \left( \frac{L}{\ell} \right)^{\frac{1}{2}} \]

\[ d_s \to d - 1 = 1 \]

In physics, write

\[ \mu = w(n) \ell^{-d} \]
\[ W(L) \propto L^x \]

for large \( L \).

For von Koch snowflake, \( x = 0.76 \)
For random walk (an\( \uparrow \)

\( x = 0.5 \)

Real systems in \( d = 2 \) obey this.

Fractal change of
structure within structure.
2. Distributions and the central limit theorem.

Averages involve distributions. We have, for example

\[ \langle Q(x) \rangle = \int dx \ Q(x) \ S(x) \]

where \( S(x) \) is the distribution function, or weight, such that

\[ \int dx \ S(x) = 1 \]

Usually we are interested in the moments of the distribution

\[ \langle x^n \rangle = n \text{th moment of } S \]

and usually only in

\[ \langle x \rangle \text{ and } \langle x^2 \rangle \]

It is easy to show that \( S(x) \) can be constructed from all positive integer moments of \( S \).

Going back to the definition of the average, note

\[ \langle S(x-x') \rangle = \int dx \ S(x-x') S(x) \]

\[ = S(x') \].

average over \( x \)
but \[ S(x-x') = \int \frac{dk}{2\pi} e^{-ik(x-x')} \]

so

\[ S(x') = \langle S(x-x') \rangle_x = \int \frac{dk}{2\pi} e^{-ikx'} \langle e^{ikx} \rangle \]

or, on dropping the primes

\[ S(x) = \int \frac{dk}{2\pi} e^{-ikx} \langle e^{ikx} \rangle \]

But \[ e^y = \sum_{n=0}^{\infty} \frac{y^n}{n!} \]

so

\[ S(x') = \int \frac{dk}{2\pi} e^{-ikx} \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle \]

And \( S(x) \) can be constructed from all positive integer moments of the distribution.

Most important example is in the central limit theorem, where \( S(x) \) is a Gaussian.

One important property of many systems is that they consist of many independent parts.

Energy = Total = \( E_1 + E_2 \)
Temperature = $T = T_1 = T_2$

Volume = $V = V_1 + V_2$

Pressure = $P = P_1 = P_2$

→ Extensive: $E, V$ etc.
   Intensive: $T, P$ etc.

Let us say $N$ is the number of independent parts in a system of big size (macroscopic).

$$N = \left( \frac{L}{\xi} \right)^d$$

$d$ is the dimension of space, $L$ is the linear dimension of the system, and $\xi$ is the scale over which things are correlated. $\xi >$ size of atom.

Of course, so

$$N \leq 10^{23} \text{ or so.}$$

For the ripping paper example:

$$\frac{\xi}{\xi} \approx 1 \mu m$$

In a sheet of $12 \times 10^5 \text{ cm}$ size, so

$$N \approx 10^8 \text{ or so.}$$
Typically, but not always

\[ N \sim 10^n \]

where \( n \approx 10^{-20} \). This big number exponentiation is key.

Consider an extensive quantity \( E \) (like the energy). Clearly

\[
E = \sum_{i=1}^{N} E_i, \quad \text{and}
\]

\[
\langle E \rangle = \sum_{i=1}^{N} \langle E_i \rangle = O(N),
\]

\[
\text{known nothing about } N.
\]

as it should. If we have an intensive quantity (the energy per unit volume for example)

\[
e \equiv \frac{E}{N} = O(1).
\]

Now let us look at the fluctuations around the average value

\[
\Delta E \equiv E - \langle E \rangle.
\]

Obviously

\[
\langle \Delta E \rangle = 0.
\]
\[ \left\langle (\Delta E)^2 \right\rangle = \sum_{i=1}^{N_1} \sum_{j=1}^{N_1} \left\langle \Delta E_i \Delta E_j \right\rangle \]

As before:
\[ = \sum_{i=1}^{N_1} \left\langle \Delta E_i^2 \right\rangle + \sum_{i=1}^{N_1} \sum_{j=1}^{N_1} \left\langle \Delta E_i \Delta E_j \right\rangle \]

But if \( i \) and \( j \) are different boxes, they are independent and:
\[ \left\langle \Delta E_i \Delta E_j \right\rangle = \left\langle \Delta E_i \right\rangle \left\langle \Delta E_j \right\rangle = 0, \quad i \neq j. \]

And:
\[ \left\langle (\Delta E)^2 \right\rangle = \sum_{i=1}^{N_1} \left\langle \Delta E_i^2 \right\rangle = O(N). \]
Likewise, the intensive quantity $e$ satisfies
\[
\langle (\Delta e)^2 \rangle = \mathcal{O}\left( \frac{1}{N} \right)
\]
and
\[
\frac{\langle (\Delta E)^4 \rangle}{\langle E \rangle^2} = \mathcal{O}\left( \frac{1}{N^{1/2}} \right)
\]
or equivalently
\[
\frac{\langle (\Delta e)^4 \rangle}{\langle e \rangle^2} = \mathcal{O}\left( \frac{1}{N^{1/2}} \right)
\]
so the fluctuations around $\langle E \rangle$ or $\langle e \rangle$, in a system of many independent points are very very small.

It is straightforward to show that
\[
\langle (\Delta E)^4 \rangle = 3 \langle (\Delta E)^2 \rangle^2
\]
and
\[
\langle (\Delta E)^{2n} \rangle = \frac{2^{n-1}}{2^n n!} \langle (\Delta E)^2 \rangle^n
\]
simply assuming $N$ is big. So for a symmetric distribution (where all odd moments vanish)
all moments are known when one knows only $\langle E \rangle$
and $\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$.
Consider the humble Gaussian distribution

$$\langle \ldots \rangle \propto \int dE (\ldots) e^{-\frac{(E-\langle E \rangle)^2}{2\langle (\Delta E)^2 \rangle}}$$

This can be easily checked to give the results above for the moments. Hence a system of many independent parts gives a Gaussian (the odd moments turn out to be negligible).

To be clear on the context, put it in terms of the intensive variable $e$ and let $\langle (\Delta e)^2 \rangle \equiv \frac{\sigma^2}{N}$
where $N = O(1)$. Then the distribution is

$$\rho(e) \propto e^{-N \frac{(e-\langle e \rangle)^2}{2\sigma^2}}$$

Note that $N'$. 
So the fluctuations around the average value are incredibly small.

So we have our first two results:

1) the random walk, a short step away from Brownian motion and nonequilibrium statistical mechanics

2) the central limit theorem and the typical size of fluctuations, a short step away from equilibrium statistical mechanics.
Second law of thermodynamics

$S$, entropy, is maximized in isolated system (energy $E$, volume $V$, number of particles $N$, all fixed) in equilibrium.

It can be shown that the Helmholtz free energy $F = E - TS$ is minimized in equilibrium in a system with fixed temperature $T$, and volume $V$. This follows from the above.

It can be shown that the Gibbs free energy $G = E - TS + PV$ where $P$ is pressure. Again, this follows from the above for system fixed $T$, $P$.

In general, one can obtain a free energy which is, for example, minimized relative for appropriate variables following from the second law involving entropy.

Entropy is rarely used, except to develop other concepts, as most systems have fixed temperature, for example.
Consider an isolated system (E, V, N fixed). Then the entropy is maximized.

Assume the probability of being in a state depends on $S$ alone:

$$\text{Probability} = e^S.$$

Note $S$ is extensive, so consider a system of two independent parts. Clearly

$$S_{\text{tot}} = S_1 + S_2.$$

But they are independent, so we multiply the constants:

$$S(S_{\text{tot}}) = e^{S_1} e^{S_2},$$

or

$$\ln S(S_{\text{tot}}) = \ln e^{S_1} + \ln e^{S_2}.$$  \[
\\]

Solution by inspection

$$\ln e^S = S$$

or

$$e^S = S/k_B$$

where $k_B$ is the positive Boltzmann constant.
Our sloppiness with multiplicative constants has no consequence because $S$ is defined up to an additive constant.

The probability of being in a state is proportional to the number of microscopic states which have the same macroscopic state. This gives the usual well-known result:

$$S = k_B \ln \left( \frac{\text{# of states with}}{E, V, N} \right),$$

again there is a little sloppiness here for the case of the continuous limit where one considers weights and the number of states in $(\ldots) \to \infty$ as $N \to \infty$.

This is called the microcanonical ensemble. It is possible to work things out with this ensemble, but it is tricky to deal with. A much handier ensemble is the canonical ensemble, obtained by considering fixed $T$ rather than constant $E$.

Little canonical ensemble exchanging heat, fixed $T$. 

(sloppy) microcanonical ensemble, fixed $E$. 
As is standard, call the large part of the system the heat reservoir, which is responsible for holding the temperature constant.

\[
S(E_{\text{reservoir}}) = S(E_{\text{total}} - E)
\]

"little" system

\[
= S(E_{\text{total}}) - \frac{\partial S}{\partial E} \bigg|_{E_{\text{total}}}
\]

\[
= \text{const} - \frac{E}{T}
\]

So,

\[
\text{Prob(state)} \propto \exp\left(\frac{-E}{kT}\right)
\]

the famous Boltzmann factor. Normalizing this we have

\[
\text{Prob}(\text{state}) = \frac{e^{-E/kT}}{\sum_{\text{states}} e^{-E_{\text{state}}/kT}}
\]

where by \(E\) we mean \(E_{\text{state}}\) of course. The normalization factor is called the partition function!
\[ Z = \sum_{\text{states}} e^{-\frac{E_{\text{state}}}{k_B T}} \]

This has a thermodynamic meaning which is relatively easy to establish:

\[ = \sum_{i=1}^{i=n} \sum_{E_{\text{state}}, \text{with some energy} E} e^{-\frac{E_{\text{state}}}{k_B T}} \]

So by all these:

\[ = \sum_{E_{\text{state}}} e^{-\frac{E_{\text{state}}}{k_B T}} \left( \text{# of states with } E \leq E_{\text{state}} \right) \]

\[ = e^{\frac{S_{\text{state}}}{k_B}} \]

\[ Z = \sum_{E_{\text{state}}} \left( E_{\text{state}} - TS \right) / k_B T \]

But the Helmholtz free energy is \( F = E - TS \)

\[ Z = \sum_{E} e^{-\frac{F}{k_B T}} \]
Say this is dominated by the most probable value, to find out what $Z$ is,

$$E = \langle E \rangle \left( 1 + \frac{\langle E \rangle}{E_{\text{max}}} \right)$$

Jointly from above

$$\frac{1}{Z} = e^{-\frac{E}{k_B T}}$$

$$F = -k_B T \ln Z$$

These give the tool chest for doing statistical mechanics.

The generalization to the grand canonical ensemble will be quickly done later, but no essential concepts need be introduced further.
Non-interacting systems.

Let's do some examples to show how useful this is. First we will consider non-interacting systems. We'll start with a paramagnet.

A paramagnet does not spontaneously magnetize, but only magnetize when forced to do so by an external magnetic field.

For simplicity assume the paramagnet consists of \( N \) dipoles, which can point up or down, called +1 and -1, on a regular lattice, here a square 2d lattice.

\[
\begin{array}{cccc}
+ & + & - & + \\
- & - & + & + \\
\end{array}
\]

Sides on the lattice are denoted by the index \( i = 1, 2, 3, \ldots N \).

At each site there is a dipole which can point up or down; \( M_i = \pm 1 \).

The energy of a state of the paramagnet is given by
\[ \mathcal{E}_{\text{stat}} = -\mathcal{H} \sum_{i=1}^{N} m_i = -\mathcal{H} \mathbf{M}_{\text{stat}} \]

where \( \mathbf{M} = \sum_{i=1}^{N} m_i \) gives the magnetization of the state, and \( \mathcal{H} \) is a constant external field. Note that if \( \mathcal{H} > 0 \), \( \mathbf{M} > 0 \) makes \( \mathcal{E} \) negative, and \( \mathcal{H} < 0 \), \( \mathbf{M} < 0 \) makes \( \mathcal{E} \) positive.

Let's look at the sum over states

\[ \sum = \sum_{\text{state}} \sum_{m_i = 1}^{+1} \sum_{m_i = -1}^{-1} \sum_{m_i = 1}^{+1} \cdots \sum_{m_i = 1}^{+1} = \frac{N}{2} \sum_{i=1}^{N} m_i \]

Each sum has only two terms of course.

\[ = 2^N \quad \text{Note this is a really big number as } N \approx 10^{23} \]

Now we have defined the model, it is straightforward to solve

\[ Z = \sum_{\text{state}} e^{-\mathcal{E}_{\text{stat}} / k_b T} \]
\[ Z = \sum_{m_1 = -1}^{+1} \sum_{m_2 = -1}^{+1} \cdots \sum_{m_N = -1}^{+1} e^{-\frac{H_{m_1}}{k_B T}} e^{-\frac{H_{m_2}}{k_B T}} \cdots e^{-\frac{H_{m_N}}{k_B T}} \]

\[ = \left( \sum_{m = -1}^{+1} e^{-\frac{H_{m}}{k_B T}} \right)^N \]

\[ = \left( e^{\frac{H}{k_B T}} + e^{-\frac{H}{k_B T}} \right)^N \]

\[ = \left( 2 \cosh \frac{H}{k_B T} \right)^N \]

Hence

\[ F = -N \log T \ln \left( 2 \cosh \frac{H}{k_B T} \right) \]

Everything we want can be obtained from derivation of \( F \), but instead let us get the average magnetization per spin, and the average energy directly.

\[ \langle m \rangle = \langle m_1 \rangle = \sum_{m_1 = -1}^{+1} \sum_{m_2 = -1}^{+1} \cdots \sum_{m_N = -1}^{+1} e^{-\frac{H_{m_1}}{k_B T}} \sum_{m_2 = -1}^{+1} \cdots \sum_{m_N = -1}^{+1} e^{-\frac{H_{m_1}}{k_B T}} \cdots e^{-\frac{H_{m_N}}{k_B T}} \]

Note: everything cancels except terms
Involving \( m_i \), so

\[
\langle m \rangle = \sum_{m_i = -1}^{+1} m_i \frac{e^{\frac{H_i}{k_B T}}}{e^{\frac{H_i}{k_B T}} + e^{-\frac{H_i}{k_B T}}} = \frac{e^{\frac{H}{k_B T}} - e^{-\frac{H}{k_B T}}}{e^{\frac{H}{k_B T}} + e^{-\frac{H}{k_B T}}} = \tanh \left( \frac{H}{k_B T} \right)
\]

In passing, note \( \langle E \rangle = -\partial \langle \sum_{i=1}^{N} m_i \rangle \)
so

\[
\langle E \rangle = -HN \tanh \left( \frac{N}{k_B T} \right).
\]

Plotting \( \langle m \rangle = \tanh \left( \frac{H}{k_B T} \right) \)

\[
\begin{align*}
\text{low} & \quad \text{medium} & \quad \text{high} \\
H/k_B T & \quad H/k_B T & \quad H/k_B T
\end{align*}
\]

All scale onto universal curve.
for fun, we'll go back to our result

$$S(n) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-ikx} e^{ikn}$$

$$S(0n) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-ikn} e^{ikn}$$

$$\langle e^{ikn} \rangle = \frac{e^{ik\mu/kT} e^{-ik\mu/kT}}{e^{k\mu/kT} + e^{-k\mu/kT}}$$

$$S(\Omega) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-ik(\Omega - 1)} e^{k\mu/kT}$$

$$+ \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-ik(\Omega + 1)} e^{k\mu/kT}$$

$$S(\Omega) = \frac{e^{k\mu/kT} S(\Omega - 1) - e^{-k\mu/kT} S(\Omega + 1)}{2 \cosh \frac{\Delta}{kT}}$$

So, up to constants:

$$S(0)$$
Just to show everything is okay,

\[ \langle \text{ln} \rangle = \sum_{m_1} \sum_{m} \left[ \frac{e^{\frac{\text{H}(\text{ln})}{k_B T}} + e^{\frac{-\text{H}(\text{ln})}{k_B T}}}{e^{\frac{\text{H}(\text{ln})}{k_B T}} + e^{\frac{-\text{H}(\text{ln})}{k_B T}}} \right] \]

\[ = \sum_{m_1} \left[ \frac{e^{\frac{\text{H}(\text{ln})}{k_B T}} - e^{\frac{-\text{H}(\text{ln})}{k_B T}}}{e^{\frac{\text{H}(\text{ln})}{k_B T}} + e^{\frac{-\text{H}(\text{ln})}{k_B T}}} \right] \]

\[ \langle \text{ln} \rangle = \tanh \frac{\text{H}}{k_B T} \], as above.

Now we'll go onto the other non-interacting cases.

Note that in general for a non-interacting system,

\[ Z = (Z_1)^N \]

for each non-interacting part.
Since $F$ is extensive, this means there is almost always but not always, some way of defining a non-interacting system with "quasi-particles" that can be treated as independent.

Gibbs' Paradox

Entropy increases

Volume of phase space for each system

So total volume of phase space is $\sqrt{N}$. 
But if particle 5 is in the same position as particle 1, phase space does not increase. Overcounting by N! corrects quasi-classical counting of phase space, giving
\[ \frac{V^N}{N!} \]
Note N! = N x N x ... x 1, so \[ \frac{V^N}{N!} \approx \text{(volume per particle)}^N \]

I said exactly identical, as this is a quantum concept. A bag of oranges is not a bag of identical oranges. But all helium atoms are identical. We need this factor of N! to do the classical limit correctly.

Let's say we have N atoms of momentum \( p_1, p_2, ..., p_N \), and positions \( x_1, x_2, ..., x_N \). In the classical limit where \( \delta^3p \) is macroscopically small but microscopically big, the volume of phase space is
\[
\text{const.} \frac{1}{N!} \prod_{i=1}^{N} \int dV_i \int dp_i
\]
What is the constant? Evidently it is something like Planck's constant or $\hbar$.

I will not work it out, but it is

Volume of phase space in classical = \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d\rho_i}{2\pi\hbar} \frac{d\phi_i}{2\pi\hbar}

in three dimensions. It is done in many books. Now the energy of atoms is

$$E = \text{kinetic energy} + \text{potential energy} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} \Phi(V)$$

Typically $\Sigma V(r_i) = \frac{1}{2} \sum_{i,j} V_{i,j}(r_i - r_j)$, schematically

short range repulsion. But we will not be looking at interactions between atoms.

At $0^\circ$ C: 1 mole water mass $= 18.0$ mg
$= 6.02 \times 10^{23}$ mol
$\approx 3.3 \times 10^{-30}$ C

Test

$C = 4 \pi \epsilon_0 \frac{N}{\ell^3}$

$= 3.0 \times 10^{-27} \text{C} = 3.0 \times 10^{-19} \text{F} \cdot \text{m}^3$

$\epsilon_0 = 8.85 \times 10^{-19} \text{F} \cdot \text{m}^2 \text{C}^{-1}$

For argon, $E = 15 \text{ eV}$, $\sigma = 0.32$ nm.
The probability is

$$\text{Prob} = \frac{e^{-\frac{1}{2\sigma^2} \left( \sum_{i} \frac{p_i^2}{m_i} + \sum V(q_i) \right)}}{\sqrt{\frac{N}{2\pi \sigma^2}} \prod_{i=1}^{N} e^{-\frac{1}{2\sigma^2} \left( \frac{p_i^2}{m_i} \right)}}$$

Note the $p_i$ part and the $q_i$ part are separable.

$$\text{Prob} = \left( \frac{f(p_i)}{g(q_i)} \right)^N$$

So the momentum and position are independent in the classical limit. The momentum part is easy to do as they are all Gaussian integrals. The position part is very hard to do. Solving this for the ideal gas limit $V = 0$, gives the Maxwell-Boltzmann distribution - which is true for the momentums in the classical limit even with interactions.

The partition function in

$$Z = \frac{1}{N!} \left[ \frac{V}{(2\pi m)^{3N}} \int d^3p \ e^{-\frac{p^2}{2m}} \right]^N$$

where $V^N = \int d^3q_1 \int d^3q_2 \ldots \int d^3q_N$
and of course all the momentum integrals are identical and separable.

Using $N! \approx N^N$, we have

$$Z = \left[ \frac{V}{N} \left( \frac{1}{2\pi m} \right)^{3/2} \left( \frac{2\pi m k_B}{h} \right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{\mathbf{p}^2}{2m}} \right]_N$$

where $\frac{\mathbf{p}}{\hbar} = \frac{\mathbf{v}}{\sqrt{2m k_B}}$.

But $\int_{-\infty}^{\infty} e^{-\frac{\mathbf{p}^2}{2m}} = \left( \int_{-\infty}^{\infty} e^{-\frac{x^2}{2}} \right)^3 = \pi^{3/2}$

so

$$Z = \left( \frac{V}{N k_B} \right)^N$$

with the thermal wavelength

$$\lambda = \sqrt{\frac{2\pi k_B T}{m}}$$

and

$$Z = \left( \frac{V}{N k_B} \right)^N$$

Hence $F = -N k_B T \ln \left( \frac{V}{N k_B} \right)$.

We can obtain thermodynamic quantities using:

$$P = -\left. \frac{\partial F}{\partial V} \right|_T, \quad S = -\left. \frac{\partial F}{\partial T} \right|_V, \quad E = F + TS$$

and $C_V = \left. \left( \frac{\partial E}{\partial T} \right) \right|_V$.
Clearly, \( P = \frac{Nk_B}{V} \)
the ideal gas law, and in

\[
S = -\frac{1}{T} \left( -Nk_B \ln \frac{V}{N} + Nk_B T \left( \frac{2\pi m}{m k_B T} \right)^{3/2} \right)
\]

\[
= Nk_B \ln \frac{V}{N} - k_B T + \frac{3}{2} Nk_B
\]

so

\[
E = F + TS
\]

\[
= \frac{3}{2} Nk_B T
\]

and

\[
C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk_B.
\]

The usual results, but now from first principles.

- Equipartition theorem.

The result for the energy can be obtained much more easily, and a general version of it is called the equipartition theorem.

It the classical energy is a quadratic dependence on a variable, the average
Energy has \( kT \) for each independent degree of freedom. The proof is easy.

\[
< E > = \sum_{\text{state}} \frac{E_{\text{state}}}{kT} \text{ e}^{-\frac{E_{\text{state}}}{kT}}
\]

Say \( E_{\text{state}} = \sum a_i \frac{q_i^2}{b_i} \)

where \( q_i \) is in -\( \infty \) to \( \infty \). Then

\[
< E > = \frac{\prod_{i=1}^{n} \left[ a_i \cdot q_i^2 \cdot e^{-\frac{a_i \cdot q_i^2}{b_i} / kT} \right]}{\prod_{i=1}^{n} \left[ e^{-\frac{a_i \cdot q_i^2}{b_i} / kT} \right]}
\]

\[
< E > = -\frac{2}{\beta} \ln \prod_{i=1}^{n} a_i \int_{-\infty}^{\infty} q_i^2 \text{ e}^{-\frac{a_i \cdot q_i^2}{b_i} / kT}
\]

where \( \beta = (kT)^{-1} \)

\[
< E > = -\frac{2}{\beta} \ln \prod_{i=1}^{n} a_i \sum_{i=1}^{n} \frac{a_i}{b_i} \pi^2
\]

\[
= \frac{2}{\beta} \left( \ln \prod_{i=1}^{n} a_i \beta^{\frac{1}{2}} + \text{ const} \right)
\]
\[ \langle E^{-} \rangle = \frac{\beta}{\delta \beta} \]

and
\[ \langle E^{+} \rangle = \frac{k_B T}{2} \]

This quadratic dependence is not unusual. Say \( E \) depends on \( q \), close to \( q = 0 \)

\[ E(q) = E(0) + E'(0) q + \frac{E''(0)}{2} q^2 + \ldots \]

Constant of the a minimum

\[ E(q) = E''(0) q^2 \]

and
\[ \langle E^{-} \rangle = \frac{k_B T}{2} \]

In passing, a classical solid can be thought of as a bunch of springs connecting atoms

\[ E = \sum \frac{1}{2} k s^2 \]

\[ \sum s = 0 \]

so there are (in 3 dimensions) 6 quadratic dependencies per atom, and

\[ E_{\text{classical solid}} = (6N) \times \frac{1}{2} k_B T = 3 N k_B T \]

and
\[ C_V = 3 N k_B \quad \text{classical solid} \]

Owens' Peit 'law'
In contrast, the experiment finds that the Cu vanishes at low temperature. This is due to quantum effects which we will get to soon.

We'll have to do one more classical result. From the probability for the ideal gas above, the probabilities of each atomic momentum is the same. Writing the drift as a velocity, \( \bar{v} = \frac{\bar{p}}{m} \), give

\[
\langle \ldots \rangle = A \int d\bar{v} \langle \ldots \rangle \exp \left[ - \frac{\bar{p}^2}{2kT} \right]
\]

where \( A \) is the normalization factor:

\[
A = \frac{1}{\int d\bar{v} \exp \left[ - \frac{\bar{p}^2}{2kT} \right]} = \left( \frac{m}{2\pi kT} \right)^{3/2}
\]

\[
\langle \ldots \rangle = \left( \frac{m}{2\pi kT} \right)^{3/2} \int d\bar{v} \langle \ldots \rangle \exp \left[ - \frac{\bar{p}^2}{2kT} \right]
\]

Using \( \int d\bar{v} = \int d\bar{p} v \cdot d\bar{v} = \int d\bar{p} \int d\bar{v} = \int d\bar{p} \int d\bar{v} \int d\bar{v} \) angular integrals.
From above
\[ \langle \frac{1}{2} m \dot{v}^2 \rangle = \frac{1}{2} k_{\text{eff}} T \]
and,
\[ \langle v^2 \rangle = \left\langle \frac{1}{m} \frac{k_{\text{eff}}}{T} \right\rangle \text{ as before.} \]

Let's go back to the specific heat of solids. Einstein said, the solid is just a bunch of harmonic oscillators, ignoring all interactions between the oscillators. So we'll do one oscillator, and then use that to get the result for all of them.

For an oscillator with frequency \( \omega \), the energy is
\[ E_n = \left( \frac{1}{2} + n \right) \hbar \omega \]
where \( n = 0, 1, 2, \ldots \)

So the partition function is