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 — much too hard!)

Thermodynamics:
axioms
\[
\frac{\partial S}{\partial V_A} = \frac{\partial P}{\partial T} V
\]

kinetic theory of gases
\[PV = Nk_B T\]

Classical statistical mechanics
\[S = k_B \log \Omega \]

quantum statistical mechanics

Modern statistical mechanics / thermodynamics

why: not "classical" statistical mechanics?

READ GOODSTEEN

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 \textit{state variables}. For example, for a gas in a box, these might be:

\begin{itemize}
  \item pressure $P$
  \item volume $V$
  \item temperature $T$
  \item internal energy $U$
  \item number of particles $N$
  \item entropy $S$
\end{itemize}

\text{not all independent}

Organize

\begin{itemize}
  \item \textit{extensive}
    \begin{itemize}
      \item $N$
      \item $V$
      \item $S$
    \end{itemize}
  \item \textit{intensive}
    \begin{itemize}
      \item $T$
      \item $P$
      \item color?
    \end{itemize}
\end{itemize}

\text{neither}

\begin{align*}
\text{mass} & \quad \text{mass} \\
\text{energy} & \quad \text{speed} \\
\text{momentum} & \quad \text{time}
\end{align*}

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

\begin{align*}
\text{intensive quantity} & \quad \text{same in 1 \& 2} \\
\text{if two systems can exchange} & \quad \text{how (example)}
\end{align*}

\begin{itemize}
  \item pressure
  \item chemical potential
  \item temperature
  \item volume
  \item particles
  \item energy
\end{itemize}

piston

none in container; electrical

thin rigid wall (barometric)

\text{Steady state: no change in any state variables.}

\text{Equilibrium: steady state AND no net flow of exchanged quantities with ANY other system (individually, not just collectively).}
What is temperature? A (pre)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.

   - 2nd law (special application): heat flows hotter to colder until equilibrium reached.
   - Still doesn't tell us how to measure it
   - Combined with 1st law, eventually get to hot engines (below)

2. Practical expansion type thermometer

   - Gabriel Daniel Fahrenheit 18th c.
   - Previously used alcohol for very calibration.
   - 0°F = freezing of salt water (solid ice in colder) vs. 32°F = body temp.
   - 100°F = body temp.

   So Fahrenheit was intended to be a centigrade scale.

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

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

\[ \text{Define temperature } k_B T = \frac{3}{2} \langle \frac{1}{2} m v^2 \rangle \text{, } \text{Then } \frac{PV}{N k_B T} \rightarrow \text{gas thermometer} \]

\[ \text{Note: } T \sim 0 \]

arbitrary constant to convert energy units into temperature units.

\[ k_B \text{ set } k_B = 1 \text{ to define } \left( \frac{3}{2} \langle \frac{1}{2} m v^2 \rangle = k_B T \right) \]

\[ \text{I.e., measure temperature in ergs} \]

\[ k_B = 1.38 \times 10^{-16} \text{ erg/} \text{K} \]

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

- Observer

  - N fast but 

    - gas in box

    - state function

    - Thermal energy

    - not gas in box

    - state function

    - Thermal energy

    - not gas in box

  - not gas in box

  - state function

  - Thermal energy

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  - not gas in box
We do NOT add \( u \) 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 \( v \ll c \).)

4. Heat Engine

\[
\begin{align*}
\text{Hot reservoir:} & \quad \frac{T_2}{1} \\
\downarrow & \quad Q_2 \\
\text{Reversible engine} & \quad \rightarrow \text{mechanical work } W = Q_2 - Q_1 \\
\downarrow & \quad Q_1 \\
T_1 \quad \text{cold}
\end{align*}
\]

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:
(carry around a reference reservoir at \( T_1 \); measure \( Q_1 \) & \( Q_2 \) to get \( T_2 \).) e.g. triple point of \( \text{H}_2\text{O} \)

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

- internal energy
  - macrostate: \( P, V, T, U, \ldots \) not all independent
  - small \#
  - Assume \( U \) determines all the rest (e.g., \( \text{ideal gas in rigid box} \))

- microstate: \( \{ x_1, x_2, \ldots \}, \{ p_1, p_2, \ldots \} \), \( \text{large \#} \)

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

Two systems in thermal equilibrium - can exchange energy but not volume or particles. 

$T$ will be "that thing" which is the same @ equilibrium

![Diagram](image)

- $U = U_1 + U_2$ 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 

$$C = \left( \frac{\partial g(U_1)}{\partial U} \right)_N = g_1'(U_1)g_2(U-U_1) - g_1(U_1)g_2'(U-U_1)$$

$$= \frac{g_1'}{g_1} \frac{g_2'}{g_2}$$

**Intuitively** hot $\rightarrow$ big cells & small $\rightarrow$ cold.

**Property**:

- $g_1$ & $g_2$ are same func.

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

where $S \equiv k_B \ln g$

Agree that $\lim_{g' \rightarrow 0} \frac{g'}{g} = 0$ or $U \rightarrow 0$ 

$$T = \left( \frac{\partial U}{\partial S} \right)_N$$
Start on counting microstates

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

Each classical spin $\uparrow +1$ or $\downarrow -1$ will be useful later when we turn on magnetic field.

1) very simple - exactly solvable
2) other similar systems aren't so easy (but)
3) generic features of $g(n)$ are good for large # of spins

<table>
<thead>
<tr>
<th>One spin</th>
<th>$\uparrow$</th>
<th>+1</th>
<th>$g(1) = 1$</th>
<th>Probability $P_{B=0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\downarrow$</td>
<td>-1</td>
<td>$\frac{1}{2^1}$</td>
<td>50%</td>
</tr>
<tr>
<td>Two spins</td>
<td>$\uparrow \uparrow$</td>
<td>+2</td>
<td>1</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>$\uparrow \downarrow$</td>
<td>0</td>
<td>2</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>$\downarrow \uparrow$</td>
<td>0</td>
<td>2</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>$\downarrow \downarrow$</td>
<td>-2</td>
<td>$\frac{1}{2^2}$</td>
<td>25%</td>
</tr>
<tr>
<td>Three spins</td>
<td>$\uparrow \uparrow \uparrow$</td>
<td>3</td>
<td>$g(3) = 1$</td>
<td>12.5%</td>
</tr>
<tr>
<td>Eight states</td>
<td>$\uparrow \uparrow \downarrow$</td>
<td>1</td>
<td>$g(3) = 1$</td>
<td>12.5%</td>
</tr>
<tr>
<td></td>
<td>$\uparrow \downarrow \uparrow$</td>
<td>1</td>
<td>$g(1) = 3$</td>
<td>37.5%</td>
</tr>
<tr>
<td></td>
<td>$\downarrow \uparrow \uparrow$</td>
<td>1</td>
<td>$g(-1) = 3$</td>
<td>37.5%</td>
</tr>
<tr>
<td></td>
<td>$\uparrow \uparrow \downarrow$</td>
<td>-1</td>
<td>$g(-1) = 3$</td>
<td>37.5%</td>
</tr>
<tr>
<td></td>
<td>$\downarrow \downarrow \uparrow$</td>
<td>-1</td>
<td>$g(-1) = 3$</td>
<td>37.5%</td>
</tr>
<tr>
<td></td>
<td>$\uparrow \downarrow \downarrow$</td>
<td>-1</td>
<td>$g(-1) = 3$</td>
<td>37.5%</td>
</tr>
<tr>
<td></td>
<td>$\downarrow \uparrow \downarrow$</td>
<td>-1</td>
<td>$g(-1) = 3$</td>
<td>37.5%</td>
</tr>
<tr>
<td></td>
<td>$\downarrow \downarrow \downarrow$</td>
<td>-3</td>
<td>$g(-3) = \frac{1}{8}$</td>
<td>12.5%</td>
</tr>
</tbody>
</table>

As you can see, all 8 states are equally likely. However, it is 3x more likely that $m = +1$ than $m = +3$. 

$\text{energy} U = -\mu mB$
1/16/03

Monday: intro; 4 definitions of T

Today: 5th def. of T

counting, (states)

Fri.: sharpness of distribution

(pp4-6 left over)

* Say something about tuning on mag. field. At $T=0$, all in ground state $\ldots$ However, we'll see that for $B \neq 0$, $T > 0$, then some probability for each state.

For general $N$:

Let $N_u = \# \text{up spins}$, $N_d = \# \text{down spins} = N - N_u$

How many ways are there to have $N_u$ up & $N_d$ down?

answer: $g(N; N_u) = \frac{N!}{N_u! \cdot N_d!} = \frac{N!}{N_u! (N-N_u)!} = \binom{N}{N_u}$

read "$N$ choose $N_u$"

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

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

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

$\vdots$

$N-N_u+1$ " " " last " "

so far we have $g \propto N (N-1) (N-2) \cdots (N-N_u+1)$

$= \frac{N (N-1) (N-2) \cdots (N-N_u+1) (N-N_d-1) \cdots 3 \cdot 2 \cdot 1}{(N-N_u) (N-N_d-1) \cdots 3 \cdot 2 \cdot 1}$

$= \frac{N!}{(N-N_u)!}$

However, we've overcounted, because

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

It counts by a field of $N_u$ \rightarrow same above
Sometimes it's convenient to define

\[ a = \frac{N_u - N_d}{2} \]

2a is called "spin excess." For example, if I have 40 spins, and 22 are up, \( a = \frac{22 - 40}{2} = \frac{-18}{2} = -9 \),

\[ N_u = \frac{N}{2} + a \]
\[ N_d = \frac{N}{2} - a \]

so \( q(N, a) = q(N; \frac{N}{2} + a) = \frac{N!}{(\frac{N}{2} + a)! (\frac{N}{2} - a)!} \)

\( q(N; N_u) \) called "binomial coeff." because in formal product

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

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

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

Pascal's triangle to calculate binomial coeffs:

```
N=0   1
1  1
2  1  2
3  1  3  1
4  1  4  6  4
```

Note:
A sharpness of coin toss (I don't mean what is chance, 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

<table>
<thead>
<tr>
<th>Heads</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \frac{1}{16} = 0.0625 )</td>
</tr>
<tr>
<td>1</td>
<td>( \frac{4}{16} = 0.25 )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{6}{16} = 0.375 )</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{4}{16} = 0.25 )</td>
</tr>
<tr>
<td>4</td>
<td>( \frac{1}{16} = 0.0625 )</td>
</tr>
</tbody>
</table>

Only a 3.125% chance of exactly 50%-50%, but an 87.5% chance it's between 25%-75%.

How about 1000 coins?

According to my calculations:

Exactly 50%-50% (i.e., 500 heads, 500 tails): only 0.00001 chance

But since it's between 25%-75% (125 heads, 875 tails) and 75%-25% (875 heads, 125 tails)

is about \( 1 \times 10^{-5} \), i.e.,

\[ 99,999 \cdots 9996 \]

(38)

Show histogram, unscaled or scaled - correct on sharpness

Verification approach
Graphs \( g(n, \frac{N}{2}) \) need for continuum approach.

First step in algebra: take big number by taking log.

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

Two approximations:

1) Stirling series: \( \ln(n!) \approx n\ln n - n + \frac{1}{2}\ln n + \frac{1}{2}\ln(2\pi n) + \frac{1}{12n} \)

2) \( n/N \ll 1 \) justified by what we've seen so far: away from center \( \pm \frac{N}{2} \),

\[ \ln\left(\frac{N}{2}+1\right)! \approx \ln\left(\frac{N}{2}-1\right)! \]

Experimental test of Stirling:

<table>
<thead>
<tr>
<th>n</th>
<th>\ln(n!)</th>
<th>n\ln n - n</th>
<th>\ln n + \frac{1}{2}\ln n + \frac{1}{2}\ln(2\pi n)</th>
<th>\frac{1}{12n}</th>
<th>\frac{1}{24n^2}</th>
<th>\frac{1}{240n^3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.7918</td>
<td>0.2958</td>
<td>1.7641</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>15.104</td>
<td>13.026</td>
<td>15.096</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>148.48</td>
<td>145.60</td>
<td>148.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>363.74</td>
<td>360.52</td>
<td>363.74</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Contrast Taylor vs asymptotic series:

\[ \ln(1 + \frac{1}{n}) < \frac{1}{n} \]

derivation of Stirling

1. K&K upper tail
tail not elementary

2. Bender & Orszag
AN. MR. METADYNAMICAL PEG
3. Methods
\[ \ln \left[ g(N,v) \right] = N \ln N - N + \frac{v}{2} \ln v - \left( \frac{v}{2} + \frac{1}{2} \right) \ln \frac{N}{2\pi} + \frac{v}{2} 
\frac{N}{v} 
\left( \frac{v}{2} - 1 \right) \ln \frac{v}{2} - \frac{v}{2} - \frac{1}{2} \ln(2\pi) \]

Write \( \ln(1 + ax) = \ln(1) = ax \) where \( a = \frac{v}{2} \) assumed << 1.

\[ \ln v \approx \ln N - v + \ln(1 + ax) \]

Thus \( \ln v \approx \ln N - v + \frac{1}{3} v^2 + \frac{1}{5} v^3 - \ldots \) keep \( v^2 \) term just to estimate our errors at the end.

\[ \ln \left[ g(N,v) \right] \approx \left( N + \frac{1}{2} \right) \ln N - \left( \frac{N}{2} + 1 \right) v + \left( \frac{1}{2} \right) \ln v + \left( \frac{1}{2} \right) v^2 + \frac{1}{3} v^3 - \frac{3}{5} v^4 - \frac{1}{2} \ln(2\pi) \]

\[ = N \ln N - v + \frac{1}{2} \ln v(2N) - 2^{1/2} N + 2(2N)^{1/2} \]

For \( n \to 0 \), \( \ln \left[ g(N,v) \right] \approx N \ln N + \frac{1}{2} \ln \left( \frac{2}{N} \right) + \Theta \left( \frac{1}{N} \right) \) from Stirling.

Take exponential:

\[ g(N,v) \approx 2^N \sqrt{\frac{2\pi N}{v}} \left( \text{e}^{-N/v} \right) \]

Generally,

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

What's left is a Gaussian (normal, bell-shaped curve).

Recall we assume \( \mu \) to be normal.

\[ g(N,v) \propto g(N,0) \exp \left[ -\frac{(N - \mu)^2}{2} \right] \]

Put in form of a normal distribution:

\[ \mathcal{P}_N(x) \propto \frac{1}{\sqrt{2\pi} \sigma} \exp \left[ -\frac{(x - \mu)^2}{2\sigma^2} \right] \]

\[ \frac{1}{\sqrt{\pi}} \exp \left[ -\frac{1}{\sqrt{\pi}} \right] \]

Total prob: \( \int_{-\infty}^{\infty} \mathcal{P}_N(x) \, dx = 1 \)

Note: endpoints are \( \pm \infty \) outside

\[ \text{Standard deviation} \]

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

\[ \text{So a probability} \]

\[ \frac{1}{\sqrt{2\pi}} \]

\[ \pm \frac{1}{\sqrt{2\pi}} \]
Natural mode is not $x$ but rather $x = \frac{N_0 - N_\bar{z}}{N}$

(i.e., magnetization PER SPIN rather than TOTAL)

Standard deviation $\sigma = \frac{\bar{z}}{\sqrt{N}}$

so $68\%$ prob $\frac{x}{\sigma}$ lies between $\pm \frac{\bar{z}}{2N}$

$95\%$ " " " " $\pm 1.96 \sqrt{N}$

$99.7\%$ " " " " $\pm 3 \sqrt{N}$

7/10/03, 1pm

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

$\langle x \rangle = \frac{1}{2} \sum_{x=-1}^{1} x = 0$

Now say coin is weighted so that prob(+1) = $0.55\%$, prob(-1) = $4.5\%$. 

$\langle x \rangle = \sum_{x=-1}^{1} x P(x) = -1 \cdot 0.45 + 1 \cdot 0.55 = 0.1$

For a continuous prob. distri. $P(x)dx$ means "prob. at exact $x$ is $P(x)dx$"

$\langle x \rangle = \int P(x)dx$

For our binary spin prob, $P(z) = \frac{1}{\sqrt{2\pi} \sigma} e^{-z^2/(2\sigma^2)}$, $\sigma = \frac{1}{2} \sqrt{N}$

$\langle z^2 \rangle = \int_{-\infty}^{\infty} 2z^2 e^{-z^2/(2\sigma^2)} \frac{1}{\sqrt{2\pi} \sigma} e^{-z^2/(2\sigma^2)} dz$ 

$\langle z^2 \rangle = \frac{2}{\sigma^2}$

$\langle z \rangle^2 = \frac{2}{\sigma^2} \cdot \frac{1}{\sigma^2} = \frac{2}{\sigma^4}$ (see below)

$P(z)$ is prob. density of $z$.

Shaded = prob. that $z_0 \leq z \leq z_0 + \delta z$

$\int_{z_0}^{z_0+\delta z} P(z)dz = 1$

$\langle f(z) \rangle = \int f(z) P(z)dz$
1. A few minutes on problem 2 of HW 1

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

Example: flipping 4 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:

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

E.g., binary spin system, \( N=4 \), ispin excess \( z=2 \):

\[ \begin{array}{ccc}
\uparrow & \downarrow & \downarrow \\
\downarrow & \uparrow & \downarrow \\
\downarrow & \downarrow & \uparrow \\
\downarrow & \downarrow & \uparrow \\
\end{array} \]

represented by 4 copies, one for each accessible state:

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

Examples of inaccessible: 1) glass — even though fused silica could turn into quartz with the correct energy, it can't yet turn into even one million (?) of years

2) planetary system consisting of our sun & one planet — many orbits have the same energy, but even over billions of years, there is dynamical reason for going from one to another, or

start over, not used. (In this case, there are other conserved quantities: angular momentum & the Laplace-Runge-Lenz vector. Add a 3rd body, and motion could become either ergodic or chaotic.)
3) QM exact stationary state — \( \gamma(t) = e^{-iE_0t}\gamma(t=0) \) stop the same (time-independent).

However, if \( \gamma \) is a stationary state only of an approximate Hamiltonian, \( H' \), with \( H' = H + \Delta H \), the perturbation \( \Delta H \) may "ergodically" couple all stationary states of \( \gamma \) with the same energy (quantum chaos - current research).

**Ensemble average:**
\[
\langle \gamma \rangle = \frac{1}{\text{system}} \sum_{\text{states}} \gamma(a) = \frac{1}{N} \sum_{a=1}^N \gamma(a)
\]

Other ways to view quantum ensemble:

- As many copies of the system, each started at \( a \) with a different initial state (or of the same energy (and other macroscopicons)):
  \[
  \langle \gamma \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{a=1}^N \gamma(a)
  \]

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

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

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

In this chapter, we used canonical ensemble (\( T \) fixed).
In ch.3, we used canonical ensemble (\( T \) fixed).
Later, over grand canonical ensemble (\( \beta \) fixed).

Sometimes, we might need a quantum expectation value; it's necessary to distinguish, we can write \( \langle \cdot \rangle_{\text{normal}} \), e.g., \( \gamma \).

Recall last week's derivation of Temp.

**Proof:** I wrote \( \gamma(U_1) = \gamma_1(U_1) \gamma_2(U - U_1) \) for the most probable partition of energy between the two subsystems. At thermal equilibrium, this and a similarly small coterie are the only partitions that matter. To be completely correct, \( \gamma = \sum_{a_1} \gamma_{a_1}(U_1) = \sum_{a_1} \gamma_1(U_1) \gamma_2(U - U_1) \).
We found \( \left( \frac{\partial S_i}{\partial H_j} \right) = \left( \frac{\partial S_j}{\partial H_i} \right) \), were \( S \neq H \).

We give a few examples of spin systems in thermal contact.

- \( \mathbf{N}_1, \mathbf{N}_2 \) fixed; \( \mathbf{S}_1 \), \( \mathbf{S}_2 \) fixed, \( \mathbf{S} \) allowed to vary
- \( \mathbf{B}' \) has form flipping \( \mathbf{S}_{1 \downarrow} \mathbf{S}_{2 \uparrow} \rightarrow \mathbf{S}_{1 \uparrow} \mathbf{S}_{2 \downarrow} \) (total spin conserved)

For \( i = 1, 2 \), \( g_i(\tau) = g_i(0)e^{-2\tau^2/\mathcal{N}_i} \), \( g_i(0) = 2^{\frac{1}{2}} \mathcal{N}_i^{-\frac{1}{4}} \).

Most likely config. satisfies

\[
\frac{2}{\mathcal{N}_1} \left[ g_1(\tau) g_2(2-2\tau) \right] = 0
\]

Extremum occurs in some place for \( g_1 g_2 \) as for \( log(g_1 g_2) \), so

\[
0 = \frac{2}{\mathcal{N}_1} \left[ \text{log} g_1(\tau) + \text{log} g_2(2-2\tau) \right] = \frac{2}{\mathcal{N}_1} \left[ \text{log} g_1(0) - 2\tau^2/\mathcal{N}_1 + \text{log} g_2(0) - 2(2-2\tau)^2/\mathcal{N}_2 \right]
\]

\[
= -4\tau^2/\mathcal{N}_1 + 4 \left[ 2 - 2\tau \right]^2/\mathcal{N}_2
\]

So

\[
\frac{\mathcal{N}_1}{\mathcal{N}_2} = \frac{\tau^2}{4}
\]

i.e., magnetization per spin equals to the spin sum.

Converting to energy (with magnetic field),

\[
\mathcal{U} = -\frac{1}{2} \sum_{\mathcal{N}_1} m_i B
\]

where \( m_i = \pm 1 \), \( \sum m_i = \mathcal{N}_1 - \mathcal{N}_2 = 2\mathcal{N}_1 \), so

\[
\mathcal{U} = -\mathcal{N}_1 B
\]

This

\[
\frac{\mathcal{U}_1}{\mathcal{N}_1} = \frac{\mathcal{U}_2}{\mathcal{N}_2}
\]

equivalent energies. This needn't be the case in general, because systems for \( \mathbf{N}_1 \neq \mathbf{N}_2 \) may not have the same magnetic moment, or may not even be made of the same material. We may be able to adjust the system to approach an equilibrium state. In general, however, it will be true that, at equilibrium,

\[
\mathcal{U}_1 = \mathcal{U}_2
\]

where \( \mathcal{U}_j = \mathcal{U}_j(0) \).
Temperature for this case:

\[ T_1 = \left( \frac{\partial U}{\partial N} \right)_V = \frac{1}{N} \left( \frac{\partial U}{\partial N} \right)_V = \frac{1}{k_B} \frac{\partial}{\partial N} \left[ k_B \frac{U}{N} \right] \]

\[ = \frac{1}{k_B \left( -\frac{U_1}{N} \right) \frac{N}{k_B^2}} = - \frac{N_1}{U_1} \left( \frac{\mu B^2}{\beta B} \right) \]

Similarly, \( T_2 = - \frac{N_2}{U_2} \frac{\mu B^2}{\beta B} = T_1 \).

Is this negative?

Lowest energy \( \Rightarrow \) all spins \( \uparrow \) \( \Rightarrow \) \( s = N \) \( \Rightarrow \) \( U \) negative

so config \( \frac{1}{2} \to 0 \) have \( T > 0 \)

config \( \frac{1}{2} \to 0 \) have \( T < 0 \)

1/15/03

Mon.: averages

Ergodic hypothesis

Microcanonical ensemble

Tues.: entropy

Temperature

Law of thermodynamics

Fri.: C.P. Snow

\[ e^{-\beta} \text{/(kgT)} \]

2

Discuss Homework 2

Same thing graphically:

\[ S + \text{const} = \text{const} - 2k_B \frac{\mu B^2}{N} \]

To get slope at edge, we cannot use Gaussian approx., since \( \mu B \) is not \( \pm N \).

(Indeed, Gaussian cannot separate down forever.)

Slope at \( \pm N \) \[ \frac{\Delta S}{\Delta U} = \frac{S(\pm N) - S(0)}{U(\pm N) - U(0)} = \frac{k_B \left[ \ln \left( \frac{\beta N}{N-1} \right) - \ln \left( \frac{\beta N}{N+1} \right) \right]}{\mu B N} \]

\[ = \beta U - \mu B \rightarrow \text{parabolic} \]

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

Is it two-steps or finite??
\[ \frac{k_B \left[ \ln \left( \frac{N}{N-1} \right) - \ln \left( \frac{N}{N} \right) \right]}{MB} = \frac{k_B \left( \ln (N) - 0 \right)}{MB} \rightarrow \infty \]

In limit of \( \infty \) system, slope \( \to +\infty \), so \( T = 0 \)

For \( T = 0 \), slope \( = 0 \), so \( \ln (N) - 0 \)

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

For \( T < 0 \), slope \( < 0 \), so \( \ln (N) - 0 \)?? See Appendix E & HW 2.2

Inverted population impossible in \( U \geq 0 \) system with arbitrarily high energy levels (e.g., particle in a box):

\[ \text{Since } \frac{\partial S}{\partial U} \geq 0 \text{ grows monotonically with } U. \]

See HW 2.3

Two subsystems again:

\[ \begin{array}{ccc}
U_1 & & U_2 = U - U_1 \\
\bar{g}_1 (U_1) & & \bar{g}_2 (U_2) \\
\end{array} \]

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

What will happen to the macrostates of the two subsystems?

Oh, so they've reached thermal equilibrium.

Is it possible for them to return to original state? [Laws of physics are reversible.] Is it likely? All macrostates 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, either direction

At each step, system can move to any connected point. It's possible but unlikely for it to evolve back to equilibrium.

\[ N_p = N; U_1 = U \]
\[ N_p = N-1 \]
\[ N_p = N-2 \]
\[ U_1 = N-3 \]
2nd law of thermodynamics: entropy "never" decreases (Anon. Hamlet)

In a small system, it rarely decreases in a system with 10^2 degrees of freedom, "never."

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

\[ \text{Reversible: processes: only infinitesimal deviations from equilibrium macrostate} \]

\[ \text{irreversible: - dropping expensive Greek vase} \]

\[ \text{over time} \]

\[ \text{- it appears that microscopic laws of physics don't provide it - only statistics} \]

\[ \text{Ways of thermodynamics:} \]

0) If A B B are in thermal equilibrium, and B C C are,
so are A B C. (Immediate consequence of
\[ T = (0/38)_m \]

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 stood on in course).

3) Entropy \[ \text{constant (usually zero)} \]
monotonically increases \[ T \rightarrow 0 \]

\[ \text{IT'S A ZERO-SUM GAME} \]
(perpetual-motion machines are
the first and)

\[ \text{YOU CAN'T WIN} \]
(Dilbert : perpetual-motion
machine of the second
kind?)

\[ \text{YOU MUST BREATHE} \]
(EVEN)
1/9/03

Well, entropy, temperature.

Today: laws of thermodynamics.

Boltzmann

Final pp?

L. R. Snow 1959 Red Lecture → Flinders + Swan

Background to proven C.3

Classical harmonic oscillator:

\[ U = \frac{p^2}{2m} + \frac{1}{2} k x^2 \]

\( q.m.: \) \[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k x^2, \quad k = \omega^2/m \]

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

With simplifies the algebra slightly by ignoring the 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 \( m_j = 0, 1, 2, \ldots \)

Subject to \( m_1 + m_2 + \ldots + m_N = n \) fixed.

Mentioning: partitioning the integer \( n \) among \( N \) rules.

\[ y(n, m) = \# \text{ ways to partition } n \]

"Generating function"

\[ \sum_{m=0}^{\infty} t^m = \frac{1}{1-t} \quad \text{for } \quad 0 < |t| < 1 \] - it is just a tool.

\[ \text{Denote: } 1 - \Delta t = e^t, \quad A = \sum_{m=1}^{\infty} \Delta t^m \]

Conside a product of \( N \) of these sums:

\[ \left( \sum_{m=1}^{\infty} t^m \right)^N = \left( \frac{1}{1-t} \right)^N \]

After expanding in powers of \( t \), we get

\[ \binom{x}{n} \cdots \binom{y}{n} = \binom{x+y}{n} \]

Expanding this to some sort of \( \# \) has some exponent. We would like to be free of some constraints for \( t \) is greater than...
\[ \left( \frac{1}{1-e} \right)^3 = \sum_{n=0}^{\infty} f(n) e^n. \]

How can we pick out the one term we want? Take a derivative wrt \( t \) \( n \) times, set \( t \rightarrow \infty \). Any term with \( e^n \cdot n \geq 0 \) will go to zero. Any term \( n \cdot m \) will be wiped out by the deriv. The term \( m \cdot n \) will have \( n! \cdot n \) term. So

\[ g(N, m) = \lim_{t \rightarrow \infty} \frac{1}{n!} \frac{d^n}{dt^n} \sum_{m=0}^{\infty} g(N, m) e^n = \lim_{t \rightarrow \infty} \frac{1}{n!} \frac{d^n}{dt^n} (1 - t)^{-N} \]

\[ = \frac{1}{n!} N (N+1) \ldots (N+n-1) \quad \text{(cancel factor \(-t\) from the exponent and \(-1\) from \(-t\))} \]

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

Part a): 
- \( \sigma = \text{bogus in Stirling approx. straight forward (5 lines)} \)

Part b): 
- Using \( \frac{1}{T} = \left( \frac{d\sigma}{dU} \right)_V \), 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) intrinsic capacity
  - Energy \( E \)
  - Energy \( T \)
  - Energy \( U = E - F \)

Possible energy levels of system are \( E_1, E_2, \ldots \) assume all distinct (just to simplify math)

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

\[ \sum_x P(E_x, T) = 1 \text{ because } \text{system must be in some state} \]
To find $P(E_2)$, fix $\beta$. Then

$multiplicity \quad J_{\text{total}} = J_{\text{res}} \cdot J_{\text{source}}$, but since we have $x$, $y_{m} > 1$.

\[ J_{\text{source}} = J_{\bar{E}_2}, \quad \bar{E}_2 = E_0 - E_2 \]

\[ P(E_2) \propto \delta(E_2) = \exp \left( \frac{1}{k_B} \bar{E}(E_2) \right) \quad \text{when mean energy} \]

\[ \bar{E} = k_B \beta \ln g \]

Consider states $x_1, x_2$ with nearly same energies.

What is ratio of their probabilities?

\[ \frac{P(E_{21})}{P(E_{22})} = \exp \left[ \frac{1}{k_B} (\bar{E}(E_{21}) - \bar{E}(E_{22})) \right] \equiv \exp \left( \frac{1}{k_B} \Delta \bar{E} \right) \]

change in energy of system \quad $\Delta E = E_{22} - E_{21}$

"source" \quad $\Delta \bar{E} = -\Delta E$\n
Since $\Delta \bar{E}$ is small quantity, we may write

\[ \Delta \bar{E} = \left( \frac{\partial \bar{E}}{\partial E_2} \right) \Delta E \]

\[ = \frac{1}{k_B} \Delta E \]

\[ = -\frac{1}{k_B} \Delta E \]

Part 3:

\[ \frac{P(E_{21})}{P(E_{22})} = \exp \left[ -\Delta E / (k_B T) \right] \quad \text{so} \quad P(E_2) = \exp \left[ -E_2 / (k_B T) \right] \]

absolute prob. \quad $P(E_2) = \frac{\exp \left[ -E_2 / (k_B T) \right]}{Z}$

where $Z = \sum \text{partition function} = \sum \exp \left[ -E_2 / (k_B T) \right]$

"Z" (or $Z$)
Fri: laws
canonical ensemble
today: heat work in the canonical ensemble
Fri: heat capacity, ideal gas

Uncanonical ensemble (Ch 2): fixed \(N\), all microstates equally likely
Canonical ensemble (Ch 3, problem 4 just studied): \(U\) can be exchanged with \(N\)
at fixed \(T\)

\[
P_j = \text{Prob. of microstate } j = \frac{e^{-E_j / (k_B T)}}{Z} \quad \gamma = \frac{k_B T}{\hbar}
\]
\[
Z = \sum_{j} e^{-E_j / (k_B T)}
\]

Average of any quantity \(a\):
\[
\langle a \rangle = \sum_j a_j P_j = \frac{\sum_j a_j \cdot e^{-E_j / (k_B T)}}{Z}
\]

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

less trivial: (do hw 2.4?)

Another expression for \(U\) directly from \(Z\) (eqn 3.1a):
\[
U = \langle E \rangle = \frac{\sum_j E_j e^{-E_j / (k_B T)}}{Z} = \frac{1}{Z} \frac{\partial (Z \cdot \sum_j E_j e^{-E_j / (k_B T)})}{\partial \beta}
\]
\[
= \frac{1}{Z} \frac{\partial Z}{\partial \beta} \cdot \langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \langle E \rangle
\]
\[
= \left( \frac{\partial Z}{\partial \beta} \right) \langle E \rangle
\]

Reversible processes: entropy of system not changed

Two special cases:
1) isentropic: entropy of system not changed (adiabatic)
- quantum states map on to each other
before

\[ \text{piston} \quad \text{slow} \quad \text{to transition} \]

\[ n=2 \]

\[ n=2 \]

Energy has increased, but if transition, same as before unchanged

2) Isochoronic

Add an infinitesimal amount of heat -

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

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

Reservoir \( E \) at \( T \) only infinitesimally higher than that of system (the inversion)

Another example of an irreversible process:

\[ \text{no work done on piston} \]

\[ \text{sudden expansion} \]

Picture and remember now

\[ \text{top view} \]

\[ \text{side view} \]

We'll change state by means of a piston, and change just one of the state

\[ \text{pure L, V good state variable (V fixed). It does matter how we} \]

\[ \text{change V} \text{ (is any useful when we test). Before changes shape in all 3 dim.} \]
Move piston slowly — not underwriting 

\[
\text{force on gas on piston} = \text{force on piston on gas} = P A .
\]

\[
\text{work done on gas} = (\Delta U)_g \quad \text{adds energy to gas}
\]
\[= \int \left( -\Delta U \right) dV \quad \text{no change in energy}
\]
\[= -P A \Delta V \]
\[= -P \Delta V,
\]
\[P = -\left( \frac{\Delta U}{\Delta V} \right) = - \left( \frac{\partial U}{\partial V} \right)_n
\]
\[\Rightarrow \delta s = k_B \]

State vars: \(U, V, N\), \(N\) fixed, so just \(U, V\)
\[S = S(U, V)
\]

Nstatistic change in \(S\) could involve both \(dU\) and \(dV\), so
\[dS = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV
\]
\[dS = S(U, V) \quad \Rightarrow \quad \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV
\]
\[\text{I'll stop now herewith until later content.}
\]

Can we write \(dU = (\delta U)_S\) and \(dV = (\delta V)_S\), together such that there's no change in entropy of system?
\[dS = - \left( \frac{\partial S}{\partial U} \right)_V \left( \delta U \right)_S + \left( \frac{\partial S}{\partial V} \right)_U \left( \delta V \right)_S
\]
\[\left( \frac{\partial S}{\partial U} \right)_V = - \left( \frac{\partial U}{\partial V} \right)_S \left( \frac{\partial S}{\partial U} \right)_V
\]
\[\left( \frac{\partial S}{\partial V} \right)_U = \frac{\left( \frac{\partial S}{\partial U} \right)_V}{T}
\]
\[\left( \frac{\partial S}{\partial V} \right)_U = - \frac{1}{T}
\]
\[S = \int \left( 1 - \frac{\partial S}{\partial V} \right)_U
\]
\[\text{going back to } dS,
\]
\[dS = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV
\]
\[\Rightarrow \int_S
\]
\[ dU = TdS - PdV \]

**Thermodynamic Identity**

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

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


Physics students like minimization principles: E.g., in QM, we are often interested in minimizing the energy, \( U \). Why? We imagine a system in thermal contact with a reservoir at \( T, \), so at least very cold, so that we have a possible state of the energy flow and reservoir.

To have \( T \neq 0 \), we don't minimize \( U \) e.g., problem 2.4, since only \( 0 \) minimizes energy, but we are not the most possible state.

Define [Helmholtz free energy] \( F = U - TdS = U - \text{intake} \)

Intuitively, minimizing \( F \) over \( U \) is good, but so is negative \( \text{intake} \).

- At \( T=0 \), \( F=U \), so only energy counts
- At \( T \neq 0 \), minimizing \( F \) becomes increasingly important

Does it succeed?

\[
\frac{dF}{dT} = \left( \frac{dU}{dT} \right)_{\text{intake}} + P \frac{dV}{dT} - \left( \frac{dP}{dT} \right)_V
\]

1) \( \text{constant volume} \Rightarrow dV=0 \)

\[
\left( \frac{dF}{dT} \right)_V = -S
\]

Since

2) \( \text{constant pressure} \Rightarrow dT=0 \)

\[
\left( \frac{dF}{dT} \right)_P = \psi
\]

State functions (e.g., \( F \), \( U \), etc.)

\[ F \]

\[ U \]

\[ T \]

\[ S \]

\[ P \]

\[ V \]

\[ \text{intake} \]

\[ \text{constant} \]

\[ dF = dU - TdS \]

If we hold \( T \) cont., \( dF = dU - \text{intake} \).

If we had \( V \) cont., \( dF \Rightarrow \psi \) of \( T \) cont.

Thus, at equilibrium, if \( dT=0 \), we have \( \Delta F=0 \).

\( F \) has an extremum at equilibrium.

\( dT \) shows that it is a minimum.

Context: \( F \) is the "thermodynamic potential" when \( dT=dV=0 \). There are others when \( dT \neq 0 \), for different purposes (e.g., \( dT=dP=0 \)
Wed: \[ U(\Phi) = \frac{\sum_{i=1}^{N} e_i \Phi_i}{Z} \]
\[ P = -\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T \]
\[ dU = TdS - PdV \]

Today: Helmholtz F
polymer
Problems

Mon: ideal gas
UV catastrophe

Finish old

Problem 3.10
Most solids expand when heated:

However, polymers — pseud 1-dim — shrink:

Model: random walk — can hit or tied 1 as - 1 (purely entropic model — no energy)

1-dim TD identity: \[ dU = TdS + Fdl \]
"volume" = length
right units: dyn cm = erg

Instead of \[ P = +T\left(\frac{\partial S}{\partial V}\right)_T \]

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

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

a) With \( N \) lines, each of length \( l \), how many ways are there to get total length \( L \)?

No. dist. from \( \pm 1 \) binary spin pair:

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

We don't care if \( +1 \) or \( -1 \), so:

\[ G = g(N, -1) + g(N, 1) = \frac{2N!}{(\frac{1}{2}N+1)!(\frac{1}{2}N-1)!} \]
A) In Gaussian approx., \( C = \frac{1}{2} \rho (\rho^2 / N) \approx - \frac{1}{2} \ln N \)

\[
\rho' = k_b \ln C = k_B \left[ \ln (2\rho / \rho^2) - 2\rho / \rho^2 \right] = k_B \left[ \ln (2\rho / \rho^2) - \frac{\rho}{\rho^2} \right]
\]

e) string tension \( f = -T \left( \frac{\partial f}{\partial T} \right)_F \)

No energy is at all in this world exception

\[
f = \frac{k_B T \rho}{\rho^2 N}
\]

\( \rho \to \text{tension} \to \text{curl up} \)

(is yield equilibrium, so we'd need a more realistic model with \( F \) in it.)

Getting \( F \) directly from \( \rho \) w/o having to calc. \( S \) in \( U \):

\[
\begin{align*}
U &= F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_V \\
\text{outer: a diff. eqn. for } F
\end{align*}
\]

which boils down to get \( F = -\frac{\beta E_0}{Z} \).

Here's an alternative derivation, but it relies on an identity. Let \( Z = \frac{e^{-\beta E_0}}{Z} \) be the prob. of being in state \( \alpha \). Then

\[
S = -k_B \sum_{\alpha} \ln \rho \rho \rho
\]

Proof: Use canonical ensemble with total \( \rho \) systems

\( \rho \) systems (or many nth. \text{Ch. 2})

\( \rho_1 = \rho_1 \rho \rho \) of them are in state 1

\( \rho_2 = \rho_2 \rho \rho \rho \rho \) of them are in state 2

Total \( \rho \)

\[
S_{\text{macro}} = \frac{\rho_1! \rho_2}{\rho_1! \rho_2} ...
\]

\[
S_{\text{macro}} = k_B \ln S_{\text{macro}} = k_B \left[ \ln (\rho_1!) - \sum \ln (\rho_1^\rho_2) \right]
\]

\[
= k_B \left[ \rho_1 \ln \rho_1 - \frac{\rho_1 \rho_1}{\rho_2} (\rho_1 \rho_1 - \rho_1) \right]
\]

\[
= k_B \left[ \rho_1 \ln \rho_1 - \frac{\rho_1 \rho_1}{\rho_2} \rho_1 \rho_2 \right]
\]

since \( \sum \rho_1 = \rho \)
Now write \[ \sum_{\alpha} u_{\alpha} \ln n_{\alpha} = \sum_{\alpha} u_{\alpha} \ln (u_{\alpha}) \]

so \[ S_{\text{env}} = \nu k_B \left[ \mu \nu - \sum_{\alpha} \omega_{\alpha} (\mu \nu + \hbar \omega_{\alpha}) \right] \]

\[ = \nu k_B \left[ \mu \nu - \frac{\mu \nu \sum_{\alpha} \omega_{\alpha} - \sum_{\alpha} \omega_{\alpha} \hbar \omega_{\alpha}}{1} \right] \]

\[ = -\nu k_B \sum_{\alpha} \omega_{\alpha} \hbar \omega_{\alpha} \]

but \[ S = \frac{S_{\text{env}}}{\nu} \]

so \[ S' = -k_B \sum_{\alpha} \omega_{\alpha} \hbar \omega_{\alpha} \]

Now to get F.

\[ S = -k_B \sum_{\alpha} \omega_{\alpha} \ln \left( \frac{e^{-\beta E_{\alpha}}}{Z} \right) \]

\[ = -k_B \sum_{\alpha} \omega_{\alpha} \cdot (-\beta E_{\alpha} - \hbar \omega_{\alpha} Z) \]

\[ = -k_B \sum_{\alpha} \frac{E_{\alpha} \omega_{\alpha}}{k_B T} - \frac{\hbar \omega_{\alpha} Z \omega_{\alpha}}{1} \]

\[ = \frac{U}{T} + k_B \hbar \omega \]

\[ TS = U + k_B T \hbar \omega \]

\[ U - TS = \begin{cases} -k_B T \hbar \omega \end{cases} \]

\[ F = \begin{cases} \end{cases} \]
Talking points on problems:

1) Give them \( Z = 1 + e^{-\beta E} \)

Show how to get \( Z \) directly (NOT the way problem asks then to do):
\[
Z = \langle E \rangle = \frac{0 + e^{-\beta E} + \sum e^{-\beta E}}{1 + e^{-\beta E}} = \frac{e^{-\beta E}}{e^{-\beta E} + 1} \quad \text{as usual}
\]

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

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

I did this problem essentially the same way as #1.

Review of hyperbolic functions:
\[
\cosh x = \frac{e^x + e^{-x}}{2}
\]
\[
\sinh x = \frac{e^x - e^{-x}}{2}
\]
\[
\tanh x = \frac{\sinh x}{\cosh x}
\]
\[
\text{sech} \ x = \frac{1}{\cosh x}
\]
\[
\text{coth} \ x = \frac{1}{\sinh x}
\]
\[
\text{csch} \ x = \frac{1}{\sinh x}
\]

\[
\cosh^2 x - \sinh^2 x = 1
\]

3) Remember that from last week \( e^{x} + e^{-x} + 1 - e^{-x} - e^{x} = 1 - e^{x} + e^{-x} \)
1/27/23

Last week:

Pressure \( P = -\left( \frac{\partial U}{\partial V} \right)_S = T \left( \frac{\partial S}{\partial V} \right)_T = -\left( \frac{\partial E}{\partial V} \right)_T = -\left( \frac{\partial U}{\partial V} \right)_T + T \left( \frac{\partial S}{\partial V} \right)_T \)

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

Helmholtz \( F = U - TS = -b \beta T \ln Z \)

\[ S = -k_B \sum_x \ln \omega_x \omega_x \quad \left( \omega_x = e^{-\beta E_x/Z} \right) \]

Today: heat capacity, ideal gas

Web: UV catastrophe + Planck

**Heat Capacity** \( C_V = T \left( \frac{\partial S}{\partial T} \right)_V \) per KBK [Note: they use same symbol \( U \) for:

- Dimensionless heat capacity, \( \frac{1}{2} \left( \frac{\partial T}{\partial V} \right)_U \)]

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

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

i.e., how much heat per unit change in temp.

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

\( H_2O: \text{large } C_V, \text{ air: small } C_V \)

In *chemical* chemistry, \( C_p = T \left( \frac{\partial S}{\partial T} \right)_p \) more important except when \( S \) cont. pressure

\( C'_V \neq C_p \)

gases: noticeably different

liquids: somewhat different

solids: badly different, so people usually use \( C_V \), since easier to calc.

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

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

heat flow \( \Delta Q \) not a full differential, because \( T \) is so defined "\( U \)"

\[ \Delta Q = T \Delta S \quad \text{the heat term in } dU = T dS - P dV \]

from which

\[ \left( \frac{\partial Q}{\partial T} \right)_X = T \left( \frac{\partial S}{\partial T} \right)_X \]

for any thermal variable \( X \)

\( \text{except } dV, dT \)

\[ X = \frac{V}{T} \]

\[ \Rightarrow \left[ C_V = T \left( \frac{\partial S}{\partial T} \right)_V \right] \]
Since $dU = TdS - PV$, at 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

\[
\frac{dU}{dT} = \left( \frac{\partial U}{\partial T} \right)_V
\]

Set $x = P$:

\[
G_p = \left( \frac{\partial Q}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P
\]

Note that $\frac{dU}{dT} \neq \left( \frac{\partial U}{\partial T} \right)_V$. Instead, consider

\[
U = U(T, P) \quad \text{(so} \ V \text{ and} \ T \text{ are} \ \text{functions of} \ T \text{ and} \ P)\
\]

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

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

\[
TdS = dQ = \frac{dU + PV}{V} \]

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

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

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

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

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

where enthalpy $H = U + PV$

**Specific heat**

\[
C = \begin{cases} \text{C/mass} & \text{depending on book} \\ \text{C/mole} & \text{C/mole of mole} \end{cases}
\]

\[
\text{Example cell of} \ V = x + xP
\]
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 the weak interaction.)

Difference between interacting and non-interacting particles in a box $N = \# \text{ particles}$ spinless, eq. of mass $M$

Interacting: $H = \left[-\frac{\hbar^2}{2m} \left( \nabla_i^2 + \nabla_j^2 + \cdots + \nabla_i^2 \right) + V(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) \right] \Psi$  

Non-interacting: $H_i = -\frac{\hbar^2}{2m} \nabla_i^2 \Psi_i(\vec{r})$

$H \Psi = E \Psi$

Solution: $\Psi_i(\vec{r}_i^0) = \sum_{n_x, n_y, n_z} \frac{n_x \pi^{1/2} \sin(n_x \pi \xi)}{\sqrt{n_x !}} \sin(n_y \pi \eta) \sin(n_z \pi \zeta) \psi_{n_x, n_y, n_z}(\vec{r}_i)$

$n_x, n_y, n_z > 0$

wave functions guaranteed to vanish at $x, y, z = \pm \frac{\pi}{2}$

$H = \sum_i H_i$

$\Psi = \left( \sum_{n_x, n_y, n_z} \right) \left( \psi_{n_x, n_y, n_z}(\vec{r}_1) \cdots \psi_{n_x, n_y, n_z}(\vec{r}_N) \right)$

Total energy $E = \sum_i E_i$

$E_i = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 (n_i^2 + n_i^2 + n_i^2)$

Partition function for atom (set $g_i = 1$ and drop non-factors subscript $i$)

$Z_i = \sum_{n_x, n_y, n_z} \exp(-\beta E_i)$  

where $\beta = \frac{\hbar^2}{2m \left( \frac{\pi}{L} \right)^2}$
\[ Z_1 = \left( \int_0^\infty dk \, e^{-\alpha^2 k^2} \right)^3 = \frac{\pi^{\frac{3}{2}}}{8\alpha^3} \]

Solved integral, appendix

\[ = L^3 \left( \frac{\pi^2 M}{\beta^3 \hbar^2} \right)^{\frac{3}{2}} = \sqrt{\frac{M \tau}{2\pi\hbar^2}} \frac{3}{2} \equiv \frac{\alpha L^3}{n} \quad \text{with} \quad n = \frac{1}{\beta} = \text{concentration (density)} \]

Since \( Z_1 \) dimensions, \( \alpha L^3 \) also has units of concentration

"Quantum concentration"

\[ n_q = \left( \frac{\alpha L^3}{2\pi\hbar^2} \right)^{\frac{3}{2}} \]

If \( n \ll n_q \), gas is essentially classical

If \( n \gg n_q \), QM indispensable (some states may try to have multiple occupations and QM does it for you)

Thermal average energy

\[ U = k_B T^2 \left( \frac{\partial Z_1}{\partial T} \right)_V \]

\[ = \gamma^2 \left( \frac{\partial n Z_1}{\partial T} \right)_V \]

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

Energy for a gas of 1 atom \( \rightarrow \) entropy

For ideal gas

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

\[
\begin{array}{c|c|c}
\text{He} & \text{H}_2 & \text{Ar} \\
\hline
\text{He} & \text{Kr} & \text{H}_2 \\
\end{array}
\]

would be different configurations, so

Partition function would be

\[ Z = \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_n} e^{-\frac{\beta E_1}{\alpha_1}} e^{-\frac{\beta E_2}{\alpha_2}} \cdots e^{-\frac{\beta E_n}{\alpha_n}} \]

\[ = \left( \sum_{\alpha_1} e^{-\beta E_1} \right) \left( \sum_{\alpha_2} e^{-\beta E_2} \right) \cdots \left( \sum_{\alpha_n} e^{-\beta E_n} \right) \]

\[ = Z_1 Z_2 Z_3 \cdots Z_n \]

However, typically we have only one kind of atom, and the two become same (with all the atom He), use the same sorting. Since we've predicted, inside by \( \alpha \)
\[ Z = \frac{Z_{i}^{n}}{N!} = \frac{1}{\sqrt{N}} (\frac{n_{0}V}{N})^{N} \]

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

Free energy \( F = -k_{B}T \ln Z = -Nk_{B}T \ln Z_{i} + k_{B}T \ln(N!) \)

\[ = -Nk_{B}T \ln(\frac{n_{0}V}{N}) + k_{B}T (Nk_{B}T - NV) \]

Pressure \( P = -\left( \frac{\partial F}{\partial V}\right)_{T} = Nk_{B}T \frac{n_{0}V}{N} = Nk_{B}T / V \)

or \( PV = \frac{Nk_{B}T}{V} \) ideal gas law

\[ 197/63 \text{ Mon. Gv, Gp} \]
\[ PV = \frac{Nk_{B}T}{V} \]

today: \( \text{5V catastrophe, phase} \)

\[ \text{What: thermal radiation, other quanta?} \]
\[ \text{Classical equipartition: each mode } \frac{1}{2} k_{B}T \text{ (e.g., } U = \frac{3}{2} Nk_{B}T \text{ ideal gas, } \text{3V mode,)} \]

\[ E_{0} = \frac{1}{2} \left( \frac{E^{2}_{0}}{k_{B}T} + \frac{B^{2}}{g_{B}} \right) + \frac{1}{2} k_{B}T \frac{1}{\text{mass}} \]

\[ E_{1} = 2k_{B}T \]

\[ E_{2} = 2k_{B}T \]

\[ \text{Note: } \text{gyr (oscillating) and } \]

\[ \text{Ideal gas energy } \epsilon = \epsilon_{0} k_{B}T \not \text{ good} \]

\[ \text{Careful classical treatment by Boltzmann & Landau} \]

\[ \text{Energy density} \]

\[ \text{State of medium varying with exp.} \]
Standing wave solution:

\[ E_a = E_0 \cos k x \cos \omega t \sin \theta \sin \phi \left( \cos \frac{\pi y}{L_y} - 1 \right) \sin \left( \frac{\pi z}{L_z} \right) \]

Constraint on choice of \( E_0, E_0', E_o \):

\[ \nabla \cdot E = 0 \]

\[ \nabla \times E = 0 \]

Similarly, \( \nabla \cdot E = 0 \). Furthermore, \( E_0'' = E_0' \) by curl parts of Maxwell equations.

With \( E_0 \) fixed \( \Rightarrow \) 3 choices for \( E_0' \).

Dispersion:

\[ c^2 \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} \]

\[ - c^2 \frac{\partial^2}{\partial y^2} (n^2(x, y) + i \gamma) - c^2 \frac{\partial^2}{\partial z^2} \]

\[ \text{Term}\text{ }1: \text{ } c^2 \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2} \]

\[ \text{Term}\text{ }2: \text{ } c^2 \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2} \]

I assume that there is no particle energy in each wave mode.

\[ \text{Mode} = \Omega \text{ } \lambda = 2 \pi \frac{L_y}{L_z} \]

Possible modes:

\[ \text{Continuous: } \Omega = \frac{\pi}{L_z} \text{ } n, \text{ } \lambda = 2 \pi \frac{L_y}{L_z} \text{ } \text{continuous} \]

\[ \text{Perpendicular: } \Omega = 2 \pi \frac{L_x}{L_z} \text{ } n, \text{ } \lambda = 2 \pi \frac{L_y}{L_z} \cdot \text{ continuous} \]
The major thing in terms of interactions between the field and atomic states is the field on atomic states. In the case of atomic states, we attempt to explain them by considering how we partition the field into various parts. The zero-point energy \( \hbar \omega / 2 \) is needed to make sense of it.

- \( n_{\alpha} \): The \( n^{th} \) mode of the cavity.
- \( c_{\alpha} \): Occupation of the \( n^{th} \) mode.
- \( a_{\alpha} \): Photon in the \( n^{th} \) mode.

A way to count occupation numbers:

\[ \begin{array}{c|ccc}
 & 0 & 1 & 2 \\
\hline
1 & & & \\
2 & & & \\
3 & & & \\
& 1 & 2 & 3 \\
\end{array} \]

The modes, like the photons, are the physical objects. It makes sense to think in terms of "particular" photons and their interaction with other modes.

If we have many fields, each field has its own occupation number.

When we say "one photon" or "one electron," it's shorthand for a mode with some occupation number. It is an analogy, not a precise equality. However, we usually mean that one mode has a single particle, and another mode has zero.

For a field of \( n \) modes:

\[ Z = \sum_{n_1} \cdots \sum_{n_N} \frac{(-\hbar \omega)^{n_1}}{n_1!} \cdots \frac{(-\hbar \omega)^{n_N}}{n_N!} \]

In general:

\[ Z = \sum_{n} \frac{(-\hbar \omega)^n}{n!} \]

or equivalently:

\[ Z = \frac{e^{-\frac{1}{2} \hbar \omega}}{1 - e^{-\hbar \omega}} \]
\[ P_n = \frac{\exp(-\frac{\beta \cdot h_n x}{\hbar})}{Z} \]

\[ \langle x \rangle = \frac{\exp(-\frac{\beta \cdot h_n x}{\hbar}) Z}{Z} = \frac{\exp(-\frac{\beta \cdot h_n x}{\hbar})}{1 - e^{-\beta \cdot h_n}} \]

\[ = \frac{1}{e^{\beta \cdot h_n} - 1} \]

\[ = \frac{e^{-\beta \cdot h_n} - e^{-\beta \cdot h_n x}}{(1 - e^{-\beta \cdot h_n})^2} \]

\[ \langle x^2 \rangle = \frac{\exp(-\frac{\beta \cdot h_n x}{\hbar}) Z}{Z} = \frac{\exp(-\frac{\beta \cdot h_n x}{\hbar})}{e^{\beta \cdot h_n} - 1 + \frac{1}{2} e^{\beta \cdot h_n}} \]

\[ \Rightarrow \text{classical limit: } \beta T \rightarrow h_0 \text{ so that} \]

\[ \delta \text{ discrete occupied levels } \rightarrow \langle x \rangle = \frac{1}{e^{\beta_0 T} - 1} = \frac{h_0}{m} \]

\[ \text{occupied energy levels } n \leq h_0 \langle x \rangle = \frac{k_{B} T}{h_0} \]

\[ k_{B} T \text{ : classical temperature} \]

\[ 1/k_{B} T \text{ : classical temperature} \]

\[ \text{Subtract two-point energy } \frac{1}{2} \text{ (this partial)} \]

\[ \text{annihilation} : \text{create } \beta_0 T \text{ of } \beta_0 \text{: population} \]

\[ \text{creation} : \text{destroy } \beta_0 T \text{ of } \beta_0 \text{: population} \]

\[ \text{create } \beta_0 T \text{ of } \beta_0 \text{: population} \]

\[ \text{destroy } \beta_0 T \text{ of } \beta_0 \text{: population} \]

\[ \text{create } \frac{1}{2} h_0 \text{ of } \frac{1}{2} h_0 \text{: population} \]

\[ \text{destroy } \frac{1}{2} h_0 \text{ of } \frac{1}{2} h_0 \text{: population} \]

\[ \text{create } \frac{1}{2} h_0 \text{ of } \frac{1}{2} h_0 \text{: population} \]

\[ \text{destroy } \frac{1}{2} h_0 \text{ of } \frac{1}{2} h_0 \text{: population} \]
Plug in $\omega_0 = \frac{e n}{m}$, $L^3 = \nu$ (vacuo).

$$U_{\text{Bond}} = \nu \frac{\pi^2}{15\hbar^3 c^3} (\sigma T)^4$$

An energy density in vacuo

$$\frac{U}{\nu} = \frac{\pi^2}{15\hbar^3 c^3} (\sigma T)^4$$

$\sigma T^4$: Stefan-Boltzmann

Go back to integral over $n$ to find out how much energy density & each freq.

$$\frac{U}{\nu} = \frac{\pi^2}{15\hbar^3 c^3} \frac{\hbar}{m} \int \frac{n^2 \rho_{-\hbar}}{\exp(\hbar \nu / kT) - 1}$$

Change var. $n = \frac{\hbar}{mc} \omega = \frac{\sqrt{3} \omega_0}{Hc}$

$$\frac{U}{\nu} = \frac{\pi^2}{15\hbar^3 c^3} \frac{\hbar}{m} \int \frac{1}{\exp(\hbar \nu / kT) - 1}$$

$$= \int d\omega \lambda(\omega)$$

where $\lambda(\omega) = \frac{\text{energy flux}}{\text{wavelength} \times \text{wavelength}}$ is a spectral density

$$= \frac{1}{\pi^2 c^3} \frac{L^3}{\exp(\hbar \omega / kT) - 1}$$

Planck radiation law

$$U(\omega)$$

Starts out line

Rephrased

Ends out constant

$\omega$-independent energy
How hot is orange hot?

The Wien's displacement law states that the wavelength at which the intensity of a blackbody is maximum is inversely proportional to the temperature of the blackbody.

\[ \lambda_{max} = \frac{2 \pi c \nu_{max}}{k_B T} \]

where \( \lambda_{max} \) is the wavelength of maximum intensity, \( c \) is the speed of light, \( \nu_{max} \) is the frequency of maximum intensity, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature of the blackbody.

Given that \( c = 3 \times 10^8 \text{ m/s} \), \( k_B = 1.38 \times 10^{-23} \text{ J/K} \), and \( \nu_{max} = 4 \times 10^{14} \text{ Hz} \), we can solve for \( T \).

\[ T = \frac{c}{k_B \nu_{max}} = \frac{3 \times 10^8}{1.38 \times 10^{-23} \times 4 \times 10^{14}} \approx 8800 \text{ K} \]

Thus, the temperature of the object is approximately 8800 Kelvin.

Reason: the temperature is a characteristic number, and it should be kept high to ensure the object is orange hot. If it is not, it will appear redder.
Blackbody radiation

Flux density \( J_0 = \frac{\text{total power}}{\text{area of hole}} \) in ergs/cm² or watts/m²

\( J_0 \propto \frac{1}{\lambda^4} \) energy density in Heliumann

\( J \propto a \) faster to get energy out

proportionality factor turns out to be \( \frac{1}{8} \) (prob. 4.15)

\[ J_0 = \sigma T^4 \]

Stefan-Boltzmann law

\[ \sigma = \frac{1}{8} \times \frac{8}{60\pi c^2} \]

\[ \times 5.67 \times 10^{-5} \text{ ergs} \text{ cm}^{-2} \text{ s}^{-1} \text{ K}^{-4} \]

Blackbody: perfect absorber or light (it doesn't have to be neutral, or equally)

blackbody emits as much as it absorbs. So to test whether something is a

blackbody, we need non-equilibrium light - e.g. flashlighk.

Small hole is ideal black surface because very little of the incident

radiation will escape reflected back.

Consider non-black plane \( \varepsilon \)

absorbivity \( 0 < \varepsilon < 1 \) : a means perfect reflector, 1 means

black, like hole

Hole not absorbed is reflected, so \( \varepsilon = 1 - \varepsilon \)

Thus, we don't know \( \varepsilon \) but it is a function of how well we

are absorbing. It's continually absorbing energy from the

environment at a rate \( k \) such that \( k \varepsilon \) is a real body. For a

perfect conductor, it must end up the same (i.e. \( \varepsilon = 1 \))

in reality, the flux density from a non-black body is

\[ J_0 = \sigma T^4 \]

This is very frictional radiation where every piece of anything but

shiny objects will obey this law. But it is not a law of nature.

Precipitate some of the flux from a body in various of eerie objects,