today: What is this course?
What is temperature?
Start counting microstates.

W,F: counting microstates

This course.
The problem: how to extract information from far too many degrees of freedom.

Historical currents (course not historical - nuch too hard!)

- Prehistory: phlogiston: Caloric
- Classical Statistical Mechanics
  \[ S = k_B \log \Omega \]

Thermodynamics

\[ \frac{\partial S}{\partial V} = \frac{\partial P}{\partial T} \]

Kinetic Theory of Gases

\[ PV = Nk_B T \]

Quantum Statistical Mechanics

Modern Statistical Mechanics/Thermodynamics

why: A "classical" statistical mechanics?

READ GOODSTEIN

Administrative: Hand out syllabus + HW
policies (in syllabus): HW
cheating
PREREQ:
books - library

Roll call
Replace too many degrees of freedom with a small number of measurable (or
interable) state variables. For example, for a gas in a box, these might be

\[
\begin{align*}
\text{pressure} & : P \\
\text{volume} & : V \\
\text{temperature} & : T \\
\text{internal energy} & : U \\
\text{no. molecules} & : N \\
\text{entropy} & : S
\end{align*}
\]

\[
\text{not all independent}
\]

Organize

<table>
<thead>
<tr>
<th>extensive</th>
<th>intensive</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>(T)</td>
</tr>
<tr>
<td>(V)</td>
<td>(P)</td>
</tr>
<tr>
<td>(S)</td>
<td>color (?)</td>
</tr>
<tr>
<td>mass</td>
<td>(\sqrt{\text{mass}})</td>
</tr>
<tr>
<td>energy</td>
<td>speed (?)</td>
</tr>
<tr>
<td>momentum</td>
<td>time (?)</td>
</tr>
</tbody>
</table>

Equilibrium & connection between intensive quantity and something conserved that
they can exchange:

\[
\begin{array}{c}
\text{intensive quantity} \\
\text{same in 1, 2}
\end{array}
\]

if two systems can exchange

<table>
<thead>
<tr>
<th>how (example)</th>
</tr>
</thead>
<tbody>
<tr>
<td>piston</td>
</tr>
<tr>
<td>hose in contain; electrical</td>
</tr>
<tr>
<td>thin rigid wall (flame, combustion)</td>
</tr>
</tbody>
</table>

Steady state: no change in any state variables.
Equilibrium: steady state AND no net flow of exchangeable quantities with ANY other system
(individually, not just collectively).
What is temperature? A (p)review (mostly a review of Physics I, but we'll do all of this more carefully later).

1. "That scalar quantity shared by two objects in equilibrium if they can exchange energy." Not unique, doesn't even tell about ordering.

   So - 2nd law (special application): heat flows hotter to colder until equilibrium reached;

   Still doesn't tell us how to measure.

   Combined w/ 1st law: eventually get to IPTS (below).

2. Practical expansion type thermometer

   Gabriel Daniel Fahrenheit: 18th C.

   Prev. used alcohol - too big. Rhenium:

   OFF = freezing of salt water (solder liquid in wall-glass),

   100 F = body temp.

   So Fahrenheit was intended to be a centigrade scale.

3. From kinetic theory of gases, we find for [ideal gas] (expand) that

   \[ PV = N \cdot \frac{2}{3} \langle \frac{1}{2} mv^2 \rangle \]

   regardless of gas.

   Define temperature \( k_B T = \frac{2}{3} \langle \frac{1}{2} mv^2 \rangle \); Then \[ \frac{PV}{Nk_B T} \rightarrow \text{Gas thermometer.} \]

   Note: TBD.

   Arbitrary constant to convert energy units into temperature units:

   \[ k_B \text{ set } k_B = 1 \text{ to define } \gamma = \frac{1}{2} \langle \frac{1}{2} mv^2 \rangle = k_B T \]

   \( \gamma \), measure temperature in ergs.

   I'll usually keep the \( k_B \) in class.

   \[ k_B = 1.38 \cdot 10^{-16} \text{ erg/N} \]

   Subtlety: temperature is not exactly the same thing as kinetic energy. For example,

   - Gas in boy at same temp.
   - Thermal radiation.

   Inadequacies of ideal gas:
   - Real gases interact
   - Way at low temp even for ideal gas because of VM.
We do NOT add \( \bar{v} \) to the rms velo. of the gas molecules in the box: \( T' = T \). So the relevant k.e. is the "random part," not the center-of-mass motion. (In fact, the temp. is Lorentz contracted, but we've kept \( v \approx c \).)

4. Heat Engine

\[
\begin{align*}
\text{Hot reservoir} & \quad \frac{T_2}{Q_2} \\
\downarrow & \\
\text{reversible engine} & \rightarrow \text{mechanical work } W = Q_2 - Q_1 \\
\downarrow & \\
\text{cold} & \frac{T_1}{Q_1}
\end{align*}
\]

You found in Physics I that \( \frac{Q_2}{Q_1} = \frac{T_2}{T_1} \). Taking this as a definition gives a way of measuring temperature:

(Consider a reference reservoir at \( T_1 \); measure \( Q_2 \) to \( Q_1 \) to get \( T_2 \) at triple point of \( \text{H}_2\text{O} \).)

5. Stat. Mech.: to develop in detail this week and next

\[ \text{internal energy} \]

\[ \text{macrostate: } P, V, T, U, \ldots \text{ not all independent} \]

\[ \text{microstate: } \hat{x}_1, \hat{p}_1, \hat{x}_2, \hat{p}_2, \ldots, \hat{r}_{10u}, \hat{p}_{10u} \text{ large #} \]

Many microstates per macrostate - let \( g(U) \) be "number" of ways to pick \( \{\hat{x}_i, \hat{p}_i\} \) consistent with \( U \).
Ergodic hypothesis: All microstates consistent with a given macrostate are equally likely; a system goes through "all" of them on a time scale short compared to the experiment ("all" = arbitrarily close, or close enough, in phase space).

Two systems in thermal equilibrium can exchange energy but not volume or particles. The temperature will be "that thing" which is the same at equilibrium.

\[
g_1(U_1) \quad g_2(U_2) \quad \text{total } U = U_1 + U_2 \text{ fixed}
\]

["Microcanonical ensemble" to explain later.]

Total # configs \( g(U_1, U_2) = g_1(U_1)g_2(U_2) = g_1(U_1)g_2(U-U_1) = g(U_1) \)

Ansatz: if all microstates are equally likely, then the equilibrium macrostate is the one corresponding to the largest number of microstates.

Set \( 0 = \left( \frac{\partial g(U)}{\partial U} \right)_N \),

\[ i.e., \quad \frac{g_1'}{g_1} = \frac{g_2'}{g_2} \quad \text{looks like log deriv.} \]

\[ \text{propor} \quad \text{t}\quad \text{y of}\quad \text{num} \]

So \( T = f(g'/g) = f \left( \frac{\partial S}{\partial U} \right)_N \)

where \( S = k_B \ln g \)

Intuitively, \( h = \text{large} \) and \( c_\text{cl} = \text{small} \); so we define \( f(x) = 1/x \); i.e., \( T = \left( \frac{\partial U}{\partial S} \right)_N \)
Start on counting microstates

We'll follow KBW considering a very simple system, the binary-spin model.
("Izing" usually reserved for interacting spins. Ours will interact only with
a magnetic field, not with each other)

\[ \uparrow \uparrow \uparrow \downarrow \downarrow \downarrow \]

Each classical spin  \( \uparrow  \uparrow \) or  \( \downarrow \downarrow \) will be useful later when we turn on mag. field.

1) Very simple - exactly solvable.
2) Other similar systems aren't so easy (HW)
3) Specific features of  \( g(v) \) are good for large "j" spins

<table>
<thead>
<tr>
<th>Energy ( V = -\mu_B mB )</th>
<th>Contd.</th>
<th>Dimensionless moment</th>
<th>( g(n) )</th>
<th>Probability</th>
<th>If ( B=0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O'r spin</td>
<td>( \uparrow )</td>
<td>+1</td>
<td>1</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>Two states</td>
<td>( \downarrow )</td>
<td>-1</td>
<td>( \frac{1}{2} )</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \uparrow \uparrow \downarrow \downarrow )</td>
<td>+2</td>
<td>1</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>( \uparrow \downarrow \downarrow \downarrow )</td>
<td>0</td>
<td>2</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \downarrow \downarrow \downarrow \downarrow )</td>
<td>0</td>
<td>2</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \downarrow \uparrow \downarrow \downarrow )</td>
<td>-2</td>
<td>( \frac{1}{4} )</td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>Three spins</td>
<td>( \uparrow \uparrow \uparrow \downarrow \downarrow \downarrow )</td>
<td>3</td>
<td>( g(3) = 1 )</td>
<td>12.5%</td>
<td></td>
</tr>
<tr>
<td>Eight states</td>
<td>( \uparrow \uparrow \downarrow \downarrow \uparrow \uparrow \downarrow \downarrow \downarrow \uparrow \uparrow \downarrow \downarrow )</td>
<td>1</td>
<td>( g(1) = 3 )</td>
<td>37.5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \downarrow \downarrow \uparrow \downarrow \downarrow \uparrow \downarrow \downarrow \downarrow \uparrow \downarrow \downarrow )</td>
<td>-1</td>
<td>( g(-1) = 3 )</td>
<td>37.5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \downarrow \uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \downarrow \downarrow \uparrow \downarrow \downarrow )</td>
<td>-3</td>
<td>( g(-3) = \frac{1}{8} )</td>
<td>12.5%</td>
<td></td>
</tr>
</tbody>
</table>

As you can now find, all 8 states are equally likely. However, it is 3x more likely that \( m_1 = +1 \) than \( m_2 = +3 \).
1/8/03

Monday: intro; 4 definitions of T

Today: 5th def. of T
country, states

Fri.: sharpness of distribution

(4p. 6 left-over)

Say something about tuning on mag. field. At T=0, all in ground state 🍎. However, we'll see that for B≠0, T>0, there's some probability for each state.

For general N:

Let $N_\uparrow =$ # up spins, $N_\downarrow =$ # down spins = $N - N_\uparrow$

How many ways can there be to have $N_\uparrow$ up & $N_\downarrow$ down?

Answer: $g(N; N_\uparrow) = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{N_\uparrow!(N-N_\uparrow)!} = \binom{N}{N_\uparrow}$ read "$N$ choose $N_\uparrow"

Argument: $N$ choices of where to put 1st up spin

$N-1$ " " " " 2nd " " because one slot's taken

$N-2$ " " " " 3rd " "

... 

$N-N_\uparrow+1$ " " last " "

So far we have $g \propto N(N-1)(N-2) \ldots (N-N_\uparrow+1)$

\[
= \frac{N(N-1)(N-2) \ldots (N-N_\uparrow+1)(N-N_\uparrow)(N-N_\uparrow+1) \ldots 3 \cdot 2 \cdot 1}{(N-N_\uparrow)(N-N_\uparrow-1) \ldots 3 \cdot 2 \cdot 1}
\]

\[
= \frac{N!}{(N-N_\uparrow)!}
\]

However, we've overcounted, because

I don't care which was the first up spin, which the second, etc.

1) cancels by a factor of $N_\uparrow!$ \implies answer above
Sometimes it's convenient to define

\[ \Delta = \frac{N_+ - N_-}{2} \]

"spin excess" - for example, if I have 40 spins, and 22 are up, \( \Delta = \frac{22 - 18}{2} = \frac{4}{2} = 2 = N_+ - N_- \)

\[ N_+ = \frac{N}{2} + \Delta \]
\[ N_- = \frac{N}{2} - \Delta \]

So \( g(N, \Delta) = g(N; \frac{N}{2} + \Delta) = \frac{N!}{(\frac{N}{2} + \Delta)! (\frac{N}{2} - \Delta)!} \)

\( g(N; N_{\uparrow}) \) called "binomial coef." because in formal product

\[ (\uparrow + \downarrow)^N = (\uparrow + \downarrow)(\uparrow + \downarrow) \ldots (\uparrow + \downarrow) = \uparrow^N \cdots \uparrow + \downarrow^N \cdots \downarrow + \ldots \]

If we collect terms by total numbers of up & down, we have

\[ (\uparrow + \downarrow)^N = \sum_{N_\uparrow=0}^{N} \binom{N}{N_\uparrow} \uparrow^{N_\uparrow} \downarrow^{(N-N_\uparrow)} \]

Pascal's triangle to calculate binomial coef.:

\[
\begin{array}{cccccc}
N = 0 & 1 \\
1 & 1 & 1 \\
2 & 1 & 2 & 1 \\
3 & 1 & 3 & 3 & 1 \\
4 & 1 & 4 & 6 & 4 & 1 \\
\vdots & \vdots & & & & \\
\end{array}
\]
Sharpness of coin flips (I don't mean what it will land on edge)

Assume coin unbiased.
Most likely outcome is 50% heads, 50% tails, but I might not get exactly 50-50.

Example: 4 coins
0 heads 1/16 = 6.25%
1 head 4/16 = 25%
2      6/16 = 37.5%
3      3/16 = 18.75%
4      1/16 = 6.25%

only a 37.5% chance of exactly 50%-50%, but an 87.5% chance it's between 25%-75% & 75%-25%.

How about 1000 coins?
According to my calc:

Exactly 50%-50% (i.e., 500 heads, 500 tails) : only 25% chance
but chance it's between 25% - 75% (750 heads, 750 tails)
    and 75% - 25% (250 heads, 250 tails)

is about 1 - 4*10^{-5} , i.e.,

99.99999...9996                            58
\[ \leftarrow\]

Show histogram, unscaled & scaled - comment on sharpness

Next: continuity approximation
Today: Binomial approach, 


g(N, n) = \frac{N!}{(\frac{n}{2}+n)! \cdot (\frac{n}{2}-n)!} \quad \text{graph of need for continuum approach}

First step in algebra: 

\ln [g(n, n)] = \ln (N!) - \ln (\frac{1}{2}N!) - \ln (\frac{1}{2}N!)

Two approximations:

1. Stirling's series

\ln (n!) \sim n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln (2\pi) - \frac{1}{2n} - \frac{1}{12n^2} + \frac{1}{12n^3} + \ldots

2. n/N \ll 1 \text{ justified by what we've seen so far: away from center, } n = 0,

\frac{g(n, n)}{2^n} \ll 1.

Empirical test of Stirling:

<table>
<thead>
<tr>
<th>n</th>
<th>ln(n!)</th>
<th>nlnn-n</th>
<th>nlnn-n + 1/2lnn + 1/2ln(2\pi) + 1/12n</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.7918</td>
<td>0.2958</td>
<td>1.7641</td>
</tr>
<tr>
<td>10</td>
<td>15.104</td>
<td>13.026</td>
<td>15.096</td>
</tr>
<tr>
<td>50</td>
<td>148.48</td>
<td>145.60</td>
<td>148.48</td>
</tr>
<tr>
<td>100</td>
<td>363.74</td>
<td>360.52</td>
<td>363.74</td>
</tr>
</tbody>
</table>

Contrast Taylor & asymptotic series:

\text{Taylor:}(n^2) \quad \text{asymptotic:}(1/n^2)

\text{for fixed } n \text{, better as } x \to 0,

\text{for fixed } x \text{, better with } n \text{ fixed.}

Derivation of Stirling:

1. R\&K app. A - tedious but elementary
\[ \ln [g(N, x)] = N \ln N - x + \frac{x}{2} \ln N - \left( \frac{x}{2} + \frac{x}{3} \right) \ln \left( \frac{2\pi}{x} \right) + \frac{x}{2} - \frac{1}{2} \ln (2\pi) \]

write \( \ln (x + \epsilon) = \ln (x) + \frac{1}{x} \epsilon + \frac{1}{2} \epsilon^2 \), where \( \epsilon \equiv \frac{x^2}{N} \) assumed \( \ll 1 \)

TAYLOR
\[ \approx \ln N - x + \frac{x}{2} \ln N - \frac{1}{2} \epsilon^2 + \frac{1}{2} \epsilon^2 - \frac{1}{2} \ln (2\pi) \]

keep \( \epsilon^2 \) term just to estimate our error at the end

\[ \ln [g(N, x)] \approx (N + \frac{1}{2}) \ln N - (N + 1) \ln x + (N + 1) \frac{1}{2} \ln 2 + \frac{1}{2} (N + 1) \epsilon^2 - 2x \epsilon - \frac{3}{2} \epsilon \ln x - \frac{1}{2} \ln (2\pi) \]

\[ = N \ln 2 + \frac{1}{2} \ln (\frac{2}{\pi x}) - 2x \epsilon + 2 \frac{1}{N} x^2 - \Theta (\frac{x^3}{N}) \]

For \( n = o \), \( \ln [g(n, 0)] = N \ln 2 + \frac{1}{2} \ln (\frac{2}{\pi}) + \Theta (\frac{1}{N}) \)

take the exponent:
\[ g(n, 0) = 2^n \sqrt{\frac{2}{\pi N}} \]

Generally,
\[ g(n, x) = g(n, 0) \exp \left[ -2 \frac{x^2}{N} + 2 \left( \frac{3}{2} - \Theta (\frac{1}{N}) \right) \right] \]

which is a Gaussian (normal, bell-shaped curve).

Recall we assume no way to field.

\[ P_n (\nu) = \frac{\text{probability} (N, x)}{2^n} = \sqrt{\frac{2}{\pi N}} e^{-2x^2/N} \]

Put in form of a normal distribution:
\[ P_n (\nu) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2} (\nu - \mu)^2} \]

\( \sigma = \frac{1}{2} \sqrt{N} \)

**Standard deviation**

\[ \text{total prob: } \int_{-\infty}^{\infty} P_n (\nu) d\nu = 1 \]

**Endpoints:** approximately \( \pm \nu \)

\[ \text{shaded area: } \int_{-\nu}^{\nu} P_n (\nu) d\nu = \text{erf} \left( \frac{\nu}{\sqrt{2}} \right) \approx 0.6827 \]

So it probably lies between \( \nu - \frac{\sigma}{2} \mu \pm \frac{1}{2} \sqrt{N} \)
Natural variable is not \( x \) but rather \( x = \frac{1}{2} \frac{N_1 - N_2}{N} \)

(i.e., magnetization \( \mu \) is SDV rather than total)

\[
\sigma = \frac{\sigma}{\sqrt{N}} = \frac{1}{2\sqrt{N}}
\]

so 68% prob \( \sigma \) lies between \( \pm \frac{2}{\sqrt{N}} \)

95% \( \pm \frac{4}{\sqrt{N}} \)

99.7% \( \pm \frac{6}{\sqrt{N}} \)

\[ \text{1/10/03} \]

**Averages**. If heads are worth +1, tails -1, what is our coin toss?

\[ \langle X \rangle = \frac{1}{N} \sum_{x \in \{-1, 1\}} x = 0 \]

Now say coin is weighted so that \( \text{prob}(1) = 53\% \), \( \text{prob}(-1) = 45\% \).

\[ \langle X \rangle = \sum_{x} x P(x) = -1 \cdot 0.45 + 1 \cdot 0.55 = 0.1 \]

For a continuous prob. distro., \( P(x) \, dx \) means "prob. of event between \( x \) & \( x + dx \)."

\[ \langle X \rangle = \int x \, P(x) \, dx \]

For our binomial prob. problem, \( P(x) = \frac{\lambda^x}{\sqrt{2\pi \lambda}} \, e^{-x^2/(2\lambda)} \), \( \lambda = \frac{1}{2} \sqrt{N} \)

\[ \text{corr. spin mean} \quad \langle X \rangle = \frac{1}{\sqrt{2\pi \lambda}} \int_{-\lambda}^{\lambda} dx \, x \, e^{-x^2/(2\lambda)} \quad \text{as } \lambda \to 0 \to 0 \]

\[ \text{corr. square spin mean} \quad \langle X^2 \rangle = \int_{-\lambda}^{\lambda} dx \, x^2 \, P(x) = \ell^2 \quad (\text{see book}) \]

\[ P(x) \] is prob. density of \( x \).

Shaded = prob. that \( x_0 \leq x \leq x_0 + dx \)

\[ \int_{-\infty}^{\infty} P(x) \, dx = 1 \]

\[ \langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) \, P(x) \, dx \]
last week: (p)review; counting states

today: averages

microcanonical ensemble

Wed.: the laws of thermodynamics

1. A few minutes on problem 2.63 from HW 7

It's sometimes easier to solve for the probability of something not happening.

Example: flipping four coins, what is the prob. of getting at least 1 head?

a) $P(1 \text{ head}) + P(2) + P(3) + P(4) = \frac{4+6+4+1}{16} = \frac{15}{16}$

b) $1 - P(0 \text{ heads}) = 1 - \frac{1}{16} = \frac{15}{16}$

2. Finish p12 on averages

---

Microcanonical ensemble:

K&K: for each accessible state of system, one copy of the system.

E.g., binary spin system, $N=4$, spin excess $A=1$:

represented by 4 copies, one of each accessible state:

Accessible in microcanonical ensemble means having same energy — implies furthermore some dynamical way of getting there in experimental time.

Examples of inaccessible:

1) glass — even though fused silica could turn into quartz sheet & conserve energy, it can't get there from here over our million (?) of years (for diamond — graphite).

2) planetary system consisting of one star & one planet — many orbits have the same energy, but over our billions of years, there's no dynamical mechanism for going from one to the other, so starts mean 1st useful. (In this case, there are other conserved quantities: angular momentum & the Laplace-Runge-Lenz rolls. Add in 3rd body, and motion could become either ergodic or chaotic.)
3) The exact stationary state — \( \Psi(x,t) = e^{-iHt/\hbar} \Psi(x,0) \) (time evolution).

However, if \( \Psi_0 \) is a stationary state only of an approximate Hamiltonian \( \hat{H}_a \), with
\[ \hat{H}_a = \hat{H}_0 + \hat{V}/2 \]
the perturbation \( \hat{V} \) may "ergodically" couple all stationary states
of \( \Psi_0 \) with the same energy (quantum chaos — current research).

\[ \text{Ensemble average: } \langle f \rangle = \frac{1}{\text{system}} \sum_{\text{system}} f(x) = \frac{1}{\text{state}} \sum_{\text{state}} f(x) \]

Other ways to view \( \psi_\infty \text{ ensemble:} \)

- \( N \) many copies of the system, each started at in a
different initial config. of the same energy (and often macroscopic vars):\n\[ \langle f \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{n=1}^{N} f(x_n) \] (system label)

- One system sampled at different times:\n\[ \langle f \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T f(x(t)) \]

According to the [ergodic hypothesis](#), all of these give the same average.

Comment on notation: \( \langle \cdot \rangle \) is ensemble average.

In this chapter, ave. over \( \mu \) canonical ensemble (\( U \) fixed).
In ch. 3, ave. over canonical ensemble (\( U \) fixed) later, over grand canonical ensemble (\( \mu \) fixed).

Sometimes, we might need a quantum expectation value; if it's necessary to distinguish, we can write \( \langle \cdot \rangle_{\text{thermal}} \) & \( \langle \cdot \rangle_{\text{qm}} \).

Recall last week's derivation of Temp:

Before, I wrote \( P(U_1) = g_1(U_1)g_2(U-U_1) \) for
the most probable partition of energy between the
two subsystems. At thermal equilibrium, this and a vanishing
small coterie are the only partitions that matter. To
be correctly correct, \( g = \sum_i g_i(U_i) = \sum_i g_i(U_i)g_2(U-U_i) \).
We found \( \langle \mathcal{S}_z \rangle = \left( \frac{3S_z}{2} \right)_V \) when \( \mathcal{S} = \sum \mathcal{S}_z \).

We will give an example of spin system in thermal contact:

\[ N_1, N_2 \text{ fixed; spin indices } a_1 + a_2 \text{ fixed, } a_1 \text{ allowed to vary} \]

\( B^o \) has form flipping \( \uparrow_{\text{sys_1}} \downarrow_{\text{sys_2}} \leftrightarrow \downarrow_{\text{sys_1}} \uparrow_{\text{sys_2}} \) - total spin conserved

For \( i = 1, 2 \), \( g_i(a_i) = g_i(0) e^{-2a_i^2/N_i} \), \( g_i(0) = 2^{N_i} \sqrt{\frac{2}{\pi N_i}} \)

Most likely config satisfies

\[ \frac{2}{N_1} \left[ g_i(a_i) g_i(a_2 - a_i) \right] = 0 \]

Extremum occurs in some place for \( g_i g_j \), so

\[ 0 = \frac{2}{N_1} \left[ \log g_i(a_i) + \log g_i(a_2 - a_i) \right] = \frac{2}{N_1} \left[ \log g_i(0) - 2a_i^2/N_i + \log g_i(0) - 2(a_2 - a_i)^2/N_2 \right] \]

\[ = -4a_i^2/N_1 + 4 \left[ a_2 - a_i \right]^2/N_2 \]

So

\[ \frac{2a_2}{N_1} = \frac{0}{N_2} \]

i.e., magnetization per spin equal in the two subsystems.

Converting to energy (with magnetic field),

\[ U = -\sum_{\text{spin}} \mu_n m_j B \]

where \( m_j = \pm 1 \); \( \sum m_j = N_1 - N_2 = 2a \), so

\[ U = -2a_2 B \]

Thus

\[ \frac{U_1}{N_1} = \frac{U_2}{N_2} \]

Equi-energy devices - this needn't be the case in general, however. System 1 might not have the same magnet moment \( a \), or they might not even be made of the same state - and I might be an ideal gas and system 2 a solid iron. In general, however, it will be the case that, at equilibrium,

\[ T_1 = T_2 \]

And

\[ T_j = \frac{1}{n_j} \]
Temperature for this example:

\[ T_1 = \left( \frac{\partial \mathcal{H}_1}{\partial \mathcal{S}_1} \right)_N = \left( \frac{\partial \mathcal{S}_1}{\partial \mathcal{U}_1} \right)_N = \frac{1}{k_B} \frac{\partial}{\partial \mathcal{U}_1} \left[ \mathcal{H}_1 \mathcal{S}_1 - \frac{1}{2} \mathcal{U}_1 \frac{1}{N} \frac{1}{\mu^2 B^2} \right] \]

\[ = \frac{1}{k_B} \frac{-\mathcal{U}_1}{N \mu^2 B^2} = - \frac{N_1}{\mathcal{U}_1} \frac{\mu^2 B^2}{k_B} \]

Similarly, \[ T_2 = - \frac{N_2}{\mathcal{U}_2} \frac{\mu^2 B^2}{k_B} = T_1. \]

Is this negative?

Lowest energy \( \Leftrightarrow \) all spins \( \uparrow \Leftrightarrow N = N \Rightarrow U < 0 \)

so configs \( N < 0 \) have \( T < 0 \)

 configs \( N > 0 \) have \( T > 0 \)

\[ \frac{1}{T} = \frac{2S}{\mathcal{U}}, \text{ i.e., slope.} \]

Is it \( \to \infty \) at ends or finite?

To get slope at edges, we cannot use Gaussian approx. since \( \mathcal{U}(\pm \infty) \) is not \( \ll N. \)

(Indeed, Gaussian curve would blow down forever.)

\[ \text{slope at } \pm \infty = \frac{\Delta S}{\Delta \mathcal{U}} = \frac{S(\pm \infty) - S(\pm \infty)}{U(\pm \infty) - U(\pm \infty)} = \frac{k_B [\mathcal{H}(z(N,y,\pm \infty)) - \mathcal{H}(z(N,y,\pm \infty))]}{-\mu(N-2)B - \mu N B} \]
\[ \frac{k_b \left[ \ln \left( \frac{N}{N-1} \right) - \ln \left( \frac{N}{N} \right) \right]}{2\mu B} = \frac{k_b \left( \ln N - 0 \right)}{2\mu B} \rightarrow \infty \]

In limit of infinite system, slope \( \to \infty \), so \( T = 0 \) [PENCIL IN PICTURE]

For \( T = 0 \), slope \( = 0 \), so \( T = \infty \)

At this temperature, distribution is same as if there were no magnetic field (practical limit: \( k_b T \gg \mu B \))

For \( T < 0 \), slope \( < 0 \), so \( T < 0 \) ?! See appendix E, HW 2.2

Inverted population impossible in system with arbitrarily high energy levels (e.g., particle in a box:

Since \( \frac{(2S)^{-1}}{(2S)} \) grows monotonically with \( U \),

See HW 2.3

---

Two subsystems again

Say all energy starts out in subsystem 1: \( U_1 = U \), \( U_2 = 0 \)

What will happen to the macrostates of the two subsystems?

... Ok, so they're reached thermal equilibrium.

Is it [possible] for them to return to original state? [Laws of physics are reversible.] Is it [likely]? All microstates consistent with total \( U \) are equally likely, but there are vastly fewer corresponding to \( U_1 = U \) than to thermal equilibrium.

---

Schematic:
- dots = microstates
- rows = macrostates
- lines = possible transitions in each direction

| \( N_h = N \) | \( U_1 = U \) |
| \( N_f = N - 1 \) |
| \( N_f = N - 2 \) |
| \( N_f = N - 3 \) |

At each step, system can move to any connected point; it's possible but unlikely for it to evolve from equilibrium.
2nd law of thermodynamics: entropy "never" decreases (nearby Hamlet)
In a small system, it rarely decreases in a system with $10^{22}$ degrees
of freedom, "never."

CARD GAME with students representing energy units
(or equivalently gas molecules)

Reversible processes: only infinitesimal deviations from equilibrium macrostate
Irreversible: - dropping expensive Greek vase
- it appears that microscopic laws of
  physics don't provide it - only statistics

Vings of thermodynamics:

0) If A & B are in thermal equilibrium, and B & C are,
   so are A & C. (Immediate consequence of
   $T = \frac{(\mu_B\mu_C)}{2}$)

1) Heat is a form of energy transfer, and
   energy is conserved.

2) The entropy of the whole universe
   cannot decrease in time.
   equivalent: A heat engine whose sole
   effect in one cycle of operation is
   to convert heat from some source
   into mechanical work, (equivalent to
   being an ideal heat engine).

3) Entropy $\rightarrow 0$ (constant (usually zero)
   monotonically as $T \rightarrow 0$

IT'S A ZERO-SUM GAME
(perpetual-motion machine is
the first kind)

YOU CAN'T WIN
(Dilbert: perpetual-motion
machine of the second
kind?)

YOU CAN'T BREAK
EVEN
Wed: entropy, temperature
Today: laws of thermo.
Boltzmann
Finish p19
C. P. Snow 1959 Rede Lecture \rightarrow Flanders + Swan

Background to problem 2.3

Classical harmonic oscillator:
\begin{align*}
E &= \frac{p^2}{2m} + \frac{1}{2}kx^2 \\
\mathcal{H} &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2, \\
\hbar &= 6.58 \times 10^{-34} \text{Js}
\end{align*}

Solution:
\[ E_n = (n + \frac{1}{2})\hbar \omega, \quad n = 0, 1, 2, \ldots \]

With simplified algebra, slightly by ignoring the \(\frac{1}{2}\)

For large \(N\), it will not be significant in this problem

Go over pp 24-25

\(N\) oscillators; number \(j\) can have any \(\nu_j = 0, 1, \ldots \)

Subject to \(\nu_1 + \nu_2 + \cdots + \nu_N = n\) fixed

Mathematics: partitioning the integer \(n\) among \(N\) boxes
\[ g(M, m) = \# \text{ ways to partition } m \]

"Generating function"
\[ \sum_{m=0}^{\infty} x^m = \frac{1}{1 - x} \quad \text{for } 0 < x < 1 \]

- \(x = \frac{1}{1 - \epsilon}\)

Proof:
Let \(A = \sum \epsilon^\nu \). Then \(A \epsilon = \sum \epsilon^{\nu + 1} \), so \(A - A \epsilon = \epsilon^0 = 1 \), so
\[ A = \frac{1}{1 - \epsilon} \]

Consider a product of \(V\) or these sums:
\[ \left( \sum_{m=0}^{\infty} x^m \right)^V = \left( \sum_{\mu=0}^{\infty} x^\mu \right)^V = \left( \frac{A}{1 - \epsilon} \right)^V \]

Expand l.h.s. \(\rightarrow\) various powers \(x \). A term
\[ x^n \epsilon^m \ldots \epsilon^\nu = x^{\nu_1} \]

represents a state in which one \( j \) has energy \(E_j \). We write line
above to the \(\sum_{\mu=1}^{\nu} - 1\). The sum of terms contributing to \( x^n \) is \( g(V, n) \).
\[(1 - \ell) \frac{\partial}{\partial \ell} \] 

How can we pick out the one term we want? Take a derivative w.r.t. \(\ell\), then set \(\ell \to 0\). Any term with \(\ell^n, n > 0\) will go to zero. Any term \(m \cdot n\) will be wiped out by the dew. The term \(m \cdot n\) will have an unwanted \(n!\) in front. So

\[ g(n, m) = \lim_{\ell \to 0} \frac{1}{n!} \left( \frac{\partial}{\partial \ell} \right)^n \sum_{m=0}^{\infty} g(n, m) \ell^n \]

\[ = \frac{1}{n!} \left( \frac{\partial}{\partial \ell} \right)^n (1 - \ell)^{-n} \]

\[ = \frac{1}{n!} \frac{1}{(N+1)! \ldots (N+n-1)} \]

\[ = \frac{(N+n-1)!}{n! (N-1)!} \]

Part a): yet \(\sigma = \text{func. in Stirling approx.}\)

Straightforward (3 lines)

Part b): using \(\frac{1}{T} = (\frac{\partial U}{\partial T})_s\), solve for \(U\)

Straightforward if you're careful

8 lines

When finished, it might be useful to sketch \(U(T)\)

**Canonical Ensemble**

Reservoir (the universe)

Infinite heat capacity

System state \(E_s\)

Energy \(E\)

Temp \(T\)

Energy \(U - E_s = \bar{E}_s\)

Possible energy levels of system are

\(E_1, E_2, \ldots\)

Assume all distinct (just to simplify)

to determine: prob. \(P(E_s, T)\) that system is in state \(s\)

\[ \sum_s P(E_s, T) = 1 \] because the system must be in some state
To find \( p(E^*) \), fix \( x \). Then

\[
g_{\text{total}} = g_{\text{sys}} \cdot g_{\text{reservoir}} \quad \text{but since we know} \; g_{\text{sys}} = 1,
\]

\[
g = g_{\text{reservoir}} = g_r(\tilde{E}_2), \; \tilde{E}_2 = \tilde{U}_0 - E_x
\]

\[
\frac{P(E_x)}{P(E_{x_1})} = \exp \left( -\frac{1}{k_B T} (S'(\tilde{E}_2) - S'(\tilde{E}_{x_1})) \right) \equiv \exp \left( -\frac{1}{k_B T} \Delta S_2 \right)
\]

Consider states \( x, y \) with nearly same energies:

What is ratio of their probabilities?

\[
\frac{P(E_x)}{P(E_{x_1})} = \exp \left[ \frac{1}{k_B T} (S'(\tilde{E}_2) - S'(\tilde{E}_{x_1})) \right] = \exp \left[ \frac{1}{k_B T} \Delta S_2 \right]
\]

change in energy of system \( \Delta E = E_x - E_{x_1} \)

"reservoir" \( \Delta E = -\Delta E \)

Since \( \Delta S \) is a small quantity, we may write

\[
\Delta S_2 \approx \left( \frac{\partial S_2}{\partial \tilde{E}_2} \right) \Delta \tilde{E}_2 = \frac{1}{k_B T} \Delta \tilde{E}_2 = -\frac{1}{k_B T} \Delta E
\]

Prop 1.3:

\[
\frac{P(E_{x_2})}{P(E_{x_1})} = \exp \left[ -\Delta E / (k_B T) \right] \quad \text{so} \quad \frac{P(E_x)}{P(E_{x_1})} \exp \left[ -E_x / (k_B T) \right] \quad \text{Helmholtz factor}
\]

absolute prob.:

\[
P(E_x) = \frac{\exp \left[ -E_x / (k_B T) \right]}{Z}
\]

where \( Z = \text{partition function} = \sum_x \exp \left[ -E_x / (k_B T) \right] \)

"\( Z \)" to \( \infty \)
Fri: Laws

Canonical ensemble

today: Heat work in the canonical ensemble.

FCI: Heat capacity, ideal gas.

--

Microcanonical ensemble (Ch 2): Fixed U, all microstates equally likely.
Canonical ensemble (Ch 3, problem 4 just reviewed): U can be exchanged with reservoir at fixed T.

\[ p_j = \text{Prob. of microstate } j = \frac{e^{-E_j/(k_B T)}}{Z} \]
\[ Z = \sum_j e^{-E_j/(k_B T)} \]

Average of any quantity \( x \): \( \langle x \rangle = \sum_j x_j p_j = \frac{\sum_j x_j e^{-E_j/(k_B T)}}{Z} \)

Trivial example: \( \langle q \rangle = \frac{\sum_j 2e^{-E_j/(k_B T)}}{\sum_j e^{-E_j/(k_B T)}} = 2 \)

Less trivial: (do hw. 2.4 ?)

Another expression for \( U \) directly from \( Z \) (eqn. 3.12):

\[ \gamma^2 \frac{\partial}{\partial T} \ln Z = \gamma^2 \frac{\partial Z/\partial T}{Z} = \gamma^2 \frac{\sum (-\gamma)^2 (-E_j)e^{-E_j/(k_B T)}}{Z} \]
\[ = \frac{\sum E_j e^{-E_j/(k_B T)}}{Z} = \langle U \rangle \]

Reversible processes: entropy at universe not changed.

---

Two special cases: 1) Isentropic: entropy of system not changed (additive).
- Quantum states map on to each other.
2. Isovolumetric

Add an infinitesimal amount of heat —

more energy \( \Rightarrow \) more microstates available \( \Rightarrow \) \( S \) of system increases

(Reversible \( \Rightarrow \) \( S \) of reservoir decreases)

Reservoir @ \( T \) only infinitesimally higher than that of system (see inversion)

- Another example of an irreversible process:
  - Vacuum \( \rightarrow \) pressure
  - No work done on piston
  - Sudden expansion

Pressure and mechanical work

\[ P = \frac{F}{A} \]

We'll change volume by means of a piston, which changes just one of the 3 dimensions.

Assume \( U, V \) good state variables (1st kind), so it doesn't matter how we change \( V \) (as long as it's not too fast). Both changes change in all 3 dimensions.
More piston study - not accelerating \( \Rightarrow \) force of gas on piston = force of piston on gas
\[ = PA \]

\[ \text{work done on gas} = (\Delta U)_g \]
adds energy to gas
without change in entropy (see above)

\[ = T \cdot (-\Delta L)_g \]

\[ = -PA \cdot (\Delta L)_g \]

\[ = -P (\Delta V)_g \]

or

\[ T = -\left( \frac{\Delta U}{\Delta V} \right)_g = -\left( \frac{\partial U}{\partial V} \right)_g \]

\[ S = k_B \sigma \]

State vars. \( U, V, N \) - \( N \) fixed, so just \( U, V \)

\[ S = S(U, V) \]

Infinitesimal change in \( S \) could involve both \( \Delta U \) and \( \Delta V \), so

\[ dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV \]

I'll drop \( N \) subscripts until later chapter.

Can we choose \( dU = (\delta U)_g \) and \( dV = (\delta V)_g \) together such that there’s no change in entropy of system?

\[ dS = 0 = \left( \frac{\partial S}{\partial U} \right)_V (\delta U)_g + \left( \frac{\partial S}{\partial V} \right)_U (\delta V)_g \]

\[ \left( \frac{\partial S}{\partial V} \right)_U = -\left( \frac{\partial S}{\partial U} \right)_V \]

\[ \left( \frac{\partial S}{\partial V} \right)_U = -P \]

so

\[ T = \frac{1}{P} \left( \frac{\partial S}{\partial V} \right)_U \]

Going back to \( dS \),

\[ dS = \frac{\partial S}{\partial V} dV + \left( \frac{\partial S}{\partial U} \right)_{V,T} dU \]

\[ = \frac{1}{T} \left( \frac{\partial S}{\partial V} \right)_U dV + \frac{1}{P} \left( \frac{\partial S}{\partial U} \right)_{V,T} dU \]
\[ dU = TS' - PdV \]

thermodynamic identity

Interpretation: 
- \( PdV \) is work done on gas
- \( TS' \) is heat added to gas

Heat is work and work is heat (1st law of thermodynamics)

Physics is like minimization principles. E.g., in QM, we're often interested in minimizing the energy, \( U \). Why? We imagine a system in thermal contact with a reservoir at \( T=0 \), or at least very cold, so that as much as possible of the energy flows into the reservoir.

If we're at non-zero \( T \), we don't minimize \( U \)—e.g., problem 24, where only MMM minimized energy, but was not the most probable state.

Define Helmholtz free energy \( F = U - TS' = U - \tau S' \)

Intuitive meaning/motivation: lower \( U \) is good, but so is higher \( S' \)

At \( T_0 \), \( F = U \), so only energy counts
As \( T \uparrow \), maximizing \( S \) becomes increasingly important.

Does it succeed?

\[ \delta F = \delta U - TD\delta S - SdT \]

1) constant volume \( \rightarrow \delta U = 0 \)

\[ \left( \frac{\partial F}{\partial T} \right)_V = -S \]

Since

\[ \delta F = -PdV - \tau dS \]

2) constant temperature \( \rightarrow \delta T = 0 \)

\[ \left( \frac{\partial F}{\partial V} \right)_T = -\tau \]

\[ \tau = \left( \frac{\partial F}{\partial V} \right)_T + T \left( \frac{\partial F}{\partial T} \right)_V \] for isothermal process

Cont'd: \( F \) is the "thermodynamic pollen" when \( \delta T = dV = 0 \). There are others for different pressures (e.g., \( \delta T = \delta P = 0 \) for isobaric)
Wed:

\[ U = \psi = \frac{\sum \psi e^{-\beta E \psi}}{Z} \]

\[ P = -\left(\frac{\beta}{\beta V}\right)_S = T \left(\frac{\beta S}{\beta V}\right)_U \]

\[ dU = TdS - PdV \]

Helmholtz F

polymer

Problems

Mon.: ideal gas

UV catastrophe

Finish old

Problem 3.10

Most solids expand when heated:

However, polymers — pseudo-first-order — shrink.

Model: random walk — each link at likely ±1 as -1 (purely entropic model — no energy)

Instead of \( P = -T \left(\frac{\partial S}{\partial V}\right)_U \), we get

\[ f = -T \left(\frac{\partial S}{\partial V}\right)_U \]

Goal: calculate string tension \( f \) as function of temperature

a) With \( N \) links, each of length \( \rho \), how many ways are there to get total length \( \ell \)?

No diff. from \( \pm 1 \) binary spin problem

\[ \psi = 1_{|V|} \rightarrow 2^{1/2} |\rho \]

\( n \) is "link" excess

\[ f(n, \pm 2) = \frac{N!}{(\frac{1}{2}N + n)! (\frac{1}{2}N - n)!} \]

We lose one if \( n_1 \rightarrow 0 \) or \( n_2 \rightarrow 0 \) so

\[ \mathcal{G} = \mathcal{g}(n, -2) + \mathcal{g}(n, 2) = \frac{2N!}{(\frac{1}{2}N - n_1)! (\frac{1}{2}N - n_2)!} \]

is relevant multiplicity.
1) In Gaussian approx., $G = 2g(M,0) e^{-2\omega^2} W$

$$S' = k_B \ln G = k_B \left[ \ln(2g(M,0)) - 2\omega^2/\rho^2 \right] = k_B \left[ \ln(2g(M,0)) - \frac{\rho^2}{2\omega^2} \right]$$

2) string tension $\xi = -T \left( \frac{S'}{S'} \right)_\theta$

$$= -T k_B (-1) \frac{\rho^2}{\omega^2}$$

$$\xi = k_B T \frac{T}{(\rho^2 \omega)}$$

(Tangent $\rightarrow$ tension $\rightarrow$ curl up)

To get equilibrium tensions, we need a more realistic model with $U$ in it.

Getting $F$ directly from $Z$, no having to calc. $S$ or $U$:

$$U = F + TS = F - T \left( \frac{2F}{F} \right)_\nu$$

outer: a diff. eqn. for $F$, which leads solves to get $F = -\frac{\partial E_0}{\partial \nu}$.

Here's an alternative derivation, but it relies on an identity. Let $W_a = \frac{e^{-aE_0}}{Z}$ be the prob. of being in state $a$. Then

$$S' = -k_B \sum_{\nu} W_{\nu} \ln W_{\nu}$$

Proof: use canonical ensemble with total of $N$ systems (proof in ch. 2)

$\nu_1 = \nu_1 \nu_1$ if them are in state 1
$\nu_2 = \nu_2 \nu_2$ if them ... state 2
...

$\nu_1 \nu_1 \nu_2 \nu_2 \cdots$

$S_{\text{ensemble}} = \frac{\nu_1}{\nu_1 \nu_1 \nu_2 \nu_2 \cdots}$

$S_{\text{ensemble}} = k_B \ln g_{\nu_1} = k_B \left[ \ln(\nu_1) - \sum_{\alpha} \ln(\nu_{\alpha}) \right]$

$\approx k_B \left[ \nu_1 \nu_1 - \frac{\nu_1}{\nu_1} \nu_{\nu_1} \nu_{\nu_1} \right]$ string

$= k_B \left[ \nu_1 \nu_1 - \nu_1 \nu_1 \nu_1 \right]$ since $\sum_{\alpha} \nu_{\alpha} = \nu$
Now write \[ \sum_x \nu_x \ln \nu_x = \sum \nu_x \ln (\nu_x) \]

so \[ S_{eq} = \nu k_B \left[ k_B \nu - \sum \nu_x \left( k_B \nu + k_B \nu_x \right) \right] \]

\[ = \nu k_B \left[ k_B \nu - k_B \nu \sum \nu_x - \sum \nu_x k_B \nu_x \right] \]

\[ = -\nu k_B \sum \nu_x k_B \nu_x \]

but \[ S = \frac{S_{eq}}{\nu} \], so \[ S = -k_B \sum \nu_x k_B \nu_x \]

Now to get \( F \).

\[ S = -k_B \sum \nu_x k_B \ln \left( \frac{e^{-\beta E_x}}{Z} \right) \]

\[ = -k_B \sum \nu_x \cdot (-\beta E_x - k_B Z) \]

\[ = -\frac{k_B \sum \nu_x E_x}{Z} + k_B \ln Z \sum \nu_x \frac{1}{1} \]

\[ = \frac{U}{Z} + k_B \ln Z \]

\[ TS = U + k_B T \ln Z \]

\[ U - TS = \frac{-k_B T \ln Z}{F} = F \]
Talking points on problems:

1) \( z = 1 + e^{-\beta E} \)

Show how to get \( U \) directly (NOT the way problem asks them to do):
\[
U = \frac{\langle E \rangle}{z} = \frac{0 + e^{-\beta E}}{1 + e^{-\beta E}} = \frac{e^{-\beta E}}{1 + e^{-\beta E}} = \frac{e^{-\beta E}}{e^{\beta E} + 1}
\]

2) This \( M \) is magnetization per unit volume.
\[
\frac{N}{V} = n \quad \text{number density}
\]

Let \( E_B = -mB \) (for one spin)
\[
E_B = +mB
\]
\[
z = (e^{mB/\beta} + e^{-mB/\beta})^N \quad \text{explain why}
\]
\[
= (2 \cosh [mB/\beta])^N
\]

I did this problem essentially same way as #1.

Review of hyperbolic functions:

\[
\cosh x = \frac{e^x + e^{-x}}{2}
\]
\[
\int \cosh x \, dx = \frac{e^x - e^{-x}}{2} = \sinh x
\]
\[
\frac{d}{dx} \cosh x = \sinh x
\]
\[
\frac{d}{dx} \sinh x = \cosh x
\]
\[
\cosh^2 x - \sinh^2 x = 1
\]
\[
\frac{\sinh x}{\cosh x} = \tanh x
\]
\[
\text{sech} x = \frac{1}{\cosh x}
\]
\[
\tanh^2 x = 1 - \text{sech}^2 x
\]
\[
\frac{d}{dx} \tanh x = \text{sech}^2 x
\]

3) Remember identity from last week \( 1 + x^2 + x^4 + \cdots = \frac{1}{1 - x} \) for \( |x| < 1 \).
last week:

pressure \( P = -\left( \frac{\partial U}{\partial V} \right)_S = T \left( \frac{\partial S}{\partial V} \right)_U = -\left( \frac{\partial F}{\partial V} \right)_T = \left( \frac{\partial U}{\partial V} \right)_T + T \left( \frac{\partial S}{\partial V} \right)_T \)

\[ dU = T dS - P dV = \text{heat} + \text{work} \]

Helmholtz \( F = U - T S = -k_B T \ln Z \)

\[ S = -k_B \sum_a \omega_a \ln \omega_a \quad (\omega_a = e^{-\beta E_a}/Z) \]

today: heat capacity, ideal gas

Wed: \( U \neq \text{vapor} \neq \text{Planck} \)

Heat capacity \( C_V = T \left( \frac{\partial S}{\partial T} \right)_V \) per KBK [Note: they use same symbol (!) for dimensional heat capacity, \( \gamma \left( \frac{\partial S}{\partial T} \right)_V \)]

Units: \( K \frac{J/K}{K} = J/K \)

\( \omega \), how much heat per unit change in temp.

Ask: which is easier to heat, air or water?

\( H_2O \): large \( C_V \), air: small \( C_V \).

In \( \text{physical} \) chemistry, \( C_p = T \left( \frac{\partial S}{\partial T} \right)_p \); more important (except usually @ const. pressure)

\( C_V < C_p \)

gases: noticeably different

liquids: somewhat different

solids: barely different, so people usually use \( C_V \), which is easier to calc.

KBK don't properly define or motivate \( C_V \), so I'll fill that in.

\[ C_V = \left( \frac{\partial Q}{\partial T} \right)_V \] heat flow into body per unit temp. change

\( \int Q \) not a full differential, because there's no defined "\( dQ \)"

\[ \int Q = T \Delta S \] the heat term in \( dU = \text{heat} - \text{work} \)

From which

\[ \left( \frac{\partial Q}{\partial T} \right)_X \equiv T \left( \frac{\partial S}{\partial T} \right)_X \quad \text{for any thermo. variable } X \]

\( \text{except } S \neq T \)

\[ \Gamma \]

\[ \Rightarrow \quad C_V = T \left( \frac{\partial S}{\partial T} \right)_V \]
Since $dU = TdS - PdV$, @ constant $V$, $dU = TdS'$ (heat only)

Divide by $dT$: \( \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_P \)

Thus \[ C_V = \left(\frac{\partial U}{\partial T}\right)_V \]

Set $X = P$:

\[ C_P = \left(\frac{dQ}{dT}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P \]

Note that $C_P \neq \left(\frac{\partial U}{\partial T}\right)_P$. Instead, consider

\[ U = U(T, P) \] (so $V$ and $S$ are "funs. of $T$ & $P$).

Aside: any two vars. out of $S, T, V, P, U$ determine the others.

Then $dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$

\[ TdS = dQ = \frac{dU + PdV}{V} = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \]

\[ P \left[ \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right] \]

Fix $P$, so that $dP = 0$. Then

\[ dQ = \left[ \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P \right] dT \]

\[ C_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P \]

\[ = \left(\frac{\partial H}{\partial T}\right)_P \]

where entropy $H = U + PV$

---

Specific heat

$C = \frac{C_{\text{mass}}}{\rho}$, $C_{\text{volume}}$, $C_{\text{molar}}$

depending on book.
Ideal gas: non-interacting (or almost — need to be able to exchange energy with walls until equilibrium reached. Once the gas has reached equilibrium, there is no longer any net exchange of energy, so we can turn off even this weak interaction.)

\[ N = \text{# particles} \quad \text{singly, each of mass } M \]

Interacting:
\[
\mathcal{H} = \left[ -\frac{\hbar^2}{2m} \left( \nabla_i^2 + \nabla_j^2 + \cdots + \nabla_n^2 \right) + V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)
\]

Non-interacting:
\[
\mathcal{H}_i = -\frac{\hbar^2}{2m} \nabla_i^2 \psi_i(\mathbf{r}_i)
\]

\[ \mathcal{H}_o = \mathcal{E}_i \psi_i \]

Solution:
\[
\psi_i(\mathbf{r}_i) = A \sin(n_{\xi} \pi x/L) \sin(n_{\eta} \pi y/L) \sin(n_{\zeta} \pi z/L),
\]

where \(n_{\xi}, n_{\eta}, n_{\zeta} > 0\) and \(\psi_i(\mathbf{r}_i)\) vanishes at \(x, y, z = \pm L/2\)

\[ \mathcal{H} = \sum_i \mathcal{H}_i \]

\[ \Psi = \left\{ \begin{array}{c}
\sin(n_{\xi}) \\
\sin(n_{\eta}) \\
\sin(n_{\zeta})
\end{array} \right\} \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \cdots \psi_n(\mathbf{r}_n) \]

Total energy \( \mathcal{E} = \sum_i \mathcal{E}_i \)

\[ \mathcal{E}_i = \frac{\hbar^2}{2m} \left( \frac{n_i^2}{L^2} \right)^2 (n_{\xi}^2 + n_{\eta}^2 + n_{\zeta}^2) \]

Partition function for \( N \) atoms (set \( i = 1 \) and drop most \( \mathcal{E}_i \) subscripts)

\[
Z_1 = \sum_{n_{\xi}} \sum_{n_{\eta}} \sum_{n_{\zeta}} \exp[-\beta \mathcal{E}_i] \approx \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \exp[-\alpha^2 (n_{\xi}^2 + n_{\eta}^2 + n_{\zeta}^2)]
\]

where \( \alpha^2 = \beta \frac{\hbar^2}{2m} \left( \frac{n_i}{L} \right)^2 \)
\[ Z_1 = \left( \int_0^\infty \text{d}n \, e^{-\alpha^2 n^2} \right)^2 = \frac{\pi^{3/2} \gamma}{8 \alpha^3} \]

\[ = L^3 \left( \frac{n_0}{\beta h^2 \pi^2} \right)^{3/2} = \sqrt{\left( \frac{m \gamma}{2 \pi \hbar^2} \right)^{3/2}} = \frac{n_0 \gamma}{\alpha} \text{ with } \alpha = \text{concentration} \left( \text{in density} \right) \]

Since \( Z_1 \) is dimensionless, \( n_0 \) also has units of concentration, "quantum concentration".

If \( n \ll n_0 \), gas is essentially classical.

If \( n \gg n_0 \), QM indispensable (since states must try to have multiple occupancy, and QM has something to say about that).

Thermal avg. energy \[ U = k_B T^2 \left( \frac{2n_0 Z_1}{\gamma^2} \right) \]

(022 of notes, 1/22/03)

\[ = \gamma^2 \left( \frac{2n_0}{\gamma^2} \right) \frac{1}{2} Z_1 = \frac{3}{2} \frac{\gamma^2}{k_B} T \]

Energy for a gas of \( N \) atoms \( \rightarrow \frac{\text{energy}}{\text{atom}} \) for ideal gas.

If we had 1 atom of He, 1 of Ne, 1 of Ar, 1 of Kr, etc., then

\[
\begin{array}{ccc}
\text{He} & \overline{\text{Ar}} & \text{He} \\
\text{Ne} & \text{Kr} & \text{Ne}
\end{array}
\]

would be different configurations, so partition function would be\[ Z = \sum_n \sum_n' \cdots \sum_n^{'} \sum_n e^{-\beta (E_1 + E_2 + E_3 + \cdots + E_n)} \]

\[ = \left( \frac{\sum}{n_1} e^{-\beta E_1} \right) \left( \frac{\sum}{n_2} e^{-\beta E_2} \right) \cdots \left( \frac{\sum}{n_N} e^{-\beta E_N} \right) \]

\[ = Z_1 Z_2 Z_3 \cdots Z_N. \]

However, typically we have only one kind of atom, and the two boxes above (with all the atoms He) are the same sortig. Since we've partitioned, inside by \( N \):
\[ Z = \frac{Z_N^N}{N!} = \frac{1}{N!} \left( \frac{\eta Q V}{N} \right)^N \]

Dividing by \( N! \) resolved the "Gibbs paradox," in which the entropy comes out wrong (see problem 5). This trick is OK so long as prob. of multiple occupancy of a single site is low. Correct treatment Ch.6, 7.

Free energy \( F = -k_B T \ln Z = -Nk_B T \ln Z + k_B T \ln (N!) \approx Nk_B T \ln (\eta Q V) + k_B T (N \ln N - N) \)

Pressure \( P = -\frac{\partial F}{\partial V} = Nk_B T \frac{\partial}{\partial V} \ln (\eta Q V) = Nk_B T / V \)
or \[ PV = Nk_B T \]

ideal-gas law

1/11/83
Mon: \( C_v, C_p \)
\[ PV = Nk_B T \]

today: \( \text{uv catastrophe, punch} \)

Weds: thermal radiation, after mañana Brown

classical equipartition: energy in each mode \( \frac{1}{2} k_B T \) (e.g., \( U = \frac{3}{2} Nk_B T \)) in ideal gas: 3N modes,

energy in Hohlraum

\[ E_0 = \frac{1}{2} \int \left( \frac{E^2}{2m} + \frac{B^2}{\mu_0} \right) dV \approx \frac{1}{2} k_B T \sqrt{2k_B T} = k_B T \]

Note: cgs (Gaussian) units

\[ E_1 = 2k_B T \]

\[ E_2 = 2k_B T \]

total energy \( E = \infty k_B T \)
not good

Careful classical treatment by Raleigh & Jeans

[Graph showing energy density with respect to wave number]
Classical quantized EM modes in a cavity w/ conducting walls - cube of side L:

\[
\begin{align*}
\nabla \cdot E &= \nabla \cdot B = 0 \\
\nabla \times E &= -\frac{1}{c} \frac{\partial B}{\partial t} \\
\nabla \times B &= \frac{1}{c} \frac{\partial E}{\partial t}
\end{align*}
\]

\[c^2 \nabla^2 E = \frac{\partial^2 E}{\partial t^2} = -\omega^2 E \quad \text{Wave eqns.}
\]

Standing-wave solution:

\[E_x = E_{x0} \sin(\pi n_x x / L) \sin(\pi n_y y / L) \sin(\pi n_z z / L)\]

Simulation comes from b.c. on B of surface \(B_z = 0\)

\[E_x = 0 \text{ at all faces (} y, z = \text{const.)}\]

\[E_y = E_{y0} \ldots\]

\[E_z = E_{z0} \ldots\]

Constraint on choice of \(E_{x0}, E_{y0}, E_{z0}\):

\[0 = \nabla \cdot E \Rightarrow E_{x0} n_x + E_{y0} n_y + E_{z0} n_z \equiv E \cdot \hat{n} = 0
\]

Similarly, \(\vec{B} \cdot \hat{n} = 0\). Furthermore, \(|\vec{E}| = |\vec{B}|\) by curl parts of Maxwell.

With \(\vec{E} \cdot \hat{n}\) fixed \(\Rightarrow 3\) choices for \(\vec{B}_{\text{out}}\).

Dispersion:

\[c^2 \nabla^2 E = \frac{\partial^2 E}{\partial t^2}
\]

\[
\frac{c^2 n^2}{L^2} (\sigma_1 n_1 + \sigma_1 n_1 \sigma_2 n_2) \omega^2 = \omega^2 E
\]

Mode labeled by \(3\) sim.

\[\omega(n_1, n_2, n_3) = \pm \sqrt{n_1^2 n_2^2 n_3^2}
\]

Equation \(\Rightarrow\) Serious trouble

Plan: drop freedom to put any energy in each mode.

\[\omega \Leftrightarrow \omega(n_1, n_2, n_3):
\]

Possible energies

\[\text{Classical: } \mathcal{E} = \int \frac{\vec{E}^2 + \vec{B}^2}{8\pi} dV \propto \mathcal{E}^2 \text{ continuous}
\]

Planck: \(\mathcal{E} = n \hbar \omega, \quad n = 0, 1, 2, \ldots\)
He thought in terms of interactions between $E+\Delta E$ & atomic states in wells (ad lib. on atomic spectra & attempts to explain them w/ oscillators).

Now we quantize the fields themselves & add $\hbar/2$ to all $E-(\Delta E/2)$ back to 0 to "zero-point" energy - (QED) needed to make sense of it.

$\omega_n$: the $n^{th}$ mode of the cavity

$\hat{N}_n$: occupation # of the $n^{th}$ mode

$= \# $ photons in $n^{th}$ mode

QM way to count occupation #:s:

The modes, not the photons, are the physical objects. It makes no sense to name a "particular" photon Fred and ask in which mode Fred sits.

Note: photons have no rest, mass, so they're easy to create and destroy (subject to conservation of energy, momentum, and angular momentum).

**THERE ARE NO PARTICLES IN QM, only fields (mode, state).** Each field has an occupation number.

When we say "one photon" or "one electron," it's shorthand for a mode with some occupation number. It's an $e^{-}$ makes a transition from one mode (state) to another, we really mean that one mode's occup. # up by a 1, another's down by 1.

Stat. mech. of photon modes:

Photon modes called Bose. After Satyendra Bose - each mode may have any occupation number. Further, massless $\rightarrow$ total occupation number not conserved.

| partition function | $Z = \sum_{\text{no } \hat{N}_n} e^{-\Delta E/2} + e^{-\Delta E/2} + e^{-2\Delta E/2} + \ldots = \sum_{n=0}^{\infty} e^{-(\Delta E/2)\hat{N}_n \omega}$ |

$$= \frac{e^{-\Delta E/2\hbar \omega}}{1 - e^{-\Delta E/2\hbar \omega}}$$
The thermal average is:
\[ \langle n \rangle = e^{-\frac{\hbar \omega_n}{k_B T}} \sum_{n=0}^{\infty} \frac{e^{-\frac{\hbar \omega_n}{k_B T}}}{Z} = e^{-\frac{\hbar \omega_n}{k_B T}} \frac{1}{Z} \int_0^\infty \frac{1}{1-e^{-\frac{\hbar \omega_n}{k_B T}}} (-\frac{1}{\omega_n}) \frac{d}{d\omega} \sum_{n=0}^{\infty} e^{-\frac{\hbar \omega_n}{k_B T}} \]

\[ = \frac{1}{e^{\frac{\hbar \omega_n}{k_B T}} - 1} \]  

The average energy of mode $n$ is:
\[ \langle \epsilon_n \rangle = [\langle n \rangle \times \frac{1}{2}] \hbar \omega = \left[ \frac{1}{e^{\frac{\hbar \omega_n}{k_B T}} - 1} \right] \frac{1}{2} \hbar \omega \quad (\approx k_B T \text{ if } k_B T \gg \hbar \omega) \]

**Equation**

\[ U = k_B T : \text{classical equipartition} \]

\[ U_{\text{ideal}} = \sum_{n=0}^{\infty} U_n = 2 \sum_{n=0}^{\infty} \frac{\hbar \omega_n}{\exp[\hbar \omega_n/k_B T] - 1} \]

\[ = \frac{1}{8} \int_0^{\infty} d\nu \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta \sum_{\nu_1 + \nu_2 = \nu} \frac{1}{\nu_1 \nu_2} \]

\[ = \frac{1}{4} \int_0^{\infty} 4 \nu^2 f_1 d\nu \]

\[ \nu_1 + \nu_2 = \nu \]
Plug in \( \omega_T = \frac{c}{L} \) \( n \), \( L^3 = V \) (volume)

\[
U_{\text{total}} = V \frac{n \pi^2}{15h^3c^3} (k_B T)^4
\]

- Energy density in cavity \( \frac{U}{V} = \frac{\pi^2}{15h^3c^3} (k_B T)^4 \)
- \( \propto T^4 \) : Stefan-Boltzmann

Go back to integral over \( n \) to find out how much energy density at each freq.:

\[
\frac{U}{V} = \frac{\pi}{V} \int_0^\infty dn \, n^2 \, \frac{\omega}{\exp(k_B T/\omega) - 1}
\]

Change vars.: \( n = \frac{1}{\pi c} \omega = \frac{\sqrt{3} \omega}{\pi c} \)

\[
\frac{U}{V} = \frac{\pi}{V} \hbar \int_0^\infty \frac{\omega^3}{\pi^3 c^3} \frac{1}{\exp(k_B T/\omega) - 1} \, d\omega
\]

\[= \int_0^\infty \omega \, U(\omega) \quad \text{where} \quad U(\omega) = \frac{\text{energy}}{\text{volume} \cdot \text{frequency}} = \text{spectrum density}
\]

\[
= \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp(\hbar k_B T/\omega) - 1}
\]

Planck radiation law

\[U_\omega\]

starts out like Rayleigh-Jeans, but no ultraviolet catastrophe (we've subtracted factor.)
How hot is orange hot?

Say peak of Planck at 600nm

\[ 0 = \frac{dU}{d\omega} = \frac{1}{h\beta} \frac{dU_r}{d\lambda}, \quad \lambda = h\omega / \beta \]

\[ \lambda (\text{const.}) \frac{d}{d\lambda} \frac{\lambda^3}{e^{\lambda^3} - 1} = (\text{const.}) \left( \frac{3\lambda^2}{e^{\lambda^3} - 1} - \frac{\lambda^3 e^{\lambda^3}}{(e^{\lambda^3} - 1)^2} \right) \]

So \( 3(1 - e^{-x}) = x \)

at \( x = 2.82 \) (numerical)

\[ \omega = \frac{2\pi c}{600nm} = \frac{\pi \times 6 \times 10^{10} \text{ cm/s}}{6 \times 10^2 \times 10^{-9} \text{ cm}} = 6.1 \times 10^5 \text{ sec}^{-1} \]

\[ \lambda = 1.1 \times 10^{-6} \text{ m} \]

so \( \beta = \frac{h\omega}{kT} = \frac{2.82}{h\omega} = 6.2 \times 10^8 \text{ cm}^{-1} \)

\[ b_B = 1.4 \times 10^{-6} \text{ erg/K} \]

\[ \Rightarrow T = 8800 \text{K} \]

\[ b_B T = \beta = \frac{h\omega}{kT} \]

\[ b_B T = \beta = \frac{h\omega}{kT} \]

Reason: distant rather than edge number; write \( U(\lambda) \) contributions to background integration

\[ \int U_\lambda \lambda d\lambda = \int U_\lambda d\lambda \]

\[ \omega = \frac{c}{2\pi \lambda}, \quad \text{so} \quad d\omega = -\frac{c}{2\pi \lambda^2} d\lambda \]

Thus \( U_\omega \neq U_\lambda \), and they don't ever have their max at same place

(i.e. \( U_{\lambda_{\text{max}}} \neq \frac{c}{2\pi \lambda_{\text{max}}} \))

Do integrals \( \lambda_{\text{max}} \) given by

\[ \chi' = \frac{hc}{\lambda_{\text{max}}^2} = 4.965 \]

so it most important wavelength is 600nm, \( T \approx 3500 \text{K} \)
Black body radiation

Perfectly reflecting walls do not emit
(perfect: incoming light reflects elastically; neither gain nor loses energy)

Flux density $J_u = \frac{\text{total power}}{\text{area of hole}} : \frac{\text{erg/sec}}{\text{cm}^2}$ or $\frac{\text{watt}}{\text{m}^2}$

$J_u \propto \frac{1}{r}$ energy density in thin film

$J \propto c$ faster gets energy out

propagation factor turns out to be $\frac{1}{4}$ (prob. 4.15)

So $J_u = \sigma_B T^4$

$\sigma_B = \frac{\pi^2 k_B^4}{60h^3 c^2}$

$\propto 5.67 \times 10^{-5}$ erg/sec

Stefan-Boltzmann law

Black body: perfect absorber of light (that doesn't mean no emission: at equilibrium, blackbody emits as much as it absorbs. So to test whether something is a blackbody, we need non-equilibrium light e.g. flash light).

Small hole is ideal black surface because very little of the incident radiation will be reflected back.

Consider non-black puck $\beta$

Absorptivity $0 < \alpha < 1$:
0 means perfect reflector, like walls
1 means black, like hole

Anything not absorbed is reflected, so $\alpha = 1 - \beta$, $\beta =$ reflectivity

How much does puck emit? Put it in frost or hole, wait for equilibrium. It's continually absorbing energy from the libraum at a rate $\alpha$ times that of a black body. For there to be equilibrium, it must give up the same flux. The emissivity $= \beta$, i.e., flux density from a non-black body is $\alpha J_u$

This is why thermal insulation in space probes consists of nothing but layers of highly reflective, silvered foil. They are used in low-T physics, where $T_u$ vanishes to $0$. $T_u$ the most significant source of heat flow. Also in windows of office blubs, etc.
Fri.: Planck

today: applications - Nyquist - phonons

wed.: Gibbs distribution, chem. pot.

J some questions about problem 1 - work done by gas on piston & constant prove = \( P \Delta V = -\Delta U \) if PBV both change.

\[
\begin{align*}
\text{isotherm: } \quad & PV = NkT = \text{constant} \\
& \implies RT = \text{constant}
\end{align*}
\]

An old note (??) - first recall Stefan-Boltzmann: \( J = \sigma A T^4 \) (amendatory).

Q. The cosmic black-body radiation was discovered in 1965 - 2.7K, almost isotropic. Knowing nothing at all about the experimental apparatus, you should nonetheless be able to guess one liquid that was essential for accurate measurements into A. liquid helium @4.2K, evaporates slowly = ~7K. It evaporates as it gets cold, except maybe by evaporation.

Can it see 2.7K (except maybe by conduction).

Q. Why can we see TV, radio, which is even cooler?
A. non-equilibrium energy density. TV now - radio stack not blackbody

Nyquist/Johnson noise in a resistor with zero mean current (\( \langle I \rangle = 0 \))

\[
\text{\( \Delta V \) should be zero \( \langle V \rangle = 0 \), but there will be fluctuations: \( \langle V^2 \rangle > 0 \).
\]

\[
\begin{align*}
\text{heat bath} & \quad T \\
\text{heat bath} & \quad T \\
\text{lossless emission} & \quad V_{\text{bar}} = R \langle I \rangle = \text{constant}
\end{align*}
\]

Think of line as 1-dim. cavity

\( L \) will drop out: use it just for counting.
Allowed modes, have wavelengths $\lambda_n = \frac{\lambda_0}{n}$, $n = 1, 2, 3, \ldots$

so (non-angular) frequencies $f_n = \frac{c'}{\lambda_n} = \frac{c'n}{L} \equiv n \delta f$, $\delta f = \frac{c'}{L}$

two modes for each freq., one right-moving, one left

so in freq. range $\Delta f$, # allowed modes $= 2 \frac{\Delta f}{\delta f} = \frac{2c}{c'} \Delta f$

Ave. energy in mode of freq. $\omega_n = 2 \pi f_n$ is

$$\frac{k\omega_n}{e^{\hbar\omega_n/\beta} - 1} = \frac{hf_n}{e^{h\omega_n/\beta} - 1}$$

where $\hbar = 2\pi h$

If $k_B T >> hf_n$, classical equipartition $\rightarrow k_B T$ per mode (Taylor)

Justification:
- E.g., say it's a computer circuit - don't measure freq. > 6 GHz $\sim 10^{12}$ s$^{-1}$
  - two $\sim 10^{-27}$ erg sec $\times 10^{12}$ sec $= 10^{-15}$ erg
  - $k_B = 1.4 \times 10^{-16}$ erg/deg
  - so equiv. temp. $\sim k_B$

would have been much lower for a radio freq. or lower circuit ($\sim$ MHz)

so in freq. range $\Delta f$, energy is $\frac{2\Delta f}{\delta f} \cdot k_B T = 2 \Delta f \frac{L}{c'} k_B T$

Total energy over all freqs. blows up for some reason
- Rayleigh-Jeans - at high freq., we need to use QM instead of equipartition. Note this means computer designers also getting close to having to use QM.

Rate at which energy goes to left resistor

$$\frac{1}{2} \cdot \text{energy in } \omega_n \frac{c'}{L} \cdot \Delta f \frac{L}{c'} k_B T$$  \quad \text{same rate to right}

$$\frac{1}{2} \text{ modes linear speed going left energy density (gyroscopic)}$$

$Z = R$, so no power reflected.
Power generated inside left resistor = $P_0$

and sent to line

Power absorbed from line by left resistor = $P_0 = \Delta f k_B T$

Power absorbed in a resistor = $\langle I^2 \rangle R$

$$= \frac{1}{4R} \langle V^2 \rangle$$

since $I = \frac{V}{R+R}$ in this problem

thus $\langle V^2 \rangle = 4R \Delta f k_B T$

Nyquist/Johnson noise

Example of "fluctuation-dissipation theorem" $\langle V^2 \rangle$ is fluctuation

power in $R$ is dissipation.

---

Heat capacity in insulating solids

$C_V$

- $3Nk_B$

$T$

high-temp. $3Nk_B$ "law of Debye & Pettit" is just classical equipartition

$N = \text{molecules}$

$3N$ positional deg. of freedom

$3N$ momentum

$$C_V = \frac{\partial (3Nk_B)}{\partial T} = 3Nk_B$$

(as noted before, $C_V \approx C_P$ for solids)

Volumetric specific heat $c_v = \frac{C_v}{V} = 3nk_B$

well established experimentally but fails at low $T$. How low depends on material - typically 100-300K
Comparison of light & elastic modes of solids:

light

\[ E = c \beta \lambda = \omega \]

"relativistic dispersion"

momentum \( p = h \omega / c \)

\[ E = \frac{p^2}{2m} \]

for massive free particle (non-relativistic)

result from solid-state physics:

"optical" (photonics)

acoustic

linear dispersion (acoustic)

\[ k = \frac{2\pi}{\lambda} \]

wavenumber "crystal momentum" = \( \hbar k \)

Maximum wavenumber because of minimum distance between atoms...

\[ |\lambda| \geq 2a \]

\[ \Rightarrow |k| \leq \pi/a \]

Debye approx.:

1) ignore "optical" mode

2) assume all 3 acoustic branches have equal \( \pm k_{F} \), i.e.

3) carry integration exactly as far as needed to get 3N modes
Recall photon integral:

\[ 2 \sum_{\omega/\hbar \neq 0} = 2 \int \frac{4 \pi n^3 \hbar^2}{m^2} \, \frac{d\omega}{\omega} \]

not \( w \propto k \) \quad \text{we have linear dispersion so that } \int \text{ over } n \text{ is really over } k

For Debye [Phonons], \( N \) again \( \omega / \hbar \), so we can again replace \( \int d\omega \) with \( \int d\omega \).

 multiply photon result by \( 3/2 \) since there are three polarizations instead of just two,

and cut off integral:

\[ \frac{1}{2} \pi n_D^3 = 3N \]

\[ n_D = (6N/\pi)^{1/3} \]

\[ U = \sum <\varepsilon_n> = \sum \frac{k \omega}{\exp(k\omega/\Theta_D) - 1} \quad \omega = \frac{n \pi \nu}{L} \]

\[ = \frac{3}{2} \pi \int_0^{\omega_D} \left( \frac{\pi \nu}{L} \right)^3 \omega^2 \, d\omega \frac{k \omega}{\exp(k\omega/\Theta_D) - 1} \quad \omega_D = \frac{\pi \nu}{L} \]

For low-temp limit, \( k_B T \ll \Theta_D = \kappa \omega_D \), integral is tiny when \( \omega > \omega_D \),

so might as well take integral all the way to \( \infty \). Now it's essentially

the same as for phonon gas (but \( 3/2 \))

\[ U \approx \frac{3}{2} \pi \left( \frac{\pi \nu}{L} \right)^3 \left( \frac{3}{1 \cdot 2} \right) \left( \frac{\pi \nu}{L} \right) \]

\[ = \frac{3 \pi^4 N k_B T^4}{5 \Theta_D^3} \]

low-temp heat cap \( C_v = \left( \frac{\partial U}{\partial T} \right)_V = \frac{12}{5} \pi^4 N k_B \left( T/\Theta_D \right)^4 \)

high-temp heat \( C_v \text{, see } \text{Lambor \& Petit} \)

\[ 3N k_B T \]
Until now, we've held $N$ (# particles) constant, and two thermodynamic variables determined all the others (e.g. $U$ and $V_i$ or $V$ and $T$). Clearly, adding a particle while holding $V, T$ constant will change $U, P, S, \ldots$ so we need to consider this.

We already know that $T_1 = T_2 = T$ (in equilibrium).

Write Helmholtz free energy

$$F_i = F_i(T, V_i, N_i) = U_i(T, V_i, N_i) - T_i S_i(T, V_i, N_i)$$

for each system ($i = 1, 2$).

Note: $U, S, F$ all determined by ind. vars. $T_i, V_i, N_i$.

Since $T_i, V_i$ fixed,

$$\frac{dF_i}{dN_i} = \left( \frac{2F}{2N} \right)_{T_i, V_i} dN_i$$

and

$$\frac{dF_2}{dN_2} = \left( \frac{2F}{2N_2} \right)_{T_i, V_i} dN_2 = -\left( \frac{2F}{2N_1} \right)_{T_i, V_i} dN_1$$

Total change in free energy

$$dF = \left[ \left( \frac{2F}{2N_1} \right)_{T_i, V_i} - \left( \frac{2F}{2N_2} \right)_{T_i, V_i} \right] dN_1$$

At equilibrium, $dU = dS = 0$, so $dF = 0$. A particle is as likely to move $1 \rightarrow 2$ as $2 \rightarrow 1$, so $\Delta F = 0$. Write

\[ \text{(I) Chemical potential} \quad \mu(T, V, N) \equiv \left( \frac{\partial F}{\partial N} \right)_{T, V} \text{ for each; deduce } \mu_1 = \mu_2 \text{ in equilibrium.} \]

Since particles are not infinitely divisible, maybe in part (I) we should write

$$\mu(T, V, N) = F(T, V, N) - F(T, V, N-1) = \left( \frac{\Delta F}{\Delta N-1} \right)_{T, V}$$

so chem. pot. is free energy difference due to adding one particle.

In general, $\mu$ depends on $N_i$, so

$$\mu \neq N \mu$$
Chapter 8 defines Gibbs free energy \( G = U - TS + PV = F + PV \), and we'll see that

\[
\mu(T, P) = \left( \frac{\partial G}{\partial N} \right)_{T, P} = \frac{\partial G(N, T, P)}{N}
\]

Since at constant \( T \) & \( P \), \( \mu \) is incl. of \( N \).

When to use (1) and when (2)?

(1) useful for boxes of fixed volume;
(2) useful in chem. reactions open to atmosphere held at fixed pressure.

Example: ideal gas

\[
F(T, V, N) = k_B T \left[ N k_B Z_1 - \ln N ight]
\]

\[
F(T, V, N-1) = -k_B T \left[ (N-1) k_B Z_1 - \ln(N-1)! \right]
\]

\[
\mu(T, V, N) = k_B T \ln \left( \frac{N}{n_0 V} \right) = k_B T \ln (n/n_0), \quad n = \frac{N}{V} \text{ number density}
\]

- intensive (like \( n, T, I \))
- at fixed volume, increases, but nonlinearly, with \( N \)

If \( \mu_2 > \mu_1 \), particles will flow - in which direction?

\[
\begin{array}{c|c|c}
\mu_1 & \mu_2 > \mu_1 \quad \text{Since } n_2 > n_1, \text{ more likely 2 \rightarrow 1 then reverse} \\
T & T
\end{array}
\]

Call this source of chem. pot. "internal." (\( \mu^\text{int} \))

We can counteract it w/ an "external" potential.

For example, for particles all with charge \( e \), apply an electric potential \( \varphi \) to side 1, zero to side 2. This raises energy of e⁻ particle in system 1 by \( e \varphi \) but doesn't change entropy.

Now \( F_1 = F_1^\text{old} + N_1 e \varphi \)

\[
\mu_1^\text{int} = \left( \frac{\partial F_1}{\partial N_1} \right)_{T, V} = \left( \frac{\partial F_1^\text{old}}{\partial N_1} \right)_{T, V} + e \varphi = \mu_1^\text{int} + e \varphi
\]
If we set $\epsilon_f = \mu_{1}^{\text{int}} - \mu_{2}^{\text{int}}$, then $\mu_{1}^{\text{tot}} = \mu_{2}^{\text{tot}}$, and we've restored equilibrium.

K&K give several examples:

1. Pressure as function of height $h$ in atmosphere

\[ P(h) = P(0) e^{-h/h_c} \quad h_c \approx 8.5 \text{ km} \]

Pretend isothermal $B$ equilibrium (1)

$D$ ideal gas

$D$ all $N_2$

\[ \mu_{1}^{\text{int}} = k_B T \ln(n(h)/n_0) \quad \text{(ideal gas)} \]

\[ \mu_{\text{ext}} = Mg h \quad (M \approx M_{N_2}) \]

\[ \mu(h) = \mu_{1}^{\text{int}} + \mu_{\text{ext}} \quad \text{should be ind. of height} \]

\[ 0 = \frac{d\mu}{dh} = \frac{k_B T}{n_0} \frac{dn}{n} + Mg = \frac{k_B T}{n} \frac{dn}{dh} + Mg \]

\[ \frac{dn}{dh} = -\frac{Mg}{k_B T} n \]

solution: $n = e^{-h/h_c} n(0) \quad \text{w/} \quad h_c = \frac{k_B T}{Mg}$

Since $P = \frac{N_2^0 k_B T}{V} - n k_B T$, $P \propto n$, and

\[ P(h) = P(0) e^{-h/h_c} \]

Other examples in text:

- Mobile particles in $B$ field
- Pb-acid battery
Extend thermodynamic identity.
Consider $U$ a function of $S$, $V$, and $N$.

1. $dU = \left( \frac{\partial U}{\partial S} \right)_{V,N} dS + \left( \frac{\partial U}{\partial V} \right)_{S,N} dV + \left( \frac{\partial U}{\partial N} \right)_{S,V} dN$

   What is $\left( \frac{\partial U}{\partial N} \right)_{S,V}$?

   Try $F = F(T,V,N) = U - TS$

   $dF = \left( \frac{\partial F}{\partial T} \right)_{V,N} dT + \left( \frac{\partial F}{\partial V} \right)_{T,N} dV + \left( \frac{\partial F}{\partial N} \right)_{T,V} dN$

   $= -SdT - PVdV + \mu dN$.

2. But $dF$ also $dU - TdS - SdT$

   $= \frac{\partial U}{\partial V} dV + \left( \frac{\partial U}{\partial N} \right)_{S,V} dN - TdS - SdT$

3. Equate 1 and 2:

   $-SdT - PVdV + \mu dN = -PVdV + \left( \frac{\partial U}{\partial N} \right)_{S,V} dN - SdT$

   So $\left( \frac{\partial U}{\partial N} \right)_{S,V} = \mu$

   Assume SSA problem 5:11
Yet another expression for $\mu$:

Consider $S$ as a func. of $U, V, N$. Then

$$dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV + \left( \frac{\partial S}{\partial N} \right)_{U,V} dN$$

What is $\left( \frac{\partial S}{\partial V} \right)_{U,N}$? I have an easier way to answer this, but then I'd have no excuse to prove a useful general formula, so...

For this section, keep $N$ fixed implicitly. $S, V, U$ then interdependent:

$$S = S(U, V)$$
$$V = V(S, U)$$
$$U = U(S, V)$$

General identity: \( \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1 \) for $x, y, z$ interrelated

derive: \( z = z(x, y) \), so \( dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \)

Hold $z$ constant (i.e., $dz = 0$): then

$$\left( \frac{\partial z}{\partial x} \right)_y dx \bigg|_z = -\left( \frac{\partial z}{\partial y} \right)_x dy \bigg|_z \quad \text{or}$$

$$\left( \frac{\partial z}{\partial x} \right)_y \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial x} \right)_z = -1$$

Alternative derivation not using "bare" differentials begins with facts that \( \frac{d^2 x}{d^2 y} = \frac{d^2 y}{d^2 x} = \frac{d^2 z}{d^2 x} = 0 \) since any two are independent

write \( \frac{dy}{dx} = 1 \)

apply chain rule twice

\( x \rightarrow U \)
\( y \rightarrow V \)
\( z \rightarrow S \)

\[ \left( \frac{\partial U}{\partial V} \right)_P \left( \frac{\partial V}{\partial S} \right)_U \left( \frac{\partial S}{\partial U} \right)_V = -1 \]

(Add a constant $N$, too)
\[ \left( \frac{\partial S'}{\partial V} \right)_U = \frac{P}{T} \]

Now for \( \left( \frac{\partial S}{\partial N} \right)_{U,V} \), I'll do this one the easy way:

\[
\begin{align*}
\Delta S & = \frac{1}{T} dU + \frac{P}{T} dV + \left( \frac{\partial S}{\partial N} \right)_{U,V} dN \\
\Delta U & = T \Delta S - P \Delta V - T \left( \frac{\partial S}{\partial N} \right)_{U,V} dN \\
\end{align*}
\]

so

\[
-T \left( \frac{\partial S}{\partial N} \right)_{U,V} = \mu
\]

Grand-Canonical (Gibbs) Ensemble

\[
\begin{array}{|c|c|}
\hline
\text{Total } U_0 & \text{System } E_{N_0} \\
\text{Total } N_0 & N_0 - N \\
\hline
\end{array}
\]

\[ R \text{ is much bigger than } \]

\text{Total } U_0 \text{ fixed for this derivation.}

\text{Total } N_0 \text{ state # particle ensemble: many systems } \mathcal{S}_1 = (N_1, N_1), \mathcal{S}_2 = (N_1, N_1), \ldots

What is prob \( p(N, N) \) that the system is in state \((N, N)\)?

Follow same deriv used for canonical ensemble: \( g = \frac{1}{h} \)

\[ P \propto g(U_0-E_0, N_0-N) = \exp \left( \frac{1}{k_B} S(U_0-E_0, N_0-N) \right) \]

two states, \((N_1, N_1)\) and \((N_2, N_2)\):

\[
\frac{P(N_1, N_1)}{P(N_2, N_2)} = \exp \left( \frac{1}{k_B} \left[ S(U_0-E_1, N_0-N_1) - S(U_0-E_2, N_0-N_2) \right] \right)
\]

\[ J \ll R, \text{ so } \frac{N_1-N_2}{N_0} \ll 1, \frac{E_1-E_2}{U_0} \ll 1 \]

so

\[
\Delta S = - (E_1-E_2) \left( \frac{2S}{2U_0} \right)_{N_0} - (N_1-N_2) \left( \frac{2S}{2N_0} \right)_{U_0} \]

\[ -\mu / T \]
\[ \frac{\mathcal{P}(N_1,N_2)}{\mathcal{P}(N_1,N_2)_0} = \exp \left[ N_1 \mu - N_2 \mu - \Sigma_1 \beta + \Sigma_2 \beta \right] \]

\[ = \frac{\exp \left[ (N_1 \mu - e_i) \beta \right]}{\exp \left[ (N_2 \mu - e_i) \beta \right]} \]

and

\[ \mathcal{P}(N_1,N_2) = \frac{\exp \left[ (N_1 \mu - e_i) \beta \right]}{Z} \]

where \[ Z = \sum_{N_1,N_2} \exp \left[ (N_1 \mu - e_i) \beta \right] \]

"Grand partition function" or "Gibbs sum"

Some authors use other letters, e.g. script \( \Omega \) or \( \Omega \).

Useful expression for thermal average partition function:

\[ \langle N \rangle = \frac{\sum_{N} N e^{-(e_i-\mu N)\beta}}{Z} \]

Recall trick

\[ U = \langle e_i \rangle = \frac{\sum_{i} e_i e^{-e_i \beta}}{\sum_{i} e^{-e_i \beta}} = -\frac{\partial}{\partial \beta} \ln Z \]

or

\[ = -k_B T \frac{\partial}{\partial T} \ln Z = 0 \]

We can do something similar for \( \langle N \rangle \):

\[ \langle N \rangle = \left[ k_B T \frac{\partial}{\partial \mu} \ln Z \right] \]

\( \mu \) is "conjugate" to \( N \)

Useful for fixing \( N = \langle N \rangle \) to be "right" number

Example: non-interacting \( e \)'s in a metal

It's label states (up, spin), each \( e \) can have occupancy \# 0 or 1 only (fermion).
prob. of occup. of a one-\(\epsilon\) state (incl. spin), \(n\), w/energy \(E_n\) is

\[ P_n = \frac{e^{-(E_n - \mu)/\beta}}{Z_n} \]

where \(Z_n = 1 + e^{-(E_n - \mu)/\beta} \), so \(P_n = \frac{e^{-(E_n - \mu)/\beta}}{1 + e^{-(E_n - \mu)/\beta}} = \frac{1}{e^{(E_n - \mu)/\beta} + 1} \)

\[ N = \langle N \rangle = \int d\epsilon \frac{1}{e^{(E_n - \mu)/\beta} + 1} \]

will include geometrical factor - "density of states" \(\Delta\epsilon\)

One then sets \(\mu\) such that \(N\) will be right # (determined by voltage).

Result from \(\epsilon\)'s:

\[ \mu = \mu(T = 0) - (\text{const.}) \left( \frac{k_B T}{\epsilon_F} \right)^2 \times \left( \frac{T}{\epsilon_F} \right)^4 \]

\(\epsilon_F\) = Fermi energy

\(\epsilon_F = k_B \cdot 1000\, K\)

---

2/19/03 Fri. Gibbs

today: Fermi - Dirac

Bose-Einstein

Deltammap

was: Ideal classical gas

Gibbs sum \(Z = \sum_{E_n} e^{-(E_n - \mu)/\beta} \equiv \sum_{E_n} \lambda^n e^{-\beta E_n} \)

\(\lambda = e^{\beta \mu}\) called "fugacity" (K&H call it "absolute activity", but I haven't seen this term elsewhere.)

Recall that for an ideal gas

\[ \mu = k_B T \ln (n/n \bar{n}) \]

so \(n = \bar{n}\), \(\bar{n} =\) quantum concentration

so \(\lambda = n/n \bar{n}\) (ideal gas)
Example: K&K prob. 5.4

Set Δμ = eV1, q the fundamental charge.

Taking μ = k_BT ln (n/n₀) as for ideal gas (this is just an estimate), we have:

\[ Δμ = μ_{\text{in}} - μ_{\text{out}} = k_BT \ln \left( \frac{n_{\text{in}}}{n_{\text{out}}} \right) = k_BT \ln (10^4) \]

Useful # to remember: \( k_B 300K \approx \frac{1}{40} \text{ eV} \)

So \( Δμ \approx \frac{1}{40} \ln(10) \text{ eV} \approx 0.23 \text{ eV} = eV_1 \)

or \( V = 0.23 \text{ volts} \)

Example: K&K problem 5.8

3 levels:

<table>
<thead>
<tr>
<th>State</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacant</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
<td>E₁</td>
</tr>
<tr>
<td>CΟ</td>
<td>E₂</td>
</tr>
</tbody>
</table>

Equilibriums:

\[ \frac{M_{O_2}}{M_{CO}} \] adsorbed \( O_2 = \mu_{O_2} \)
\[ \mu_{CO} \] adsorbed \( CO = \mu_{CO} \)

Fugacity \( \lambda_{O_2} = 1 \times 10^{-5} \approx e^{M_{O_2}E} \)

Fugacity \( \lambda_{CO} = 1 \times 10^{-7} \)

\[ T = 37^\circ C = 310K \] Ignoring internal degrees of freedom

e) Gibbs sum for one site (no CO):

\[ Z = e^0 + \lambda_2 e^{-βE_1} = 1 + \lambda_2 e^{-βE_1} \]

prob. occupied \( \frac{\lambda e^{-βE_1}}{2} \equiv 0.9 \equiv \alpha \) \( (\lambda = \lambda_{O_2}) \)

\[ e^{-βE_1} (\lambda - α^2) = α \]

\[ e^{-βE_1} = \frac{α}{\lambda(1-α)} = \frac{0.9}{10^{-5} \cdot 0.1} = 9 \times 10^5 \]
\[ E_n = -k_B T \ln \left( 9 \times 10^5 \right) = \frac{k_B}{3 \times 10^5} \ln \left( 9 \times 10^5 \right) = -0.37 \text{ eV} \]

b) Introduce CO \( \% \) the concentration \( n_0 \) \( (n_0 = 10^{-7}) \)

We're told that now only 1% of sites have absorbed \( O_2 \). What is CO binding energy, \( E_B \)?

\[ J = 1 + n_0 e^{-E_B/k_B} = 1 + n_0 e^{-E_B/k_B} \]

prob. occ. by \( O_2 \) \[ \frac{n_0 e^{-E_B/k_B}}{J} = \frac{9}{J} \]

\[ J = \frac{90}{10}, \text{ or } n_0 e^{-E_B/k_B} = 80 \]

\[ E_B = -k_B T \ln \left( \frac{n_0 e^{-E_B/k_B}}{n_0} \right) = -0.0268 \text{ eV} \ln (8 \times 10^{-7}) \]

\[ = -0.55 \text{ eV} \]

CO much more tightly bound than \( O_2 \):

\[ \frac{E_B - E_n}{k_B T} = \frac{0.18 \text{ eV}}{0.027 \text{ eV}} \approx 6.7 \] so it's very hard @ body temp. to dislodge a CO

---

"Quantum Statistics"

Q. Mech: Every particle has an intrinsic angular momentum, either an integer multiple (0, 1, 2, 3, etc.) or a half-integer multiple (e.g., photon has spin 1, electron spin \( \frac{1}{2} \)).

Spin-Statistics theorem (relativistic q. field theory):

- Integer spin: Bosons \( \Psi (2,1) = \Psi (1,2) \)
- Half-integer: Fermions \( \Psi (2,1) = -\Psi (1,2) \)

Consequence for Fermions:

\[ \begin{pmatrix} 1 \\ 2 \end{pmatrix} = -\begin{pmatrix} 2 \\ 1 \end{pmatrix} \]

However,

\[ \begin{pmatrix} 2 \\ 1 \end{pmatrix} = \begin{pmatrix} 2 \\ 2 \end{pmatrix} \]

because labels are arbitrary
So double (or higher) occupancies are FORBIDDEN.

BOSE case. Like photons/phonons but particle number (ingenuously) conserved \( \rightarrow \) mod. \( \lambda \).

For one state ("orbital"),

\[
\mathcal{Z} = \sum_{N=0}^{\infty} e^{-\frac{(N-\mu)\beta}{\lambda}} = \sum_{N=0}^{\infty} (\lambda e^{-\beta})^N = \frac{1}{1-\lambda e^{-\beta}} \quad \text{provided } \beta > \mu \quad \text{so } \lambda e^{-\beta} < 1
\]

occupation function:  

For a single state of energy \( \xi \):

\[
f(\xi) = \langle N(\xi) \rangle = \lambda \frac{\partial}{\partial \lambda} \ln \mathcal{Z} = \left( = \sum \frac{\lambda^N N e^{-\xi N \beta}}{\mathcal{Z}} \right)
\]

\[
= -\lambda \frac{\partial}{\partial \lambda} \ln (1-\lambda e^{-\beta})
\]

\[
= \frac{\lambda e^{-\beta}}{1-\lambda e^{-\beta}} = \frac{1}{\lambda^2 e^{\beta} - 1}
\]

Bose-Einstein distribution

Interpretation: for a level of energy \( \xi \), what is the expected occupation number?

FERMI case

Gibbs sum for one state ("closed")

occupation function:

\[
f(\xi) = \langle N(\xi) \rangle = \frac{\lambda e^{-\beta \xi}}{1 + \lambda e^{-\beta \xi}} = \frac{1}{e^{(\xi-\mu)\beta} + 1}
\]

Fermi-Dirac distribution

Interp.: we have many levels, e.g. of a diff. energy \( \xi \). \( f(\xi) \) tells

\[f(\xi) = \begin{cases} 
\frac{1}{0+1} = 1 & \xi < \mu(T=0) \text{ definitely occupied} \\
\frac{1}{0+1} = 0 & \xi > \mu(T=0) \text{ definitely unoccupied}
\end{cases}\]

At \( T=0, \beta = \infty \), so \( f(\xi) = \begin{cases} 
1 & \xi < \mu(T=0) \\
0 & \xi > \mu(T=0)
\end{cases}\)
Let $a = \frac{1}{2}$.

For $x < 0$, we have $f(x) = \frac{1}{2}$. For $x > 0$, we have $f(x) = x^2 - 1$.

The function $f(x)$ is continuous at $x = 0$ if $\lim_{x \to 0} f(x) = f(0)$.

The limit of $f(x)$ as $x$ approaches $0$ can be found using the definition of a limit.

For $x > 0$, we have

$$f(x) = x^2 - 1$$

For $x < 0$, we have

$$f(x) = \frac{1}{2}$$

For $x = 0$, we have

$$f(0) = \lim_{x \to 0} f(x) = \frac{1}{2}$$

Therefore, the function $f(x)$ is continuous at $x = 0$.

For $x > 0$, we have

$$\int_{-1}^{x} f(t) dt$$

For $x < 0$, we have

$$\int_{x}^{-1} f(t) dt$$

For $x = 0$, we have

$$\int_{-1}^{0} f(t) dt$$

Using the Fundamental Theorem of Calculus, we can evaluate these integrals.

For $x > 0$, we have

$$\int_{-1}^{x} f(t) dt = \left[ \frac{1}{2} x^2 - x \right]_{-1}^{x} = \frac{1}{2} x^2 - x - \left( \frac{1}{2} + 1 \right) = \frac{1}{2} x^2 - x - \frac{3}{2}$$

For $x < 0$, we have

$$\int_{x}^{-1} f(t) dt = \left[ \frac{1}{2} t^2 - t \right]_{x}^{-1} = \frac{1}{2} (-1)^2 - (-1) - \left( \frac{1}{2} x^2 - x \right) = \frac{1}{2} + 1 + \frac{1}{2} x^2 - x = \frac{3}{2} + \frac{1}{2} x^2 - x$$

For $x = 0$, we have

$$\int_{-1}^{0} f(t) dt = \left[ \frac{1}{2} t^2 - t \right]_{-1}^{0} = \frac{1}{2} (0)^2 - 0 - \left( \frac{1}{2} + 1 \right) = -\frac{3}{2}$$

For $x > 0$, we have

$$\int_{0}^{x} f(t) dt = \left[ \frac{1}{2} t^2 - t \right]_{0}^{x} = \frac{1}{2} x^2 - x$$

For $x < 0$, we have

$$\int_{x}^{0} f(t) dt = \left[ \frac{1}{2} t^2 - t \right]_{x}^{0} = \frac{1}{2} (0)^2 - 0 - \left( \frac{1}{2} x^2 - x \right) = -\frac{1}{2} x^2 + x$$

For $x = 0$, we have

$$\int_{0}^{0} f(t) dt = \left[ \frac{1}{2} t^2 - t \right]_{0}^{0} = \frac{1}{2} (0)^2 - 0 = 0$$
For state $\varepsilon$,
\[
Z = \sum_{N_k} \frac{1}{N_k!} e^{-\beta(\varepsilon - \mu)N_k} = \sum_{\lambda} \frac{1}{\lambda!} (\lambda e^{-\beta \varepsilon})^{N_k}
\]
\[
\langle N_k \rangle = -\frac{1}{\beta} \left( \frac{\partial}{\partial \varepsilon} \right)_{\mu, T} \mu, T
\]

Simplify: \[Z = e^{\lambda e^{-\beta \varepsilon}}\]

So \[\langle N_k \rangle = -\frac{1}{\beta e^{\lambda e^{-\beta \varepsilon}}} \lambda e^{-\beta \varepsilon}(-\beta) e^{\lambda e^{-\beta \varepsilon}}\]

\[= \lambda e^{-\beta \varepsilon} = \frac{e^{-\beta(\varepsilon - \mu)}}{e^{\beta(\varepsilon - \mu)}} \equiv f_{MB}(T, \mu)\]

Let \[\lambda = e^{\beta(\varepsilon - \mu)}\]. Then

\[f_{FP}(x) = \frac{1}{x+1}\]
\[f_{BE}(x) = \frac{1}{x-1}\]
\[f_{MB}(x) = \frac{1}{x+1}\]

Now some graphs. Convert $\frac{1}{N_i}$.

Classical is valid only when $f_{MB} \ll 1$; i.e.,

\[\lambda \gg 1\] contribute significantly, so $\frac{1}{N_i} \ll 1$.

Deduce behavior of IDEAL monatomic classical gas from $f_{MB}$
- we previously derived most of these relations from the canonical ens.

1. Using $\mu$ as knob to ensure $\langle N_k \rangle = \text{true for } N_0$:
\[ N_0 = \langle N \rangle = \sum m_0 (z_0) = \frac{2}{\lambda} \sum e^{-z_0} = \frac{2}{\lambda} z_1, \ \text{where} \ z_1 = n_0 V \] (4.3)

So \[ \lambda = \frac{N_0}{z_1} = \frac{N_0}{n_0 V} = \frac{\lambda}{n_0} \] (ideal gas)

Taking log:
\[ \mu = k_B T \ln (n/n_0) \]

Primary derived in ch.5.

2. Helmholtz free energy
\[ \left( \frac{\partial F}{\partial N} \right)_{V, T} = \mu \]

\[ F(N, T, V) = \int dN' \mu(N', T, V) = k_B T \left[ \ln \left( \frac{n}{n_0 V} \right) + \int dN' \mu(N') \right] \]

\[ = k_B T \left[ \ln \left( \frac{n}{n_0 V} \right) + N k_B T - N - \frac{\mu}{k_B T} \right] \]

\[ = N k_B T \left[ \ln \left( \frac{n}{n_0} \right) - 1 \right] \]

Agrees w/ ch.3

3. pressure (exercise as in ch.9):
\[ P = -\left( \frac{\partial F}{\partial V} \right)_{N, T} = \frac{\partial F}{\partial V} = \frac{N k_B T V^2 N}{(n/n_0) n_0^2} = \frac{N k_B T}{V} \]

or \[ PV = Nk_BT \]

4. entropy \( S = -\left( \frac{\partial F}{\partial T} \right)_{V, N} = -N k_B \left[ \ln \left( \frac{n}{n_0} \right) - 1 \right] + \frac{k_B T n_0}{n} \left( \frac{\partial n}{\partial T} \right) \]

\[ \left( \frac{\partial n}{\partial T} \right) \]

\[ S = -N k_B \left[ \ln \left( \frac{n}{n_0} \right) - 1 \right] - k_B T n_0 \left( \frac{n}{n_0} \right) \left( \frac{\partial n}{\partial T} \right) \]

\[ S = -N k_B \left[ \ln \left( \frac{n}{n_0} \right) - 1 \right] - k_B T n_0 \frac{1}{T} \left( \frac{n}{n_0} \right) \left( \frac{n}{n_0} \right) \]

\[ S = -N k_B \left[ \ln \left( \frac{n}{n_0} \right) + \frac{3}{2} \right] = \left[ N k_B \left[ \ln \left( \frac{n}{n_0} \right) + \frac{3}{2} \right] \right] \]

S. \[ U = F + TS = N k_B T \left[ \ln \left( \frac{n}{n_0} \right) - 1 + k_B \left( \frac{n}{n_0} \right) + S \right] = \frac{1}{2} TV_{k_B T} \]

Equilibrium
6. \( G_V = -T \left( \frac{\partial^2 S}{\partial T^2} \right) \pi \left( \frac{N_k}{n} \right) \frac{1}{n} \frac{\partial \mu}{\partial T} = \frac{3}{2} \frac{N_k}{N} \)  

(Or just \( \frac{\partial^2 U}{\partial T^2} \pi_N \))

7. \( C_p = \left( \frac{\partial U}{\partial T} \right)_p \pi_N + P \left( \frac{\partial V}{\partial T} \right)_p \pi_N \)  

\( = \frac{3}{2} N_k B + P \left( \frac{\partial V}{\partial T} \right)_p \pi_N \left( \frac{N_k}{2} \right) = \frac{3}{2} N_k B + N_k B = \boxed{\frac{5}{2} N_k B} \)

Ratio \( \frac{C_p}{G_V} \equiv \gamma = \frac{5}{3} \) for ideal monatomic gas

Generally, > 1.

How do we revise these results if there are internal degrees of freedom?

E.g.,

\[ \begin{array}{c}
\frac{\partial^2 U}{\partial T^2} \pi \left( \frac{N_k}{n} \right) \\
\frac{\partial V}{\partial T} \pi \left( \frac{N_k}{2} \right)
\end{array} \]

From before, for one "orbit of energy \( \varepsilon \),

\( \pi = \frac{\sum_{i=1}^{N_i} (\lambda e^{-\beta \varepsilon})^0}{N_i} \)  

(no internal deg. of freedom)

Now we need to sum over internal states as well: \( \varepsilon \rightarrow \varepsilon + \varepsilon_{i,\text{int}} \)

\( \pi = \frac{\sum_{i=1}^{N_i} (\lambda e^{-\beta \varepsilon})^0}{N_i} = \sum_{i=1}^{N_i} \frac{1}{N_i} (\lambda e^{-\beta \varepsilon} Z_{i,\text{int}})^0 \)

where \( Z_{i,\text{int}} = \sum_{i=1}^{N_i} e^{-\beta \varepsilon} \)

Occupation number for state \( \varepsilon \) including all internal states:

\( \tau_{nB} (\varepsilon) = \left< n_e \right> = -\frac{1}{\beta} \frac{\partial \mu}{\partial \varepsilon} |_{\mu_T} = Z_{i,\text{int}} e^{-\beta \varepsilon} \beta \)
\[ \lambda = \frac{n}{n_q Z_{\text{int}}} \]

\[ \mu = k_B T \left[ \ln \left( \frac{\gamma}{n_q} \right) - \ln Z_{\text{int}} \right] \]

\[ F = \int dN' \mu(N', T, V) = F_0 + F_{\text{int}} = F_0 - N k_B T \ln Z_{\text{int}} \]

\[ S = -\left( \frac{\partial F}{\partial T} \right)_{N, V} = S_0 - \left( \frac{\partial F_{\text{int}}}{\partial T} \right)_{N, V} \quad \text{(real model of } F_{\text{int}} \text{ to calculate) } \]

\[ U_{\text{int}} = N \frac{\sum e_i^{\text{int}} e^{-\beta E_i^{\text{int}}}}{Z_{\text{int}}} = N \left\langle U_{\text{int}}^{(N)} \right\rangle. \]

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**2/14/03 Wed.**

**Classical ideal gas**

- Thermodynamic quantities
- Internal degrees of freedom

*Today:*
- Finish internal deg.
- Reversible vs. irreversible examples
- Metals
- Neutron stars

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**Model just the** \( U_{\text{int}} \) **for ceramic clastic spring (not iron or steel)**

**Classical 2D phase space:**

\[ E = \frac{1}{2} m x^2 + \frac{1}{2} \alpha p^2 \]

\[ \nu \quad \text{displacement} \]

**Ex: non-linear smooth all phase**

Space is accessible with Boltzmann probability.

\[ Z_{\text{int}} = \mathcal{X} \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx \int_{-\infty}^{+\infty} e^{-\frac{\beta p^2}{2}} dp \]

\[ \mathcal{X} \text{ pos. constant on unit } \theta \quad \text{with } \frac{1}{2} \mathcal{X} \mathcal{X}^{\frac{1}{2}} = \frac{1}{\sqrt{2 \pi}} \]

\[ Z_{\text{int}} = \mathcal{X} \sqrt{\frac{4 \pi}{\beta}} \]

\[ = \sqrt{\frac{4 \pi}{\beta}} \]
\[ \langle u_{int}^2 \rangle = -\frac{1}{2m} \frac{\beta^2}{\beta^2} 2m = \beta \beta^2 = k_B T \] for springs.

\[ \frac{1}{2} k_B T \] for each of pitch and yaw (not for roll), so

\[ U_{\text{kin}}^{\text{total}} = N k_B T \left( \frac{3}{2} + \frac{3}{2} + \frac{1}{2} + \frac{1}{2} \right) = \frac{7}{2} N k_B T \]

\[ \text{So } \zeta = \frac{7}{2} N k_B \]

\[ \text{NOT } V \text{ AGILENT } \text{ with exp} \text{. except at high } T - \]

\[ \text{eq. } (3.9) \text{ p.8} \]

\[ \text{vibration "pulled out" (y. mech.) - just mean } \int_{x_0}^{x_f} dx \text{ should instead have been seen over direct v.} \]

\[ \text{quantum harmonic etc.} \]

Contrast several different expansion processes for monatomic ideal gas.

In each case, \( V_i \) = initial volume, \( V_f \) = final volume, \( N \) = fixed.

\[ \frac{V_f}{V_i} = 2 \]

1. Reversible - isothermal

\[ \text{before} \quad T \quad \text{during} \quad T \quad \text{after} \quad T \]

\[ \text{since } \frac{P_i}{V_i} = \frac{V_i u_i T}{V_i} \]

\[ \frac{P_f}{V_f} = \frac{V_i u_i T}{V_i} \quad \Rightarrow \quad \frac{P_f}{V_f} = \frac{2}{T} = \frac{1}{2} \text{ const.} \]

\[ \text{If expand, change, use Sackur-Tetrode:} \]

\[ \frac{V_i}{T} = V_i \left[ k_B \left( \frac{n_i}{N_i} \right) + \frac{1}{2} \right] \]

\[ \frac{S_f}{T} = V_i \left[ k_B \left( \frac{n_f}{N_f} \right) + \frac{1}{2} \right] \]

\[ \text{Concentration } n = \frac{2}{T}, \text{ so } n_f = \frac{1}{2} n_i. \]

\[ \text{Change } S_f = \frac{V_i}{T} - \frac{V_i}{T} = V_i \left[ k_B \left( \frac{n_i}{N_i} \right) + \frac{1}{2} \right] = V_i \left( k_B + \frac{1}{2} \right) \]
Work done by gas on piston $= \int \frac{P(V)\,dV}{V_i} = \int \frac{Nk_BT\,dV}{V_i} = Nk_B \left( \frac{V_f}{V_i} \right) = Nk_B T \ln \frac{V_f}{V_i}$

change in internal energy $\Delta U = 0$ because $U_f = U_i = \frac{3}{2} Nk_B T$

Since gas lost internal energy through mechanical work, an equivalent amount of heat must have flowed in from the reservoir: $\Delta Q = Nk_B T \ln \frac{V_f}{V_i}$

Use $P-V$ diagram (useful for reversible processes only)

Q1: How can the process be reversible if entropy increases?
A1: entropy change in reservoir is $-\Delta S$, so total entropy change is zero.
$\Delta Q = T \Delta S$.

2. Reversible - adiabatic

entropy change $\Delta S = 0$ by definition

Satistical Tetrode $S(V, T) = Nk_B \left[ k_B \left( \frac{q_0 V}{N^2} \right) + \frac{3}{2} \right] = Nk_B \left[ k_B (T^{\frac{3}{2}}V) \text{ const} \right]$

At $P = \text{const}$, $V^{\frac{3}{2}} = \text{const}$

Q2: So that, you had instead $T^{\frac{3}{2}}V = \text{const}$ for an adiabatic process.
Which was different? It is because gas is in contact with reservoir.

$p_i V_i < p_f V_f$

Adiabatic: steeper than isotherm

$P \left( V_i, T \right) = \frac{p_i V_i}{T_i}$

Substitute $T = \alpha V^{-2\alpha}$ to get $P V^\alpha$:

$\alpha V^{2\alpha} = \frac{p_i V_i}{T_i}$ & $\Rightarrow \alpha = \frac{2}{\alpha + 1}$
Change in temp. from $T_i$ to $T_f$:

$$\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} = \left( \frac{V_i}{V_f} \right)^{-\gamma} = \left( \frac{V_i}{V_f} \right)^{3/5} \quad \text{so it cools}$$

Change in internal energy:

$$\Delta U = U_f - U_i = \frac{3}{2} N k_b (T_f - T_i) \quad \text{loses energy}$$

Work done by gas on piston:

$$W = \int P \, dV = \int \frac{N k_b T(V)}{V} \, dV$$

$$P(V) \alpha \frac{1}{V^\gamma} = \frac{N k_b}{V_i} \int V^{-5/3} \, dV = -\frac{3}{2} N k_b \alpha (V_f^{-\gamma} - V_i^{-\gamma}) = -\frac{3}{2} N k_b (T_f - T_i) > 0$$

3. Reversible - isobaric

Explain how mass is added to hold $P$ fixed.

Reservoir $T$ increases slowly perhaps by means of the compression of another ideal gas.

Work done by gas on piston:

$$W = P(V_f - V_i)$$

$$P = \text{const} = \frac{N k_b T_f}{V_i} = \frac{N k_b T_i}{V_i}$$

$$\alpha \frac{V_f}{V_i} = \frac{V_i}{V_f} \quad \text{for change}$$

Change in internal energy:

$$\Delta U = U_f - U_i = \frac{3}{2} N k_b (T_f - T_i) > 0$$

2/1/2023
Contrast sudden expansion:

\[ \Delta U = 0 \] because there's no reason for work to go

\[ \text{Since } U_f = U_i = \frac{3}{2} N k_b T \text{: No change in temperature (assumed: } k \text{ ideal gas}) \]

Increase in entropy from vacuo to Tetradec:

\[ \Delta S = N k_b \ln \left( \frac{N_f}{N_i} \right) = N k_b \ln 2 \]

Q. Why can't we use \( dU = dQ - dW \)?

\[ dS = \frac{1}{T} dU \quad \text{is const, so } \int dS = \int \frac{dU}{T} \]

A. \( dU - T dS \) assumes a reversible process, which this is not.