Physics 463: Statistical Mechanics and Thermodynamics

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Contents

1 Intro to statistical methods

- Goal: Study systems consist of many particles (magnitude of moles) that interact with each other.
- Stat Mech bridges the gap between the Macroscopic and Microscopic Description of a system.

Macroscopic Description > µm:

- Temperature, Pressure, Volume Entropy, etc.

Microscopic Description Å:

Worksheet

(1) Avogadro's number: $N_A = 6.022 \times 10^{23}$ e.g. in 12g of carbon-12, there are N_A atoms!
1 mole of air : 22.4 L at 273 K, 1 atm.
e.g. Say a room is 5m x 5m x 8m = 200 m^3 = 200×10^3 L, how many moles of air are in the room? $\sim 10000 N_A$

(2) $k_B = 1.38 \times 10^{-23}$ J/K
Physical Meaning: $k_B T$ will roughly gives us the energy in one atom

(3) On a number line with 1 and $+\infty$, where is N_A?
In mathematics, we would place N_A closer to 1, but in physics we would place it closer to $+\infty$ because this number is huge in the context of physics.

(4) In the physics convention, we use θ as the polar angle and ϕ as the azimuthal angle. So a volume element in a sphere is

$$r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$

Thus the volume of a sphere is

$$V = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_0^R r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi = \frac{4}{3}\pi R^3$$

(5) The ideal gas law comes in two forms:

$$PV = N k_B T$$

$$PV = nRT$$

where $n = \frac{N}{N_A}$, and N is the number of particles in the system.

(6) The container with gas confined to half a container at $t = 0$ releases the gas to fill the whole container at $t > 0$. What is the change in entropy?
The equation for the change in entropy is

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T}$$

but this doesn't tell us much...

Basic Statistical Concepts : "statistical ensemble"

Example: Fair coin toss (50/50) N times. The expected value of heads is $N/2$. Repeating this many times gives a Gaussian distribution centered at $N/2$.

Random walk in 1D Starting at $x = 0$, we have a probability p to move one unit to the right and probability $(1-p) = q$ to move left.

For a 'trajectory'

- n_L: # of steps left
- n_R: # of steps right
- $N = n_L + n_R$
- Displacement: $x = n_R - n_L$

Each step is independent: "no memory", "Markovian/Markov process"

The probability of a specific trajectory is

$$p \cdot p \cdots p \cdot q \cdots q = p^{n_R} q^{n_L}$$

How many ways this (n_R, n_L) can be arranged?

$$\binom{N}{n_R} = \frac{N!}{n_R! n_L!}$$

So the probabilty of taking n_R steps to the right is

$$W_N(n_R) = \frac{N!}{n_R! n_L!} p^{n_R} q^{n_L}$$

Finishing the Random Walk

$$W_N(n_R) = \frac{N!}{n_R! n_L!} p^{n_R} q^{n_L}$$

is indeed the "Binomial distribution".

The mean displacement (or expected value) is

$$\bar{m} = \bar{n}_R - \bar{n}_L = pN - qN = N(p-q)$$

How do we define variance/dispersion?

$$\begin{aligned}
\overline{(\Delta n_R)^2} = \overline{(n_R - \bar{n}_R)^2} &= \overline{n_R^2 - 2n_R\bar{n}_R + \bar{n}_R^2} \\
&= \overline{n_R^2} - 2\bar{n}_R^2 + \bar{n}_R^2 \\
&= \overline{n_R^2} - \bar{n}_R^2 = Npq
\end{aligned}$$

So the deviation or width is roughly $\sim \sqrt{Npq}$

For large N, the distribution can be approximated a continuous:

$$\left.\frac{\mathrm{d}W(n_R)}{\mathrm{d}n_R}\right|_{\bar{n}_R} = 0$$

or equivalently

$$\left.\frac{\mathrm{d}\ln W(n_R)}{\mathrm{d}n_R}\right|_{\bar{n}_R} = 0$$

And using

$$n_R \equiv \bar{n}_R + \xi$$

where ξ is the deviation from the mean.

So now we can Taylor expand $\ln W$:

$$\ln W(n_R) = \ln W(\bar{n}_R) + \cancel{\left.\frac{\mathrm{d}\ln W(n_R)}{\mathrm{d}n_R}\right|_{\bar{n}_R}(n_R - \bar{n}_R)} + \frac{1}{2}B_2\xi^2 + \dots$$

where

$$W(n_R) \equiv W_{max} e^{-\frac{1}{2}B_2\xi^2}, \quad B_2 = \frac{1}{Npq}$$

This yields the Gaussian distribution approximation.

$$P(m) = W(n_R) = (2\pi Npq)^{-1/2} e^{-\frac{[m-N(p-q)]^2}{8Npq}}$$

Worksheet

1. If a coin is flipped 400 times, what's the probability of getting 215 heads?

   $N = 215 + 185 = 400$, $p = 0.5$, $q = 0.5$, $m = 215 - 185 = 30$

   Plugging in the numbers gives $P(30) = 1.295\%$

2 Statistical description of systems of particles

2.1 Statistical formulation

Essential ingredients:

1. state of the system:
   - single spin-1/2 particle. $\uparrow, \downarrow$
   - a bunch of spin-1/2 particles. $\uparrow\uparrow\downarrow\dots$
   - a simple 1D Harmonic Oscillator: $E = (n + 1/2)\hbar\omega$, with states $|n\rangle$
   - a bunch of 1D HO: $|n_1, n_2, \dots, n_N\rangle$
2. Statistical ensemble: Instead of a simple experiments, we consider an exsemble of many exps.
3. Basic postulate about a priori probabilities (relative prob of finding the system in any of its accessible states)
4. Calculate probabilities

Example: 3 spin-1/2

State	Spin	Energy	$\Omega(E)$	$y_k = \uparrow, \downarrow$
$\uparrow\uparrow\uparrow$	3/2	$-3\mu H$	1	$\Omega(-\mu H, \uparrow)$
$\uparrow\uparrow\downarrow$	1/2	$-\mu H$	3	
$\uparrow\downarrow\uparrow$				
$\downarrow\uparrow\uparrow$				
$\uparrow\downarrow\downarrow$	-1/2	μH	3	
$\downarrow\uparrow\downarrow$				
$\downarrow\downarrow\uparrow$				
$\downarrow\downarrow\downarrow$	-3/2	$3\mu H$	1	

Table 1: Energy levels of 3 spin-1/2 particles

System: *isolated*: energy cannot change *equilibrium*: prob of finding the system in any one accessible state is constant in time

A fundamental postulate:

$\boxed{\text{An isolated system in equilirbium is equally likely to be in any of its accessible states}}$

In calculating probabilities, e.g., isolated system with energy in range $[E, E + \delta E]$
$\Omega(E)$: total number of states of the system in this range
$\Omega(E, y_k)$: in this energy range and some other property y_k where the probability of having this property is

$$P(y_k) = \frac{\Omega(E, y_k)}{\Omega(E)}$$

Density of states (DOS)

$$\Omega(E) = w(E)\mathrm{d}E, \quad w(E) \sim E$$

where $w(E)$ is the density of states.

2.2 Interactions between macroscopic systems

In general: specify some macroscopic measureable paremeters $x_1, x_2, \dots x_n$

- Micostate: A particula quantum state: γ of the system with energy E_r

$$E_r = E_r(x_1, x_2, \dots, x_n)$$

- Macrostate (Macroscopic state): Specify external parameters and any other conditions, and includes all the possible microstates—e.g., from Table above the macrostate of $-\mu H$ has 3 microstates. "Microstate" is one particular specific state consistern with the macrostate.

Consider two macro systems A, A'; they can interact with each other to exchange energy.

Q: what are the different ways to exchange E? HEAT, WORK. e.g. If A, A' are in a box seperated by a wall, then the wall moving due to pressure exchanges energy as work. If the wall cannot move, then there is no work exchanged. [insert image of two boxes with a wall]

Two Cases:

- *thermal interaction*: If all the external parameters are fixed

$$\Delta E = Q, \quad \Delta E' = Q'$$

where Q, Q' are the heat absorbed by each macrosystem, and the energy of the whole system is unchanged, i.e.,

$$\Delta E + \Delta E' = 0 \implies Q + Q' = 0, \quad Q = -Q'$$

- *mechanical interaction* (thermal isolation): no heat exchange "adiabatic". I do work, negative work is done!

Example: Beaker of water, A, and a wheel attached to a pulley with a weight, A' (2.7 Example 2). The work done by the pulley decreases the energy of system A' by ws (weight times distance).

In general energy can be exchanged both as Heat and Work.

$$Q \equiv \Delta E - \mathcal{W}$$

where $\mathcal{W}$ is the work done to the system. And

$$W = \mathcal{W}$$

is the workd done by the system, i.e.,

$$Q \equiv \Delta \bar{E} + W$$

Case of small amounts interaction: Infinitesimal changes

$$đQ = d\bar{E} + đW$$

where the bar through the differential indicates the process as path dependent.

Worksheet

(1) For the infinitesimal quantity

$$dG = \alpha dx + \beta \frac{x}{y} dy$$

it is path dependent:

- $(1,1) \to (1,2) \to (2,2)$:

$$
\begin{aligned}
G &= \int_{(1,1)}^{(1,2)} dG + \int_{(1,2)}^{(2,2)} dG \\
&= \cancel{\alpha x\Big|_{(1,1)}^{(1,2)}} + \beta \ln y\Big|_{(1,1)}^{(1,2)} + \alpha x\Big|_{(1,2)}^{(2,2)} + \cancel{\beta \ln y\Big|_{(1,2)}^{(2,2)}} \\
&= \alpha + \beta \ln 2
\end{aligned}
$$

- $(1,1) \to (2,1) \to (2,2)$:

$$G = \alpha + 2\beta \ln 2$$

So the path is dependent or dG is an inexact differential.

(2) Is the following exact?

$$dF = \frac{a}{x}dx + \frac{b}{y}dy$$

General interaction process: energy is exchanged both as heat and work

$$Q = \delta E + W$$

where Q is the heat added to the system (positive ΔE adds energy) and W is the work done by the system

Very very small work/heat: infinitesimal

$$đQ = d\bar{E} + đW$$

where d is an exact differential (path independent) and $đ$ is a inexact differential (path dependent).

Math: multivariable differential

A differential form is exact if its equal to the general differential dF for some function $F(x, y)$

e.g. $A(x, y)dx + B(x, y)dy = dF(x, y)$

From last times worksheet:

$$\frac{a}{x}dx + \frac{b}{y}dy = d(a \ln x + b \ln y)$$

How to check if its exact? Assume F exists:

$$dF(x, y): \quad \text{is exact} \quad \iff \quad \left(\frac{\partial A}{\partial y}_x\right) = \left(\frac{\partial B}{\partial x}\right)_y$$

where $\iff$ means iff or if and only if. e.g. from the worksheet:

$$dG = adx + b\frac{x}{y}dy, \quad A = a, \quad B = b\frac{x}{y}$$

so

$$\frac{\partial A}{\partial y} = 0, \quad \frac{\partial B}{\partial x} = \frac{b}{y}$$

thus it is inexact.

Quasi-static process: A system interacts with other systems in a process that is so slow that A remains arbitrarily close to equilibrium at all stages!

e.g. a piston pushing very slowly in a cylinder; when the system is not in equilibrium, then the ideal gas law $pV = nRT$ does not hold.

"relaxational time τ": time system requires to reach equilibrium if it experiences a sudden change.

Recall we denote the external parameters of an isolated system

$$x_1, x_2, \dots, x_x$$

and the energy of a microstate r

$$E_r = E_r(x_1, x_2, \dots, x_n)$$

When we start to change the external parameter, energy of state r will change:

$$x_\alpha \to x_\alpha + dx_\alpha$$

and the change in energy is

$$dE_r = \sum_{\alpha=1}^{n} \frac{\partial E_r}{\partial x_\alpha} dx_\alpha$$

Now in isolated case $đQ = 0$ so

$$dE_r + đW_r = 0$$

$$\implies đW_r = -dE_r = \sum_{\alpha=1}^{n} \left(-\frac{\partial E_r}{\partial x_\alpha}\right) dx_\alpha$$

where

$$X_{\alpha,r} = -\frac{\partial E_r}{\partial x_\alpha}$$

is the "generalized force"— e.g. if x is a distance, then X is a force; if x is a volume, then X is a pressure.

NOTE all discussion above are for : state r

Consider an ensemble: in a quasi static process, $X_{\alpha,r}$ has definite value, so

$$đW = \sum_\alpha \bar{X}_{\alpha,r} dx_\alpha$$

where $\bar{X}_{\alpha,r}$ is mean of the generalized force.

Example: Cylindrical chamber in state r (height s, circular area A, pressure P_r) with a piston pushing in ds

Force on the piston: $P_r A$

Volume: $V = AS$

Thus work done is

$$\begin{aligned} đW &= Fds = (P_r A)ds \\ &= P_r dV \end{aligned}$$

and

$$dE_r = -đW_r = -P_r dV, \quad P_r = -\frac{\partial E_r}{\partial V}$$

Worksheet

1. The mean pressure p of thermally insulated gas vaires with volume V by

$$pV^\gamma = K$$

where K and γ are constants. Find work from p_i, V_i to p_f, V_f.

$$\begin{aligned} \int đW &= \int_{V_i}^{V_f} pdV \\ &= \int_{V_i}^{V_f} \frac{K}{V^\gamma} dV \\ W &= \left.\frac{KV^{1-\gamma}}{1-\gamma}\right|_{V_i}^{V_f} \end{aligned}$$

And since $p_i V_i^\gamma = p_f V_f^\gamma = K$, then

$$\begin{aligned} W &= \frac{K}{1-\gamma}\left(V_f^{1-\gamma} - V_i^{1-\gamma}\right) \\ &= \frac{1}{1-\gamma}(p_f V_f - p_i V_i) \end{aligned}$$

3 Statistical thermodynamics

Irreversibility and attainment of equilibrium

3.1 Equilibrium conditions and constraints

Equilibrium condition: The system is equally likely to be found in any accessible states.

"accessible states": some specfic conditions/constraints of sysem , these limit the numebr of states the system can be possibly found.

Furthermore, how does the change of constraints change the number of accessible states?

Examples:

- Box divided (partition) into two equal parts: left half is filled with gas, and the right half is empty. After removing the partition (constraint), the gas spreads, but the probability of the gas being in the left half is much smaller, $\frac{1}{2^N}$. Rather, we would expect an equal number of particles on each side for $N \to N_A$.
- Box with insulating wall constrained to move: If the barrier freely moves, we would expect the Pressures to equalize $P = P'$
- Box with noninsulating wall (can't move): We would expect temperature to be equal $T = T'$

After the states reach equilibrium, if we added the contraint back in, the system would not go back to the original state! (irreverssible process)

But what is temperature???

- Kinetic energy? Heat transfer?
- Perhaps macroscopically: flow of heat from one system to another by touch (thermal contact)

3.2 Distribution of energy between systems via heat

Consider two systems A and A':

- A: Energy E, Number of states $\Omega(E)$
- A': Energy E', Number of states $\Omega(E')$

where $\Omega(E)$ is the # of states in A with energy range $(E, E + \delta E)$

The total combined system $A^{(0)}$, with number of states $\Omega^{(0)}$, has a constant total energy,

$$E^{(0)} = E + E' = \text{constant}$$

where we define: $\Omega^{(0)}(E)$: # of states accessible to $A^{(0)}$ when the subsystem A has energy $(E, E + \delta E)$.

When $A^{(0)}$ is in equilibrium the probability is proportional to the number of accessible states:

$$P(E) \propto \Omega^{(0)}(E), \quad \text{or} \quad P(E) = \frac{\Omega^{(0)}(E)}{\sum_E \Omega^{(0)}(E)} = C\Omega^{(0)}(E)$$

where C is a constant.

Multiplicity

$$\Omega^{(0)}(E) = \Omega(E)\Omega'(E^{(0)} - E)$$

Now, the probability $P(E)$ with E is

$$P(E) = C\Omega(E)\Omega'(E^{(0)} - E)$$

Graphically, we would expect E vs. $\Omega(E)$ to increase (as E increases, $\Omega(E)$ increases), and same with E' vs. $\Omega'(E')$. But E vs. $\Omega'(E^{(0)} - E)$ would decrease. In addition, the probability $P(E)$ as a function of E would have a sharp peak near the equilibrium $\tilde{E}$.

Finding maximum Take the derivative (of the log because multiplication becomes addition):

$$\frac{\partial \ln P(E)}{\partial E} = 0, \quad \ln P(E) = \ln C + \ln \Omega(E) + \ln \Omega'(E^{(0)} - E)$$

hence

$$\frac{\partial \ln P(E)}{\partial E} = \frac{\partial \ln(\Omega(E))}{\partial E} - \frac{\partial \ln(\Omega'(E'))}{\partial E'} = 0$$

Thermodynamic beta (Wikipedia) Define β:

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E}$$

where at equilibrium, $\beta(\tilde{E}) = \beta'(\tilde{E}')$

Then we introduce a *dimensionless* parameter T such that

$$\boxed{kT = \frac{1}{\beta}}$$

where k (k_B everywhere else) is the Boltzmann constant. Therefore, temperature characterizes the variation of density of state with energy.

Entropy From temperature and defining entropy $S(E)$:

$$\begin{aligned} \frac{1}{T} = k\beta &= \frac{\partial k \ln \Omega(E)}{\partial E}, \quad S(E) = k \ln \Omega(E) \\ &= \frac{\partial S}{\partial E} \end{aligned}$$

Worksheet

1. # of energy levels $\Phi_1(\epsilon) \leq \frac{\epsilon}{\Delta\epsilon} = C\epsilon$
2. Average energy per molecule is $\epsilon = E/f$ (f molecules)

$$\Phi(E) = (\Phi_1(\epsilon))^f$$

3.

$$\begin{aligned} \Omega(E) &= \Phi(E + \delta E) - \Phi(E) \\ &= \frac{\partial \Phi(E)}{\partial E}\delta E, = \Phi_1^{f-1}\frac{\partial \Phi_1}{\partial \epsilon}\delta E \end{aligned}$$

4. If f is very large

$$\begin{aligned} \ln \Omega &= (f-1)\ln \Omega(\epsilon) + \ldots \\ &\approx f \ln \Omega(\epsilon) \end{aligned}$$

5. So

$$\Omega \propto \phi_1(\epsilon)^f \propto E^f$$

Review of last time: What is temperature?

For two systems A and A' that present heat exchange:

- $E^{(0)} = E + E'$: total energy is constant
- At thermal equilibrium, the temperature of the systems are the same.
- $P(E) \propto \Omega^{(0)}(E)$: probability of finding system A to have energy E is proportional to the number of accessible states in the total system A^0.
- $\Omega^{(0)}(E) = \Omega(E)\Omega'(E^{(0)} - E)$: multiplicity
- To find the maximum, take the derivative to zero:

$$\frac{\partial \ln P(E)}{\partial E} = 0$$
$$\implies \frac{\partial \ln \Omega(E)}{\partial E} = \frac{\partial \ln \Omega'(E^{(0)} - E)}{\partial E'}$$

where

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E} \quad \text{and} \quad kT = \frac{1}{\beta}$$

and at equilibrium, $\beta(\tilde{E}) = \beta'(\tilde{E}')$ Finally, we define entropy $S(E)$ as

$$S(E) = k \ln \Omega(E)$$

where $S + S' =$ maximum at equilibrium

[insert figure graph of $P(E), \Omega(E), \Omega'(E')$]

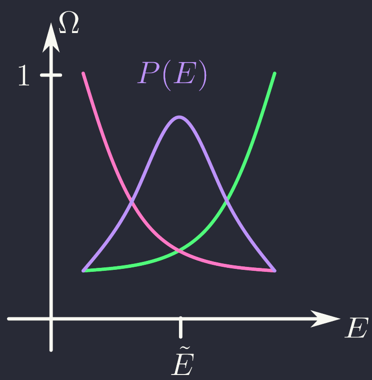

Figure 3.1: Graph of $P(E), \Omega(E)$ (green), $\Omega'(E')$

What is kT?

We replace $\Omega \sim E^f$ so

$$\frac{1}{kT} = \beta = \frac{\partial \ln \Omega}{\partial E} \approx f \frac{\partial \ln E}{\partial E} = \frac{f}{\bar{E}}$$
$$\implies kT \approx \frac{\bar{E}}{f}$$

so kT roughly represents energy per atom. Or

kT is a measure of the mean energy above the ground state per atom

- In the hydrogen atom, if $kT \geq \Delta$ (energy difference between the ground state and the first excited state), then the atom can be excited.

- Room temperature (300 K) is roughly $kT \approx 1/40$ eV $= 25$ meV
- A superconducting qubit of energy (usually in GHz) 25 µeV uses temperature in the magnitude of 15 mK: Backwards calculation: Going from 300K to 25 meV means we need to go to 0.3 K, but 0.03 K for the precision, to be in the range of the qubit.

3.3 Approach to equilibrium

Given A, A' we have average initial energy $\bar{E}_i$, $\bar{E}'_i$: At equilibrium

$$\bar{E}_f = \tilde{E}$$
$$\bar{E}'_f = \tilde{E}' = E^{(0)} - \tilde{E}$$

The heat exchange is

$$Q = \bar{E}_f - \bar{E}_i$$
$$Q' = \bar{E}'_f - \bar{E}'_i$$

where the total heat is constant, $Q + Q' = 0$.

- The system that absorbs heat is "colder"
- The system that releases (gives off) heat is "hotter"

3.4 Temperature

Properties of T:

- If the two systems have same T, they will remain in equilibrium when brought together.
- Zeroth Law of Thermodynamics: If two systems are in thermal equilibrium with a 3rd system, then they must be in equilibrium with each other.

  This allows us to use a test system as a "thermometer": a small system that has a macroscopic parameter that varies when brought into contact with another system.

3.5 Heat Reservoir

A heat reservoir A' with temp T' transfers heat to a smaller system A with temp T:

- $T \to T'$
- T' does not change!

Using the parameter $\beta' = \beta'(E')$ (where it is inversely related to temp),

$$\left| \frac{\partial \beta'}{\partial E'} Q' \right| \ll \beta'$$

which pretty much tells us that $\Delta\beta' \ll \beta'$, so the temperature of the reservoir does not change.

The change of the density of states of the reservoir is

$$\ln \Omega'(E' + Q') - \ln \Omega'(E')$$

where the Taylor expansion gives us

$$= \frac{\partial \ln \Omega'}{\partial E'} Q' = \beta' Q'$$

This is proportional to the change of entropy:

$$\Delta S' = k(\ln \Omega'(E' + Q) - \ln \Omega'(E'))$$
$$\beta' Q' k = \frac{Q'}{T'}$$

Simply,

$$\Delta S' = \frac{Q'}{T'} \quad \text{(for a heat reservoir)}$$

If one assumes an infinitesimal amount of heat $đQ$

$$\boxed{dS' = \frac{đQ'}{T'}}$$

which is the 2nd law of thermodynamics.

The first law of thermodynamics is (as we discovered)

$$dE + đW = đQ$$

3.6 Dependence on Density of States (DoS) on external parameters

$\Omega(E, x)$ where x is an external parameter. The change of energy is

$$\frac{\partial E}{\partial x} dx \quad \text{where} \quad X = -\frac{\partial E}{\partial x} \quad \text{"generalized force"}$$

Review

$$\frac{\partial \ln \Omega(E)}{\partial E} = \beta = \frac{1}{kT}$$
$$ds = \frac{đQ}{T}, \quad S = k \ln \Omega$$

3.7 Density of states on external parameters

When a parameter $x \to x + dx$ the energy of each microstate r changes by

$$\frac{\partial E_r}{\partial x} dx$$

where

$$X = -\frac{\partial E_r}{\partial x}$$

is the generalized force.

- $\Omega(E, x)$: external parameter x for the # of states in $[E, E + \delta E]$.
- $\Omega_Y(E, x)$: # of states in $[E, E + \delta E]$ *with* $Y = \frac{\partial E_r}{\partial x}$ in $[Y, Y + \delta Y]$

The total number of states is now

$$\Omega(E, x) = \sum_Y \Omega_Y(E, x)$$

Consider energy E when $x \to x + dx$:
some states r originally with energy $< E$ Can now aquire energy $> E$:

- $\sigma(E)$: # of state of originally
- $\sigma_Y(E)$: \$ of states ... with $Y = \frac{\partial E_r}{\partial x}$ in $[Y, Y + \delta Y]$

For a given E, Y; the work done is the generalized force times the change in the parameter $Y\,dx$ which is like the width of the rectangle below the energy E.

Above the energy $[E, E + \delta E]$ we can treat the total area as the total # of states $\Omega_Y(E, x)$, and dividing by the width δE kind of gives us a linear density of states per unit energy. Finally we can find σ_Y by getting the area

$$\sigma_Y(E) = \frac{\Omega_Y(E, x)}{\delta E} Y\,dx$$

and thus

$$\begin{aligned}
\sigma(E, x) = \sum_Y \sigma_Y(E, x) &= \sum_Y \frac{\Omega_Y(E, x)}{\delta E} Y\,dx \\
&= \frac{\Omega(E, x)}{\delta E} \bar{Y}\,dx \\
\bar{Y} &= \frac{1}{\Omega(E, x)} \sum_Y Y \Omega_Y(E, x)
\end{aligned}$$

The change of the DoS is

$$\frac{\partial \Omega(E, x)}{\partial x} dx = \sigma(E) - \sigma(E + \delta E) = -\frac{\partial \sigma(E)}{\partial E} \delta E$$

on the RHS

$$\frac{\partial \sigma(E, x)}{\partial E} = \frac{dx}{\delta E} \frac{\partial \Omega \bar{Y}}{\partial E}$$

and thus

$$\frac{\partial\Omega(E,x)}{\partial x} = -\frac{\partial\Omega\bar{Y}}{\partial E} = -\frac{\partial\Omega}{\partial E}\bar{Y} - \Omega\frac{\partial\bar{Y}}{\partial E}$$

dividing both sides by Ω

$$\frac{1}{\Omega}\frac{\partial\Omega}{\partial x} = -\frac{1}{\Omega}\frac{\partial\Omega}{\partial E}\bar{Y} - \frac{\partial\bar{Y}}{\partial E}$$

where

$$\frac{\partial\ln\Omega}{\partial x} = \frac{1}{\Omega}\frac{\partial\Omega}{\partial x}, \quad \frac{\partial\ln\Omega}{\partial E} = \frac{1}{\Omega}\frac{\partial\Omega}{\partial E}$$

and another trick: the second term is $\sim \bar{Y}/E$ and $\Omega \sim E^f$ so we can drop the second term

$$\frac{\partial\ln\Omega}{\partial x} = -\frac{\partial\ln\Omega}{\partial E}\bar{Y} = \beta\bar{X}$$

Recap: For a system with states $\Omega(E,x)$ we are give

$$\boxed{\frac{\partial\ln\Omega}{\partial E} = \beta}, \quad \boxed{\frac{\partial\ln\Omega}{\partial x} = \beta\bar{X}}$$

The second equation tells us that doing work will obviously increase Ω.

The rubber band example: Stretching the rubber band (work done) adds energy or heat to the system.

3.8 Equilibrium of interacting systems

$\Omega^{(0)}(E,x)$ will be maximum at $\tilde{E},\tilde{x}$.

Consider an infinitesimal quasi-static process where A and A' are brought from equiilibrium to another state $\tilde{E}+d\tilde{E},\tilde{x}+d\tilde{x}$.

The differential of the log Dos is (using math)

$$\begin{aligned}
d\ln\Omega(E,x) &= \frac{\partial\ln\Omega}{\partial E}d\tilde{E} + \frac{\partial\ln\Omega}{\partial x}d\tilde{x} \\
&= \beta(d\tilde{E} + Xd\tilde{x}) \quad Xd\tilde{x} = đW \\
&= \beta đQ \\
kd\ln\Omega(E,x) &= \frac{đQ}{T}
\end{aligned}$$

where $S = k\ln\Omega$ or equivalently

$$dS = \frac{đQ}{T}$$

Case 1 : Thermally isolated and quasi-static process

$$đQ = 0 \implies \Delta S = 0$$

thus a **reversible process**

Worksheet A gas with N atoms confined to half a box is released to fill the whole container:
Given

- Ideal gas: $PV = NkT$
- Average energy: $\bar{E}(T) = \frac{3}{2}NkT$

(i) Change in entropy $S = k\ln\Omega$: Originally we have only 1 macrostate or Ω_0 microstates, and now the total number of arrangements is $\Omega_0 2^N$ so

$$\Delta S = k\ln\Omega_0 2^N - k\ln\Omega_0 = Nk\ln 2$$

where we have a volume independence $\Omega \sim V^N X(E)$.

(ii) Defining a quasi-static process where energy doesn't change from initial to final state: We can now use

$$dS = \frac{đQ}{T}$$

and for a quasi-static process

$$\begin{aligned} đQ &= \cancel{d\bar{E}} + đW \\ đQ &= đW = PdV \end{aligned}$$

So

$$\Delta S = \int ds = \int_{V_0}^{2V_0} \frac{PdV}{T} = \int_{V_0}^{2V_0} \frac{Nk}{V} dV = Nk\ln 2$$

3.9 Fundamental Results

3.9.1 Thermodynamic laws

0th law If two systems are in equilibrium with a 3rd system, they're in equilibrium with each other. (allows us to compare temp of systems via thermometer)

1st law Energy is conserved: $đQ = d\bar{E} + đW$

2nd law An equilibrium macrostate can be characterized by S (entropy), whichhas properties that

a. In any thermally isolated process goes from one macrostate to another, entropy tends to increase

$$\Delta S \geq 0$$

b. If the system is not isolated and undergoes a quasi-static process (absorbs heat),

$$dS = \frac{đQ}{T}$$

3rd law The entropy S of a system has the limiting properties that

$$T \to 0, \quad S \to S_0 \quad \text{(Absolute entropy)}$$

Remarks All four laws are *macroscopic*. In the context of three parameters $\bar{E}, S, T$.

3.9.2 Statistical calculation of thermodynamic quantities

Statistical Relations (Microscopic nature)

- $S = k \ln \Omega$
- $\beta = \frac{\partial \ln \Omega}{\partial E}, \quad X_\alpha = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial x_\alpha}$

For the free expansion of an idea gas:

$$\Omega \propto V^N X(E)$$

where the log of the DoS is

$$\ln \Omega = N \ln V + \ln X(E) + C$$

So from the mean pressure

$$P = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial V} = \frac{1}{\beta}\frac{\partial \ln V^N}{\partial V} = \frac{1}{\beta}\frac{N}{V} = \frac{NkT}{V}$$
$$PV = NkT$$

From the beta relation

$$\beta = \frac{\ln X(E)}{E}$$

thus it is only a function of energy and not volume V:

$$\beta(\bar{E}) = E \implies \bar{E}(T) = \bar{E}$$

Extensive vs Intensive parameters For macroscopic parameters y_1, y_2 we have two cases:

- Case 1: Extensive if $y_1 + y_2 = y$
- Case 2: Intensive if $y_1 = y_2 = y$

Extensive	Intensive
Volume	T
Energy	Pressure
entropy	specific heat
mass	
heat capacity	

3.10 Heat capacity and specific heat

Suppose we add $đQ$ to the system while other parameters are fixed, the system temperature raised by dT

$$\text{“Heat capacity”} \quad \left(\frac{đQ}{dT}\right)_y = C_y$$

In general The heat capacity is defined by temperature and the parameter

$$C_y = C_y(T, y)$$

We can also relate it to the entropy change $ds = \frac{đQ}{T}$:

$$C_y = \left(\frac{đQ}{dT}\right)_y = T\left(\frac{ds}{dT}\right)_y$$

Specific heat: Intensive parameter

$$C_y = \frac{C_V}{V} \quad \text{per mole}$$
$$C_y = \frac{C_P}{\text{mass}} \quad \text{per gram}$$

or the “specific heat/heat capacity per mole/gram”

Defining some units:

- Calorie: Heat required to raise temperature of 1 g of water @ 1 atm from 14.5 → 15.5 °C.
- Joule: Applied work

$$1\,\text{cal} = 4.1840\,\text{J}$$

Worksheet

1. Increase in entropy of a cup of water as it is heated from room temp to boiling:

$$\Delta S = \int dS = \int \frac{đQ}{T} = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$
$$= C_P \ln \frac{T_2}{T_1} = C_P \ln \frac{373}{298}$$

where $q = mC_P\Delta T$

4 Macroscopic Parameters and their measurement

4.1 Work & internal energy

From the first law of thermodynamics we always talk about

$$Q = \Delta\bar{E} + W$$

Given a system, work is *easy* measure i.e. we integrate

$$W = -\int p\mathrm{d}V$$

Measure of internal energy

- Thermal isolation case: $Q = 0$

$$\Delta\bar{E} = \bar{E}_b - \bar{E}_b = -W_{ab} = \int_a^b đW$$

  e.g. a thermally isolated piston goes from state a to b.

4.2 Heat

The heat absorbed by a system going from macrostate a to b is simply

$$Q_{ab} = (\bar{E}_b - \bar{E}_a) + W_{ab}$$

Example A superconducting circuit A is connected to the circuit B with a resistor.
Adding 20 µW of heat to the system: we actuallly are doing work on a resistor.

Method of Mixers (Comparison Method)

Bring system A into contact with system B that has a known relation between its internal energy and some parameters (T).

$$Q_A = \Delta\bar{E}_B = -Q_B$$

e.g. system A is submerged in water B and we can measure the change in internal energy of water quite easily.

4.3 Entropy

We define entropy S

$$dS = \frac{đQ}{T}$$

and **Absolute entropy** from the 3rd law

$$T \to 0, \quad S \to S_0$$

Example: Tin
Two structures of a solid:

1. White tin—a metal $\to$ stable > 298 K
2. Grey tin—semiconductor $\to$ stable < 298 K

Thus it requires some amount of heat Q to transform from grey to white tin.

- Case 1: a mole of white tin from $T = 0 \to T_0$ with specific heat $C^{(w)}(T)$

$$S^{(w)}(T_0) = S^{(w)}(T = 0) + \int_0^{T_0} \frac{C^{(w)}(T)}{T} \mathrm{d}T$$

- Case 2: Grey tin from 0 K $\to T_0$ and then it transforms to white tin quasi-statically. It absorbs heat Q and the entropy change is

$$S^{(w)}(T_0) = S^{(g)}(T = 0) + \int_0^{T_0} \frac{C^{(g)}(T)}{T} dT + \frac{Q}{T_0}$$

  where

$$S^{(g)}(T = 0) = S^{(w)}(T = 0) = S_0$$

Figure 4.1: Mole of Tin (DALL-E 3)

5 Simple Applications of macroscopic thermodynamics

5.1 General relationship of thermodynamics

Fundamental thermodynamic relation for a *quasi-static process*:

$$dS = \frac{đQ}{T}$$

where

$$đQ = dE + đW = dE + pdV$$

The only external parameter of change is V

$$\implies dE = TdS - pdV$$

This specifies certain relationship between T, S, p, V i.e. S & V are independent variables

$$E = E(S, V)$$

So we have a pure mathematical relationship

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

where

$$\begin{cases} T = \left(\frac{\partial E}{\partial S}\right)_V \\ -p = \left(\frac{\partial E}{\partial V}\right)_S \end{cases}$$

which we already know! Because dE is an exact differential

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

this is known as the first Maxwell relation (wiki).

How about S, P?

From our favorite starting point

$$dE = TdS - pdV$$

we need to change $dV \to dp$ so from chain rule

$$d(pV) = pdV + Vdp \implies pdV = d(pV) - Vdp$$

so

$$dE = TdS - d(pV) + Vdp$$

or

$$d(E + pV) = TdS + Vdp$$

lets call this new parameter $H = E + pV$ the **enthalpy** i.e.

$$H = H(S, p)$$

So

$$\begin{cases} T = \left(\frac{\partial H}{\partial S}\right)_p \\ V = \left(\frac{\partial H}{\partial p}\right)_S \end{cases}$$

where dH is an exact differential

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

or the second Maxwell relation!

Worksheet We can derive the Helmholtz free energy $F = F(T, V)$ by starting with

$$d(TS) = TdS + SdT \implies TdS = d(TS) - SdT$$

so

$$\begin{aligned} dE &= d(TS) - SdT - pdV \\ d(E - TS) &= -SdT - pdV \end{aligned}$$

1. Thus the Hemholtz free energy $F \equiv E - TS$ so

$$\begin{aligned} dF &= dE - (TdS + SdT) \\ &= TdS - pdV - Tds - SdT \\ &= -SdT - pdV \end{aligned}$$

2. So $F = F(T, V)$ the we know that

$$\begin{cases} -S = \left(\frac{\partial F}{\partial T}\right)_V \\ -p = \left(\frac{\partial F}{\partial V}\right)_T \end{cases}$$

and dF is an exact differential

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Finally for independent parameters T, p:

$$dE = TdS - pdV$$

we need to change $dV \to dp$ so from chain rule

$$d(pV) = pdV + Vdp \implies pdV = d(pV) - Vdp$$

so also using $TdS = d(TS) - SdT$

$$\begin{aligned} dE &= (d(TS) - SdT) - (d(pV) - Vdp) \\ d(E - TS + pV) &= -SdT + VdP \end{aligned}$$

where $G = E - TS + pV$ is the Gibbs free energy $G = G(T, p)$

$$\begin{cases} -S = \left(\frac{\partial G}{\partial T}\right)_p \\ V = \left(\frac{\partial G}{\partial p}\right)_T \end{cases}$$

and dG is an exact differential

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

Summary of Maxwell relations

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial V}{\partial T}\right)_p &= -\left(\frac{\partial S}{\partial p}\right)_T \end{aligned}$$

or in box form Where the components are horizontal (TS) and vert (pV) give us the relations.
e.g. someothing

$$\begin{array}{c|c} \text{E} & \text{F} \\ \hline \text{H} & \text{G} \end{array}$$

Review of Maxwell relations the DoS and external parameters of the system

$$(T, S) \quad \text{and} \quad (p, V)$$

are not independent, but related through

$$dE = Tds - pdV$$

From this we can get the Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$
$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

which can be derived from the Thermodynamic functions

$$\begin{aligned} E &= E(S, V) \\ H &= H(S, p) = E + pV \\ F &= F(T, V) = E - TS \\ G &= G(T, p) = E - TS + pV \end{aligned}$$

5.2 Specific Heats

- Molar specific heat at constant volume $dV = 0$

$$C_V = \frac{1}{n}\left(\frac{đQ}{dT}\right)_V \qquad dE = đQ = nC_v dT$$

- Molar specific heat for constant pressure $dp = 0$

$$C_p = \frac{1}{n}\left(\frac{đQ}{dT}\right)_p = C_V + \frac{1}{n}p\left(\frac{dV}{dT}\right)_p$$

  When comparing the two specific heats we can infer that $C_p > C_V$ because the heat $đQ$ has to both increase the internal energy and do mechanical work to expand the volume:

$$đQ = dE + pdV = nC_V dT + pdV$$

- For an ideal gas

$$\begin{aligned} pV &= nRT \\ pdV &= nRdT \\ \implies \left(\frac{dV}{dT}\right) &= \frac{nR}{p} \end{aligned}$$

  thus

$$C_p = C_V + R$$

  where we define

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{R}{C_V}$$

For the idea gas molecule the energy is given by

$$E(T) = \frac{3}{2}nRT$$

where there is 3 degrees of freedom thus

$$C_V = \frac{1}{n}\frac{dE}{dT} = \frac{3}{2}R$$
$$C_p = C_V + R = \frac{5}{2}R$$

For a diatomimc molecule there are 2 extra degrees of freedom for rotaion so

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3}$$

5.3 Adiabatic expansion or compression

Some definitions:

- "Isothermal": T is constant $\implies pV =$ Constant.
- "Adiabatic": $đQ = 0$

$$\begin{aligned} \implies 0 &= dE + pdV \\ &= nC_V dT + pdV \end{aligned}$$

So from the ideal gas law $pV = nRT$ we can get

$$VdP + pdV = nRdT$$

and substituting dT into the adiabatic expression

$$đQ = 0 = V\frac{C_V}{R}dP + \frac{C_V P}{R}dV + pdV$$

which can be rewritten as

$$0 = (C_V + R)pdV + C_V VdP = C_p pdV + C_v Vdp$$

or dividing by $C_V PV$ we ge

$$\gamma\frac{dV}{V} + \frac{dP}{P} = 0$$

Integration then gives

$$\gamma \ln V + \ln P = \text{Constant} \implies \ln(PV^\gamma) = \text{Constant}$$

or

$$PV^\gamma = \text{Constant}$$

Worksheet

- Pumping a bike tire, a liter or air at 1 atm is compressed *adiabatically* to 7 atm. (Air is mostly diatomic gas)

- For diatomic gas

$$E(T) = \frac{5}{2}nRT$$

So the specific heats are

$$C_V = \frac{1}{n}\frac{dE}{dT} = \frac{5}{2}RC_p = C_V + R = \frac{7}{2}R$$

which gives us

$$\gamma = \frac{C_p}{C_V} = \frac{7}{5}$$

- The final volume after compression is

$$p_i V_i^\gamma = p_f V_f^\gamma$$

or

$$(1\,\mathrm{atm})(1\,\mathrm{L})^{7/5} = (7\,\mathrm{atm})V_f^{7/5} \implies V_f = 0.25\,\mathrm{L}$$

- Work done compressing air: using $p_i V_i^\gamma = 1 \implies p = \frac{1}{V^\gamma}$

$$\begin{aligned} W &= \int_{V_i}^{V_f} pdV = \int_{V_i}^{V_f} \frac{1}{V^\gamma} dV \\ &= \frac{1}{1-\gamma}\left(V_f^{1-\gamma} - V_i^{1-\gamma}\right) \end{aligned}$$

- If initial temp is 300 K, the final temp is

$$\begin{aligned} P_i V_i = nRT_i \quad P_f V_f = nRT_f \\ \implies \frac{P_f V_f}{P_i V_i} = \frac{T_f}{T_i} \end{aligned}$$

- If the compression is isothermal (pumping very slowly) how does the answers change?

General case:

$$\begin{aligned} C_V &= \left(\frac{đQ}{dT}\right)_V = T(\frac{\partial S}{\partial T})_V \\ C_p &= \left(\frac{đQ}{dT}\right)_p = T(\frac{\partial S}{\partial T})_p \end{aligned}$$

5.4 Entropy

Consider $S = S(T, P)$

$$\begin{aligned} đQ = TdS &= T\left[\left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP\right] \\ &= C_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \end{aligned}$$

5.5 Specifc heats again

General relation between C_v and C_p for non-ideal gas ($C_p - C_v = R$),

$$C_V = \left(\frac{đQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$
$$C_P = \left(\frac{đQ}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

where

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

The pressure $P(T,V)$ with temp and volume dependence has a differential

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

and since C_V acknowledges fixed volume $dV = 0$ we get

$$C_V = \left(\frac{đQ}{dT}\right)_V = C_p + T\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

where we can replace the entropy term wit the Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

We define the "volume coefficient of expansion"

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

so

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V$$

The second term is not well defined since fixing volume while increasing pressure is hard to due (e.g. filling a water bottle with more and more water). Now using the volume dependence $V(P,T)$ i.e.

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = 0$$

and moving thing around we get

$$\left(\frac{dP}{dT}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}$$

where we define another term

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

AKA the "isothermal compressibility" thus

$$\boxed{C_P - C_V = VT\frac{\alpha^2}{\kappa}}$$

One check we can do is use the Ideal gas law to calculate α and κ then see if the above equation gives us the relation $C_P - C_V = R$

5.6 Entropy and Internala energy

$S(T,V)$ doing the same thing

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$
$$= \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_N dV$$

etc.

5.7 Free expansion of a gas

For the general case

$$dE = 0$$
$$E = E(T,V)$$

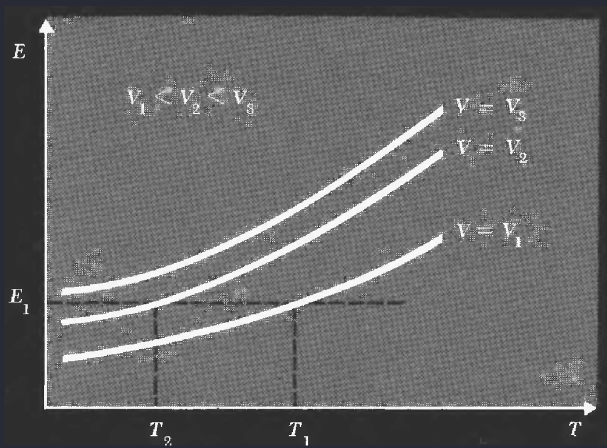

Figure 5.1: Free expansion of a gas

Van de Waals Gas

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad E = E(T,V)$$
$$v = \frac{V}{n}$$

5.8 Heat Engine

What is a heat engine? Heat → Work.

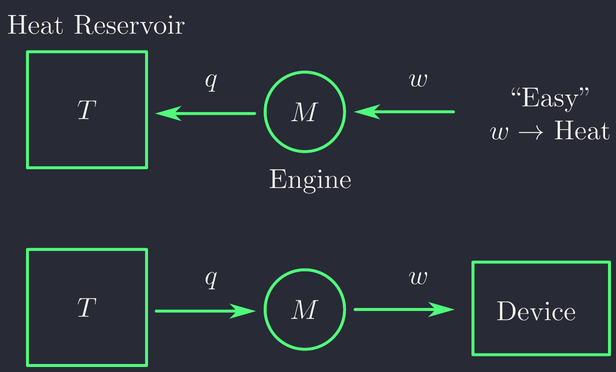

Figure 5.2: (top) reverse "easy" process converting work to heat. (botton) Heat Engine converting heat from a reservoir into work.

- For a heat engine: whatever mechanisms needed to retune to the same original condition; go through a cycle; otherwise, engine cannot continuously operate.
- Ideally perfect engine: $q = w$ or 100% efficiency

A perfect engine *violates* the 2nd law of thermodynamics $\Delta S \geq 0$.

- entropy change for engine and external device $\Delta S = 0$
- entropy change for hea reservoir $\Delta S = -q/T$ thus

$$\Delta S_{\text{tot}} = -\frac{q}{T} < 0$$

Building a heat engine: Using two heat reservoirs

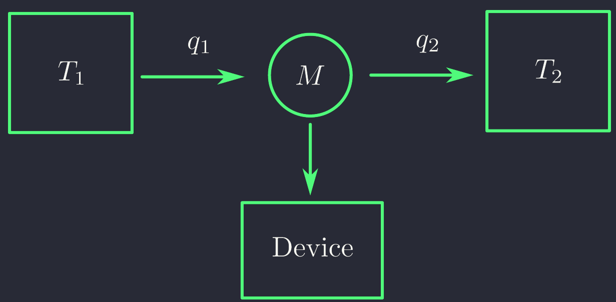

Figure 5.3: Heat engine using two heat reservoirs

Where we make $q_1 > q_2$ so that heat flows from $T_1 \to T_2$ so that

$$W = q_1 - q_2 \implies q_2 = q_1 - W$$

so the total entropy change is

$$\begin{aligned}\Delta S_{\text{tot}} &= -\frac{q_1}{T_1} - \frac{q_2}{T_2} \geq 0\\ &= -\frac{q_1}{T_1} + \frac{q_1 - W}{T_2}\\ \implies \frac{W}{T_2} &\leq q_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\end{aligned}$$

thus the efficiency of the engine

$$\eta = \frac{W}{q_1} \leq T_2\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$= 1 - \frac{T_2}{T_1}$$

Carnot Engine

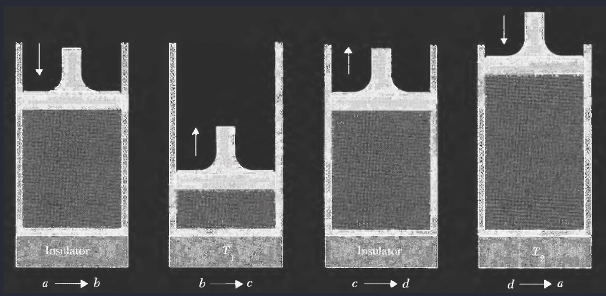

Figure 5.4: 4 stages of Carnot Engine

- $a \to b$: adiabatic (no heat exchange) bringing colder $T_2 \to T_1$
- $b \to c$: isothermal (constant temp) adding heat q_1 from hot reservoir
- $c \to d$: adiabatic (no heat exchange) cooling down $T_1 \to T_2$ as work is done through expansion
- $d \to a$: isothermal (constant temp) releasing heat q_2 to cold reservoir

Worksheet Carnot Engine using an ideal gas:

The work done is

$$W = \int_a^b PdV + \int_b^c PdV + \int_c^d PdV + \int_d^a PdV$$

- $b \to c$: Using the ideal gas law $PV = nRT$ we get

$$W = \int PdV = \int_{V_b}^{V_c} \frac{nRT_1}{V} dV = nRT_1 \ln \frac{V_c}{V_b}$$

  and since $\Delta E = 0$ we know that

$$q_1 = W = nRT_1 \ln \frac{V_c}{V_b}$$

- $d \to a$: Same as above

$$q_2 = nRT_2 \ln \frac{V_a}{V_d}$$

  so

$$W = q_1 - q_2$$

  where the work done should be the total heat of the system as we go from $a \to b \to c \to d \to a$, i.e.

$$\Delta E = 0 \implies W = \Delta Q$$

The efficiency of the Carnot engine is by definition

$$\eta = \frac{W}{q_1} = \frac{q_1 - q_2}{q_1} = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1} \frac{\ln(V_d/V_a)}{\ln(V_c/V_b)}$$

Argument:

$$\frac{V_d}{V_a} = \frac{V_c}{V_b}$$

From the adiabatic process

$$PV^\gamma = \text{Constant}$$

so

$$P_a V_a^\gamma = P_b V_b^\gamma$$
$$P_d V_d^\gamma = P_c V_c^\gamma$$
$$\implies \frac{P_a V_a^\gamma}{P_d V_d^\gamma} = \frac{P_b V_b^\gamma}{P_c V_c^\gamma}$$

And from the Isothermal process

$$PV = \text{Constant} \implies \frac{P_a V_a}{P_b V_b} = \frac{P_d V_d}{P_c V_c}$$

From the former equation we can rewrite it as

$$\frac{P_a V_a V_a^{\gamma-1}}{P_d V_d V_d^{\gamma-1}} = \frac{P_b V_b V_b^{\gamma-1}}{P_c V_c V_c^{\gamma-1}}$$

which cancels out some terms

$$\frac{V_a^{\gamma-1}}{V_d^{\gamma-1}} = \frac{V_b^{\gamma-1}}{V_c^{\gamma-1}} \implies \frac{V_d}{V_a} = \frac{V_c}{V_b}$$

5.9 Refrigerators

[insert figure of 2 fridges]

From the Thermo Laws

- 1st law:

$$W + q_2 + q_1$$

- 2nd law:

$$\Delta S = \frac{q_1}{T_1} + \frac{-q_2}{T_2} \geq 0$$

  or

$$\frac{q_1}{q_2} \geq \frac{T_1}{T_2}$$

We define the “coefficient of performance”

$$CoP \equiv \frac{q_2}{W} = \frac{q_2}{q_1 - q_2} = \frac{1}{\frac{q_1}{q_2} - 1} \leq \frac{1}{\frac{T_1}{T_2} - 1} = \frac{T_2}{T_1 - T_2}$$

Case:

- Room temp: $T_1 = 300K$
- Freezer: $T_2 = 255K$

so the CoP is roughly

$$\frac{255}{45} \approx 5.67$$

since less work is required to move heat rather than converting into heat, the number is greater than one $COP > 1$.

	$-TS \rightarrow$	
$+pV \downarrow$	E	F
	H	G

Recap: Classical thermodynamics only focuses on macroscopic parameters and their measures.
Key Points:

- $dE = đQ + đW$ from 1st law.
- $dE = TdS - PdV$, and from 2nd law $dS = đQ/T$
- Relationship between (T, S) and (P, V) where F is the Hemholtz, G is Gibbs, and H is enthalpy.

6 Stat Mech Results and Methods

Our Return to th stat mech part... with systems A and heat reservoir A' where

$$A \ll A'$$

What is the prob of finding system A in a ny particular microstate r with energy E_r?

$$E_r + E' = E^{(0)}, \implies E' = E^{(0)} - E_r$$

And from the DoS the number of states in A' is

$$\Omega'(E^{(0)} - E_r)$$

or the Multiplicity of A' given E_r. The prob P_r has a proportionality

$$P_r \propto C'\Omega'(E^{(0)} - E_r)$$

Since $A \ll A'$ and $E_r \ll E^{(0)}$ we can take the log and Taylor expand

$$\ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E^{(0)}} E_r$$

where the derivative is the thermodynamic beta

$$\left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E^{(0)}} = \frac{1}{kT} = \beta$$

which is independent of E_r. So taking the exponential again...

$$\Omega'(E^{(0)} - E_r) = \Omega'(E^{(0)})e^{-\beta E_r} = Ce^{-\beta E_r}$$

where the $\Omega'(E^{(0)})$ is a constant, i.e.

$$P_r = Ce^{-\beta E_r}$$

This must be normalized by

$$\sum P_r = 1$$

or

$$C = \frac{1}{\sum e^{-\beta E_r}}$$

where the "Partition Function" is

$$Z \equiv \sum_r e^{-\beta E_r}$$

coined by Planck (1920) as "Zustandsumme" or "Sum over all states".

The probability is

$$P_r = \frac{e^{-\beta E_r}}{Z}$$

Where we have a "Boltzmann funtion" $e^{-\beta E_r}$ and P_r is the cannonincal distribution.

The probability of A having energy E is given by

$$P(E) = \frac{\Omega E e^{-\beta E}}{Z}$$

where the partition function Z is incredibly useful for

- Average energy: From P_r, E_r

$$\bar{E} = \sum_r P_r E_r = \frac{\sum_r e^{-\beta E_r} E_r}{Z}, \quad Z = \sum_r e^{-\beta E_r}$$

Using the mathematically useful fact

$$\frac{\partial Z}{\partial \beta} = -\sum_r E_r e^{-\beta E_r}$$

So we can get

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

which is just equivalent to

$$\boxed{\bar{E} = -\frac{\partial}{\partial \beta}(\ln Z)}$$

The variance of the change in energy is (NOTE: the square is inside because $(\overline{\Delta E})^2 = 0$)

$$\overline{(\Delta E)^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2$$

where

$$\overline{E^2} = \sum_r P_r E_r^2 = \frac{\sum_r e^{-\beta E_r} E_r^2}{Z}$$

The top part is equivalent to the second derivative of Z

$$\frac{\partial^2 Z}{\partial \beta^2} = \sum_r e^{-\beta E_r} E_r^2$$

So

$$\overline{E^2} = \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)^2 = -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2$$

where we get second part of the variance from above

$$\bar{E}^2 = \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

Thus

$$\overline{(\Delta E)^2} = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

- Change in Work:

$$\begin{aligned} đW &= \frac{\sum e^{betaE_r}\left(\frac{\partial E_r}{\partial x}dx\right)}{Z} \\ &= \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}dx \\ đW &= \bar{X}dx, \quad \boxed{\bar{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}} \end{aligned}$$

Example: A spin-$\frac{1}{2}$ particle (or a two-level system) in a magnetic field B with magnetic moment μ so the two states are

- $\mu B \to |+\rangle$
- $-\mu B \to |-\rangle$

The partition function is

$$Z = \sum_r e^{-\beta E_r} = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B)$$

Thus

$$\bar{E} = -\frac{\partial \ln Z}{\partial\beta} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\mu B\frac{\sinh(\beta\mu B)}{\cosh(\beta\mu B)} = -\mu B\tanh(\beta\mu B)$$

And the temperature limits

$$\begin{aligned} T \to 0, \bar{E} &= -\mu B \\ T \to \infty, \bar{E} &= 0 \end{aligned}$$

Example: Harmonic Oscillator

$$E = \left(n + \frac{1}{2}\right)\hbar\omega$$

Thus the partition function is

$$\begin{aligned} Z = \sum e^{-\beta E_r} &= \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} \\ &= e^{\frac{1}{2}\beta\hbar\omega}\sum\left(e^{-\beta\hbar\omega}\right)^n \end{aligned}$$

We can simplify the summation using a geometric series

$$\sum_n x^2 = 1 + x + x^2 + \cdots = \frac{1}{1-x}$$

Therefore

$$Z = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

and

$$\bar{E} = -\frac{\partial \ln Z}{\partial\beta} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

Looking at the temperature limits

- $T \to 0, \beta \to \infty \quad \bar{E} = \frac{1}{2}\hbar\omega$
- $T \to \infty, \beta \to 0 \quad \bar{E} \to \infty$

Example: Particle in a Box: the solution in 1D is

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

where we get this from the Schrödinger equation wavefunction for a infinite well

$$\psi(x) = A\sin\left(\frac{n_x\pi x}{L_x}\right), \quad k_x = \frac{n_x\pi}{L_x}$$

with boundary conditions $\psi(0) = \psi(L) = 0$. For the 3D box we remember

$$\psi = A\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

where the momentum is $p = \hbar k$ and the energy is

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

In k-space the volume of a point (microstate) is

$$k_x k_y k_z = \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{V}$$

We assume the box is large, so in the range $k \to k + dk$. The volume of the "orange peel" in this range divided by the volume in k-space is

$$\Omega(k) = \frac{1}{8}\frac{4\pi k^2 dk}{\pi^3/V} = \frac{V}{2\pi^2}k^2 dk$$

Note: the k-space is spherical since the vector basis is

$$k = \sqrt{k_x^2 + k_y^2 + k_z^2}$$

and we only deal with positive k_i i.e. the positve x, y, z octant in the Cartesian k-space.

The partition function is then

$$\begin{aligned} Z &= \int_0^\infty \Omega(k) e^{-\beta\frac{\hbar^2 k^2}{2m}}\, dk = \frac{V}{2\pi^2}\int_0^\infty k^2 e^{-\beta\frac{\hbar^2 k^2}{2m}}\, dk \\ &= \frac{V}{2\pi^2}\frac{\sqrt{\pi}}{4}\left(\frac{2m}{\beta\hbar}\right)^{3/2} \end{aligned}$$

or

$$\boxed{Z = \left(\frac{2m}{\hbar^2\pi}\right)^{3/2}\beta^{-3/2}V}$$

Multiple Particles: The system

$$A^{(0)} = A + A', \quad \text{For} \quad A^{(0)}, \quad E_{r,s}^{(0)} = E_r + E_s'$$

and

$$A' \text{ has } E_s, \quad Z^{(0)} = \sum_{r,s} e^{-\beta E_{r,s}^{(0)}}$$

The partition function

$$\begin{aligned} Z^{(0)} &= \sum_{r,s} e^{-\beta(E_r + E_s')} \\ &= \sum_r e^{-\beta E_r}\sum_s e^{-\beta E_s'} = ZZ' \end{aligned}$$

So for N particles

$$Z_N = \left[\left(\frac{2m}{\hbar^2 \pi} \right)^{3/2} \beta^{-3/2} V \right]^N$$

The average Energy is now

$$\bar{E} = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{3}{2} N k T$$

Density of States For average pressure is equivalent to the generalized force so

$$\begin{aligned} \bar{P} &= \frac{1}{\beta} \frac{\partial (\ln Z)}{\partial V} = \frac{1}{\beta} N \frac{1}{V} \\ &= \frac{NkT}{V} \end{aligned}$$

thus

$$\bar{P} V = N k T$$

Connection to Thermo For $Z(\beta, x)$ the differential is mathematically stated by

$$d \ln Z(\beta, x) = \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial x} dx$$

or

$$\begin{aligned} d \ln Z &= -\bar{E} d\beta + \beta đW \\ &= (\beta đW - d(\bar{E}\beta)) + \beta d\bar{E} \\ d(\ln Z + \bar{E}\beta) &= \beta(đW + d\bar{E}) = \beta dQ \\ &= \frac{1}{k} dS \end{aligned}$$

Thus the entropy of an ideal gas system is

$$S = k(\ln Z + \bar{E}\beta)$$

so using $\bar{E} = \frac{3}{2} NkT$ we get

$$S = Nk \left[\frac{3}{2} \ln \left(\frac{2m}{\hbar^2 \pi} \right) - \frac{3}{2} \ln(\beta) + \ln(V) + \frac{3}{2} \right]$$

where

$$\frac{3}{2} \ln \beta = \frac{3}{2} \ln k + \frac{3}{2} \ln T$$

so

$$S = Nk \left(\ln V + \frac{3}{2} \ln T + \sigma_0 \right), \quad \sigma_0 = \frac{3}{2} \ln \left(\frac{2m}{\hbar^2 \pi} \right) + \frac{5}{2}$$

Two Issues:

- The second law is violated: $T \to 0$ which implies $S \to -\infty$
- Gibbs paradox: $S > S' + S''$

7 Simple Applications of Stat Mech

7.1 Gibbs Paradox

From the last lecture the Gibbs paradox $S > S' + S''$ is puzzling...

(indistinguishable) If the particles are identical we can keep track double counting with

$$Z_N = \frac{Z_1^N}{N!}$$

And from the log of the partition function

$$\begin{aligned} \ln Z_N &= N \ln Z_1 - \ln N! \quad \text{using} \quad \ln N! = N \ln N - N \\ &= N \ln Z_1 - N \ln N + N \end{aligned}$$

NOTE: This does not affect $\bar{E}, \bar{P}$ as they are still

$$\bar{E} = \frac{3}{2} NkT, \quad \bar{P} = \frac{NkT}{V}$$

The entropy is recaculated as

$$S = k(\ln Z + \beta E)$$

Using

$$Z_1 = \left(\frac{2m}{\hbar^2 \pi}\right)^{3/2} \beta^{-3/2} V$$

we have the entropy

$$S = kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_0\right], \quad \sigma_0 = \sigma + 1 = \frac{3}{2} \ln \left(\frac{2\pi mk}{h^2}\right)^{3/2} + \frac{5}{2}$$

7.2 Equipartition Theorem

Using the Boltzmann function

Consider some systems described by generalized coordinates q_k, p_k with energies

$$E = E(q_1, \ldots, q_N, p_1, \ldots, p_N)$$

- Assumption 1: The total energy is additive

$$E = \epsilon_i(p_i) + E(q_1, \ldots, q_N, p_1, \ldots, \text{no } p_i, \ldots, p_N)$$

- Assumption 2: function ϵ_i is quasi-staic in p_i or usually the energy is quadratic i.e.

$$\epsilon_i(p_i) = bp_i^2$$

The average value of ϵ_i is

$$\begin{aligned} \overline{\epsilon_i} &= \frac{1}{Z} \int \epsilon_i e^{-\beta E} dq dp \\ &= \frac{\int_{-\infty}^{\infty} e^{-\beta E(q_1, \ldots, p_N)} \epsilon_i dq_1, \ldots, dp_N}{\int_{-\infty}^{\infty} e^{-\beta E(q_1, \ldots, p_N)} dq_1, \ldots, dp_N} \end{aligned}$$

From the first assumption we know that the energy is additive so

$$\begin{aligned}\overline{\epsilon_i} &= \frac{\int_{-\infty}^{\infty} e^{-\beta\epsilon_i}\epsilon_i dp_i \cancel{\int e^{-\beta E'} dq_1, \dots, dp_N}}{\int_{-\infty}^{\infty} e^{-\beta\epsilon_i} dp_i \cancel{\int e^{-\beta E'} dq_1, \dots, dp_N}} \\ &= -\frac{\partial}{\partial\beta}\ln\left(\int e^{-\beta E} dp_i\right)\end{aligned}$$

Now using the second assumption the intgral becomes

$$\int e^{-\beta\epsilon_i} dp_i = \int e^{-\beta b p_i^2} dp_i$$

With a change of variables

$$y = \sqrt{\beta} p_i, \quad dy = \sqrt{\beta} dp_i$$

the integral becomes

$$= \frac{1}{\sqrt{\beta}} \int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\frac{\pi}{\beta}}$$

which is independent of β so

$$\int e^{-\beta\epsilon_i} dp_i = C\beta^{-1/2}$$

where C is a constant. Thus

$$\overline{\epsilon_i} = -\frac{\partial}{\partial\beta}\ln\left(C\beta^{-1/2}\right) = \frac{1}{2\beta} = \frac{1}{2}kT$$

Worksheet

1. Use the equipartition theorem to determine the molar heat capacity at constant volume of a monoatomic gas: Given

$$\bar{\epsilon} = \frac{1}{2}kT \quad \text{for} \quad q_x, q_y, q_z \implies \bar{E} = \frac{3}{2}NkT$$

so the molar heat capacity is

$$c_V = \frac{\partial\bar{E}}{\partial T} = \frac{3}{2}Nk \implies c_p = \frac{c_V}{n} = \frac{3}{2}R, \quad R = \frac{N}{n}k = N_A k$$

2. A small particle undergoing Brownian motion in a liquid. The particle is in equilibrium with a bath at temp T. Use the equipartition theorem to determine the velocity dispersion

$$\begin{aligned}\bar{E}_x &= \frac{1}{2}m\overline{v_x}^2 = \frac{1}{2}kT \\ \implies \overline{v_x}^2 &= \frac{2\bar{E}_x}{m} = \frac{kT}{m}\end{aligned}$$

7.3 Specifc heat of solids

In 3D the energy is

$$E = \sum_{i=1}^{3N}\left[\frac{p_i^2}{2m} + \frac{1}{2}mk_i^2 q_i^2\right]$$

where we have three dimensions as well as a kinetic and potential dimension (6N degrees of freedom). From the equipartition theorem the average energy is

$$\bar{E} = 3N\left(\frac{1}{2}kT \cdot 2\right) = 3NkT$$

The molar heat capacity is roughly

$$c_p = \frac{c_V}{n} = \frac{3Nk}{n} = 3R$$

The molar heat capacity of a solids at $T = 300$ K are

$$c_p = \begin{cases} 25.35 \text{ J/mol K} & \text{Ag} \\ 22.75 \text{ J/mol K} & \text{S} \\ 25.39 \text{ J/mol K} & \text{Zn} \\ 24.20 \text{ J/mol K} & \text{Al} \\ 6.01 \text{ J/mol K} & \text{C} \end{cases}$$

Einstein's Solids: All atoms have the same spring constant $\omega = \sqrt{k/m}$ From the partition function, the average energy in 3D is

$$\bar{E} = 3N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)$$

To find the heat capacity:

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right)$$

so

$$\begin{aligned} c_V &= 3N\hbar\omega\left(-\frac{1}{(e^{\beta\hbar\omega} - 1)^2} e^{\beta\hbar\omega}\hbar\omega\right)\left(\frac{1}{kT^2}\right) \\ &= 3Nk\frac{\hbar^2\omega^2}{T^2}\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \end{aligned}$$

Einstein was smart and defined an "Einstein temperature" $\Theta_E \equiv \hbar\omega/k$ and using

$$\beta = \frac{1}{kT} \implies \beta\hbar\omega = \frac{\hbar\omega}{kT} = \frac{\Theta_E}{T}$$

so the heat capacity is (using $Nk = nR$)

$$c_V = 3nR\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}$$

Temperature limits

- High T limit: $\Theta_E \ll T$

  Using the approximation $e^x \approx 1 + x$ for $x \ll 1$ we have

  $$c_V = 3nR\left(\frac{\Theta_E}{T}\right)^2 \frac{1 + \Theta_E/T}{(\Theta_E/T)^2} = 3nR\left(1 + \frac{\Theta_E}{T}\right) = 3nR$$

  For most solids $\Theta_E \approx 300$ K, but for Carbon $\Theta_E \approx 1300$ K—since the frequency of $\omega = \sqrt{k/m}$ is high for low molecular weight.

- For a low temperature limit $\Theta_E \gg T$ and $\Theta_E/T \gg 1$ so

  $$c_V \to 3nR\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T} \to 0 \quad \text{as} \quad T \to 0$$

7.4 Maxwell velocity distribution

The average velocity of a distribution of particles in a box is

$$\overline{\mathbf{v}} = 0$$

For a simple molecule in a gas

$$\epsilon = \frac{p^2}{2m} + \epsilon_{\text{int}}$$

where we can ignore this constant internal energy due to rotation and vibration of a molecule. The probablity should also be proportional to the boltzmann factor

$$P(\mathbf{r}, \mathbf{p})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p} \propto e^{-\beta\frac{p^2}{2m}}\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p}$$

Since $\mathbf{v} = \mathbf{p}/m$ we have

$$\begin{aligned} f(\mathbf{r},\mathbf{v})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v} \equiv \quad & \text{mean \# of molecules in} \\ & \mathbf{r} \to \mathbf{r} + \mathrm{d}\mathbf{r} \;\text{ and }\; \mathbf{v} \to \mathbf{v} + \mathrm{d}\mathbf{v} \\ & \propto e^{-\beta \frac{mv^2}{2}}\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v} \end{aligned}$$

So we get

$$f(\mathbf{r},\mathbf{v})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v} = Ce^{-\beta \frac{mv^2}{2}}\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v}$$

where C is the normalization factor taken from integrating over all space

$$N = \int_{\mathbf{r}}\int_{\mathbf{v}} f(\mathbf{r},\mathbf{v})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v}$$

This function only depends on velocity because it does not matter where the particle is inside the box to get the velocity distribution so

$$\begin{aligned} N &= \int_{\mathbf{r}}\mathrm{d}^3\mathbf{r}\int_{\mathbf{v}} f(\mathbf{v})\,\mathrm{d}^3\mathbf{v} \\ &= VC\iiint_{-\infty}^{\infty} e^{-\beta \frac{mv^2}{2}}\,\mathrm{d}^3\mathbf{v} \quad v = \sqrt{v_x^2 + v_y^2 + v_z^2}, \quad \mathrm{d}^3\mathbf{v} = \mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z \end{aligned}$$

and using the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-ax^2}\,\mathrm{d}x = \sqrt{\frac{\pi}{a}}$$

we get the normalization factor

$$N = VC\left(\frac{2\pi}{\beta m}\right)^{3/2}$$

or

$$C = \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2}$$

Now that we are equipped with the normalization factor we can find the *Maxwell velocity distribution*

$$f(\mathbf{v})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v} = \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta \frac{mv^2}{2}}\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v}$$

Worksheet

1. IN a laser absorption experiment

$$\begin{aligned} V f(\mathbf{v})\,\mathrm{d}v_x &= \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta \frac{mv_x^2}{2}}\,\mathrm{d}v_x \int e^{-\beta \frac{mv^2}{2}}\,\mathrm{d}v_y\,\mathrm{d}v_z \\ &= N\left(\frac{\beta m}{2\pi}\right)^{3/2}\frac{2\pi}{\beta m} e^{-\beta \frac{mv_x^2}{2}}\,\mathrm{d}v_x \\ g(\mathbf{v})\,\mathrm{d}v_x &= N\left(\frac{\beta m}{2\pi}\right)^{1/2} e^{-\beta \frac{mv_x^2}{2}}\,\mathrm{d}v_x \end{aligned}$$

Maxwell velocity distribution cont'd

8 Equilibrium between Phases

vapor $\rightleftharpoons$ water $\rightleftharpoons$ ice

8.1 Isolated System

General Aspects :

- For an isolated system, at equilibrium, the entropy is maximized
- For multiple systems, we must consider the entire system's entropy as a maximized quantity.

Case 1: Isolated System

$$Q = \Delta\bar{E} + W$$
$$W = 0, Q = 0, \Delta\bar{E} = 0$$

For some fluctuation:

$$P(y) \propto \Omega(y) = e^{S(y)/k}, \quad \frac{P(y)}{P(\tilde{y})} = \frac{e^{S(y)/k}}{e^{S(\tilde{y})/k}} = e^{\Delta S/k}$$

where the relative prob is exponentially suppressed.

8.2 System in Contact with a Reservoir

Case 2: System is in contact with a reservoir at T

$$A' + A = A^{(0)}$$

where $S^{(0)}$ is maximized

$$\Delta S^{(0)} \geq 0 = \Delta S + \Delta S'$$

Heat transfer from the heat reservoir A' (which doesn't change in Tempertature) to the system A is

$$\Delta S' = -\frac{Q}{T_0}$$

In additiion, there is no work done on the system i.e. $Q = \Delta\bar{E}$ so

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0} = \frac{T_0\Delta S - \Delta\bar{E}}{T_0} = \frac{\Delta(T_0 S - \bar{E})}{T_0} = \frac{-F_0}{T_0}$$

where

$$F_0 = T_0 S - \bar{E}$$

is the Helmholtz free energy of system A as it has the same temperature of the reservoir. Furthermore,

$$\Delta F_0 \leq 0$$

So the equilibrium condition requires a minimized free energy!

8.3 System in Contact with Reservoir at Constant Temperature and Pressure

Review :

- Case I: Isolated system:

$$S\text{maximum} : \Delta S \geq 0$$

- Case II: Systme is contact with reservoir: Minimized 'Helmholtz' free energy at constant temperature

$$\bar{F}_0 = \bar{E} - T_0 S$$

- Case III: System in contact with reservoir at constant T_0, P_0

$$\begin{aligned} A^{(0)} &= A + A' \\ \implies \Delta S^{(0)} &= \Delta S + \Delta' \geq 0 \quad \Delta S' = -\frac{Q}{T_0} \end{aligned}$$

so the entropy of the system and reservoir must increase by

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0} = \frac{1}{T_0}(T_0 \Delta S - Q)$$

where

$$Q = \Delta \bar{E} + P_0 \Delta V$$

And doing some math movement, we find

$$\begin{aligned} &= \frac{1}{T_0}(T_0 \Delta S - (\Delta \bar{E} + P_0 \Delta V)) \\ &= \frac{1}{T_0}(\Delta(T_0 S - (\bar{E} + P_0 V))) \end{aligned}$$

or

$$\Delta S^{(0)} = -\frac{1}{T_0}\Delta G_0 \geq 0 \implies G_0 \leq 0$$

So the equilibrium contision is: "Gibbs free energy is minimized"

8.4 Stability of homogeneous substance

For the homogeneous substance, the Gibbs free energy is at a minimum

$$G_0 \equiv \bar{E} - T_0 S + P_0 V$$

and assume at equilibrium, subsystem A is at $\tilde{T}, \tilde{P}$.

Fix V and change T:

$$\left(\frac{\partial G_0}{\partial T}\right)_V = 0 \quad \text{for} \quad T = \tilde{T}$$

or using the definition

$$\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V - T_0 \left(\frac{\partial S}{\partial T}\right)_V = 0$$

where $TdS = d\bar{E}$ so

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V \frac{1}{T}$$

Therefore

$$\frac{\partial G_0}{\partial T}_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V \left(1 - \frac{T_0}{T}\right) = 0$$

or $\tilde{T} = T$ at equilibrium.

Looking at the second derivative

$$\begin{aligned}\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V &= \left(\frac{\partial^2 \bar{E}}{\partial T^2}\right)_V \left(1 - \frac{T_0}{T}\right) + \left(\frac{\partial \bar{E}}{\partial T}\right)_V \left(\frac{T_0}{T^2}\right) = 0 \\ &= \left(\frac{\partial \bar{E}}{\partial T}\right)_V \left(\frac{T_0}{T^2}\right) = 0\end{aligned}$$

where

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V \geq 0$$

Worksheet

1.
$$\left(\frac{\partial G_0}{\partial V}\right)_T = \left(\frac{\partial \bar{E}}{\partial V}\right)_T - T_0 \left(\frac{\partial S}{\partial V}\right)_T + P_0 = 0$$

and from the fundamental relation

$$T\frac{\partial S}{\partial V} = \frac{\partial \bar{E}}{\partial V} + \bar{P}$$

we have (using $T = T_0$)

$$\begin{aligned}\left(\frac{\partial G_0}{\partial V}\right)_T &= \frac{\partial \bar{E}}{\partial V} - \frac{T_0}{T}\left(\frac{\partial E}{\partial V} + \bar{P}\right) + P_0 = 0 \\ &= P_0 - \bar{P} = 0 \implies P_0 = \bar{P}\end{aligned}$$

2. For the stability condition; the second derivative of G_0 must be positive

$$\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T = \left(\frac{\partial^2 \bar{E}}{\partial V^2}\right)_T - T_0 \left(\frac{\partial^2 S}{\partial V^2}\right)_T + 0 \geq 0$$

and again

$$T\frac{\partial^2 S}{\partial V^2} = \frac{\partial^2 \bar{E}}{\partial V^2} + \frac{\partial \bar{P}}{\partial V}$$

so

$$\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T = -\left(\frac{\partial \bar{P}}{\partial V}\right) \geq 0 \implies \kappa = -\left(\frac{\partial \bar{P}}{\partial V}\right) \geq 0$$

where κ is the compressibility of the system.

8.4.1 Equilibrium between Phases

Consider a single component system consisting of two phases 1, 2, e.g., liquid & gas, liquid & solid.
For certain equilibrium, phases can co-exist; the G_0 must still be a minimum

- Assume:

$$\begin{aligned} n_1 &= \# \text{ of moles in phase 1} \\ n_2 &= \# \text{ of moles in phase 2} \\ g_1 &: \text{Gibbs free energy per more of phase 1} \\ g_2 &: \text{Gibbs free energy per more of phase 2} \end{aligned}$$

- At T, P

$$\begin{aligned} G &= n_1 g_1 + n_2 g_2 \quad n_1 + n_2 = n \\ G &= (n - n_2) g_1 + n_2 g_2 \end{aligned}$$

So at equilibrium G is a a minimum

$$\begin{aligned} dG &= -g_1 dn_2 + g_2 dn_2 \\ &= (g_2 - g_1) dn_2 = 0 \implies g_1(T,P) = g_2(T,P) \end{aligned}$$

or a phase equilibrium line on the $T - P$ diagram.
At a point B on the line,

$$g_1(T + dT, P + dP) = g_2(T + dT, P + dP)$$

or

$$dg_i = \left(\frac{\partial g_i}{\partial T}\right)_P dT + \left(\frac{\partial g_i}{\partial P}\right)_T dP$$

So using the fundamental relation (where the lower case is the per molar quantity)

$$dg = d(\epsilon - Ts + Pv) = -sdT + vdP$$

And at the equilibrium point B

$$dg_1 = dg_2 = \implies -s_1 dT + v_1 dP = -s_2 dT + v_2 dP$$

or rewritten as

$$(s_2 - s_1) dT = (v_2 - s_1) dP \implies \frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta s}{\Delta s}$$

We can see that dP/dT is the slope of the line on the $T - P$ diagram AKA the 'Clausius-Clapeyron equation'. Using the definition $\Delta S = Q/T$ or latent heat of transformation from phase 1 to phase 2, $L_{12} = T\Delta S$:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{Q}{T\Delta V} = \frac{L_{12}}{T\Delta V}$$

Simple Phase Transformation: Solid $\to$ Liquid:

- Entropy $\uparrow$ increases
- Absorb heat

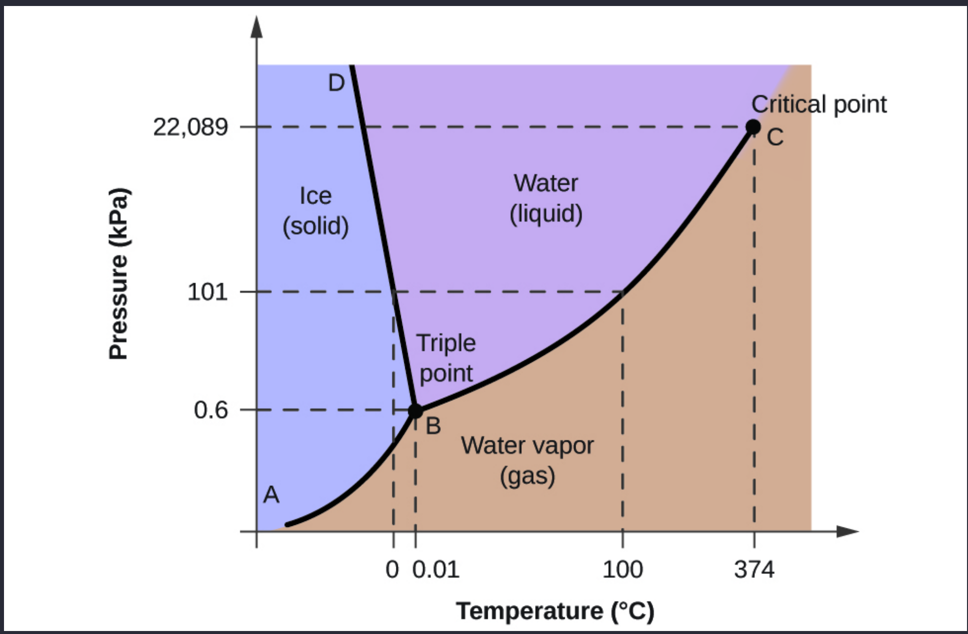

Figure 8.1: Phase diagram of water

Worksheet

- For a phase diagram similar to water, as melt from Solid to Liquid, the pressure decrease, so the material expands.
- Using the CC equation

$$dP = \frac{L_{12}}{T\Delta V} dT$$
$$\implies \Delta P = \int L_{12} \frac{dT}{T\Delta V} = \frac{L_{12}}{\Delta V} \ln \frac{T_2}{T_1}$$

As an ideal gas $pv = RT \implies v = RT/p$ so

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{pl_{12}}{RT^2}$$
$$\frac{1}{p} dp = \frac{l_{12}}{RT^2} dT$$

integrating both sides

$$\ln p = -\frac{l_{12}}{RT} + C$$

or

$$p = p_0 e^{-l_{12}/RT}$$

So pressure increases very very rapidly with T.

8.5 Chemical Equilibrium: systems with several components

E.g.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

"Chemical potential", systems with several components:

Consider a system with $\bar{E}, V$, m different kinds of components (e.g. molecules), and N_i number of each type:

$$S = S(E, V, N_1, N_2, \ldots, N_m)$$

The number N_i can change due to chemical reactions.

For general infinitesimal process

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_{j\neq i}} dN_i$$

where

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \frac{\partial S}{\partial V} = \frac{P}{T}$$

and a new quantity

$$\mu_i = -T\left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_{j\neq i}}$$

or the "chemical potential" per molecule of of the ith species. So we can rewrite to

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_i^m \frac{\mu_i}{T} dN_i$$

Other forms We can also express μ_i in different forms by moving stuff around:

$$dE = TdS - pdV + \sum_i \mu_i dN_i$$

or

$$\implies \mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

In terms of the Helmholtz free energy

$$F = E - TS \implies dF = d(E - TS)$$

or

$$\implies \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

And in terms of the Gibbs free energy

$$d(E - TS + pV) = dG$$

so

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

If there is only 1 species of a molecule then

$$G = G(T, p, N) = Ng'(T, p) \implies \mu = g'(T, p)$$

8.6 General conditions for chemical equilibrium

For m different molecules labels $B_1, B_2, \ldots, B_m$: e.g.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$
$$2H_2 + O_2 - 2H_2O = 0$$

and $b_1, b_2, \ldots, b_m$ are the stoichiometric coefficients so

$$\sum b_i B_i = 0$$

So for the water example $m = 3$:

$$B_1 = H_2, \quad B_2 = O_2, \quad B_3 = H_2O$$
$$b_1 = 2, \quad b_2 = 1, \quad b_3 = -2$$

For N_i number of B_i molecules

$$dN_i = \lambda b_i$$

where λ is a constant.

- For an isolated system, the entropy S is maximized

$$dS = 0$$
$$V = \text{constant} \implies dV = 0$$
$$\bar{E} = \text{constant} \implies dE = 0$$

so from the previous lecture

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dN_i \implies \sum \frac{\mu_i}{T}dN_i = 0$$

or

$$\sum_{i=1}^{m} \mu_i b_i = 0$$

So if we measure the μ_1, μ_2, μ_3 for the water example, we can determine the equilibrium condition

$$\sum b_i \mu_i = 0 = 2\mu_1 + \mu_2 - 2\mu_3$$

9 Quantum Statistics

9.1 Identical particles and symmetry

From Gibbs' paradox

$$Z == \frac{Z_1^N}{N!}$$

where we have indistinguishable particles.

- Classical particles: $A, B, C, \ldots$ where we have distinguishable particles
- Quantum particles: $A, A, A, \ldots$ which are indistinguishable...but we also have two types of quantum particles
  - Bosons: Integer spin, symmetric total wave function Ψ e.g. photons, gamma rays
  - Fermions: Half-integer spin, antisymmetric total wave function $\Psi \to$ pauli exclusion principle, e.g. electrons

Worksheet

1. Assume 2 partilces and each particle can be in one of three possible staes,

$$r = 1, 2, 3$$

(1) Maxwell-Boltzmann statistics (classical particle) total number of available states

$$\Omega = 3^2 = 9$$

(2) Bose-Einstein statistics (bosons) total number of available states

$$\Omega = 3 + 3 = 6$$

(3) Fermi-Dirac statistics (fermions) we take away the same states occupations

$$\Omega = 6 - 3 = 3$$

9.2 Formulation of quantum statistical problem

Consider a gas of particles in volume V at temperature T.

- ϵ_r: is the energy of a particle in state r
- n_r: # of particles in state r
- R: specify all possible states of the whole system

So the total energy of the system is

$$E_R = n_1\epsilon_1 + n_2\epsilon_2 + \cdots = \sum_r n_r\epsilon_r$$

where $\sum_r n_r = N$. The partition function is

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta \sum_r n_r \epsilon_r}$$

Since the probability of having $\{n_1, n_2, \ldots, n_r, \ldots\}$ state is

$$\frac{e^{-\beta E_R}}{Z}$$

for a state R, the mean number of particles in states S is

$$\bar{n}_S = \frac{\sum_R n_S e^{-\beta E_R}}{Z}$$

or

$$= \frac{1}{Z}\sum_R \left(-\frac{1}{\beta}\frac{\partial Z}{\partial \epsilon_S}\right)$$

- Bose-Einstein Statistics (BE)

$$\sum n_R = N$$

- Photon statistics: no restriction of particle number
- Fermi-Dirac Statistics (FD): for $n_r = 0, 1$

Using the mulitplication math thing

$$e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\dots)} = e^{-\beta n_s \epsilon_s} e^{-\beta n_1 \epsilon_1 + \dots}$$

where the second term doesn't have a n_s term. So the mean number of particles in state S is

$$\begin{aligned}
\bar{n}_S &= \frac{1}{Z} \sum_R n_S e^{-\beta E_R} \\
&= \frac{1}{Z} \sum_R n_S e^{-\beta n_s \epsilon_s} e^{-\beta n_1 \epsilon_1 + \dots} \\
&= \frac{\sum_R \left(n_s e^{-\beta n_s \epsilon_s} e^{-\beta n_1 \epsilon_1 + \dots}\right)}{\sum_R \left(e^{-\beta n_s \epsilon_s} e^{-\beta n_1 \epsilon_1 + \dots}\right)} \\
&= \frac{\sum_{n_s} \left(n_s e^{-\beta n_s \epsilon_s} \sum^{(S)}_{n_1, n_2, \dots} e^{-\beta n_1 \epsilon_1 + \dots}\right)}{\sum_{n_s} \left(e^{-\beta n_s \epsilon_s} \sum^{(S)}_{n_1, n_2, \dots} e^{-\beta n_1 \epsilon_1 + \dots}\right)}
\end{aligned}$$

Photon statistics No restriction on # of particles $\implies$ the sum $\sum_{n_1, n_2, \dots}$ is always infinite, so the second term cancels out

$$\bar{n}_S = \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s}}{\sum_{n_s} e^{-\beta n_s \epsilon_s}} - \frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln\left(\sum_{n_s=0}^{\infty} e^{-\beta n_s \epsilon_s}\right)$$

and using the geometric series

$$\begin{aligned}
&= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln \frac{1}{1 - e^{-\beta \epsilon_s}} \\
&= \frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln\left(1 - e^{-\beta \epsilon_s}\right) \\
&= \frac{1}{\beta} \frac{\beta e^{-\beta \epsilon_s}}{1 - e^{-\beta \epsilon_s}} \\
&= \frac{1}{e^{\beta \epsilon_s} - 1}
\end{aligned}$$

Fermi-Dirac statistics For $n_r = 0, 1$ (the easier one)

$$\begin{aligned}
\bar{n}_S &= \frac{0 + e^{-\beta \epsilon_s} Z_S(N-1)}{Z_S(N) + e^{-\beta \epsilon_S} Z_S(N-1)} \\
&= \frac{1}{\left(\frac{Z_S(N)}{Z_S(N-1)} e^{-\beta \epsilon_s} + 1\right)}
\end{aligned}$$

where the Z_S ommits the n_s term

$$Z_S(N) \equiv \sum^{(S)}_{n_1, n_2, \dots} e^{-\beta n_1 \epsilon_1 + \dots}$$

To relate $Z_S(N)$ and $Z_S(N-1)$ for large N:

$$\ln Z_S(N-1) = \ln Z_S(N) - \frac{\partial \ln Z_S(N)}{\partial N} \cdot 1$$

where the $\frac{\partial \ln Z_S(N)}{\partial N} = \alpha_S$ so

$$Z_S(N-1) = Z_S(N)e^{-\alpha_S}$$
$$\implies \frac{Z_S(N)}{Z_S(N-1)} = e^{\alpha_S}$$

ASSUMPTION: Since the sum of Z_S includes *many* states, α_S cannot does not depend too much on S, so we assume a constant

$$\alpha_S = \alpha = \frac{\partial \ln Z}{\partial N}$$

So the mean number of particles in state S is

$$\bar{n}_S = \frac{1}{e^{\alpha + \beta\epsilon_s} + 1}$$

Since we know the relation

$$F = -kT \ln Z \implies \frac{\partial F}{\partial N} = -kT\frac{\partial \ln Z}{\partial N} = \mu \implies \alpha = -\beta\mu$$

So we get the Fermi-Dirac distribution

$$\bar{n}_S = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}$$

Worksheet Bose-Einstein stats using

$$\frac{Z_S(N)}{Z_S(N-1)} = e^{\alpha}$$

The average number of particles in state S is

$$\bar{n}_S = \frac{0 + e^{-\beta\epsilon_s}Z_S(N-1) + 2e^{-\beta\epsilon_s}Z_S(N-2) + \dots}{Z_S(N) + e^{-\beta\epsilon_s}Z_S(N-1) + e^{-2\beta\epsilon_s}Z_S(N-2) + \dots}$$

taking out a $Z_S(N)$ term for each e.g.

$$e^{-\beta\epsilon_s}Z_S(N-1) = Z_S(N)\left(e^{-\beta\epsilon_s}\frac{Z_S(N-1)}{Z_S(N)}\right) = Z_S(N)e^{-\beta\epsilon_s}e^{-\alpha}$$

and for the next term

$$\begin{aligned}
e^{-2\beta\epsilon_s}Z_S(N-2) &= Z_S(N)e^{-2\beta\epsilon_s}\frac{Z_S(N-2)}{Z_S(N)} \\
&= Z_S(N)e^{-2\beta\epsilon_s}\frac{Z(N-2)}{Z(N-1)}e^{-\alpha} \\
&= Z_S(N)e^{-2\beta\epsilon_s}e^{-2\alpha}
\end{aligned}$$

So

$$\bar{n}_S = \frac{Z_S(N)\big(0 + e^{-\beta\epsilon_s}e^{-\alpha} + e^{-2\beta\epsilon_s}e^{-2\alpha} + \dots\big)}{Z_S(N)(1 + e^{-\beta\epsilon_s}e^{-\alpha} + e^{-2\beta\epsilon_s}e^{-2\alpha} + \dots)}$$

From last time

- Photon Statistics (Boson):

$$\bar{n}_s = \frac{1}{e^{\beta\epsilon_s} - 1}$$

- Bose-Einstein Statistics:

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1}$$

- Fermi-Dirac Statistics:

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}$$

Today: Partition function for quantum statistics...

$$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

where for BE and FD, $\sum n_r = N$

9.3 Photon statistics

$$\begin{aligned} Z &= \sum_{n_1, n_2, \dots} e^{-\beta n_1 \epsilon_1 + \dots} \\ &= \underbrace{\sum_{n_1=0}^{\infty} e^{-\beta n_1 \epsilon_1}}_{1 + e^{-\beta\epsilon_1} + e^{-2\beta\epsilon_1} + \dots} \sum_{n_2=0}^{\infty} e^{-\beta n_2 \epsilon_2} \dots \\ &= \frac{1}{1 - e^{-\beta\epsilon_1}} \frac{1}{1 - e^{-\beta\epsilon_2}} \dots \end{aligned}$$

So the log of the partition function is

$$\begin{aligned} \ln Z &= \sum_r \ln \frac{1}{1 - e^{-\beta\epsilon_r}} \\ &= -\sum_r \ln\left(1 - e^{-\beta\epsilon_r}\right) \end{aligned}$$

The mean number of particles in one state ϵ_S is

$$\begin{aligned} \bar{n}_S &= -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_S} \\ &= \frac{1}{\beta} \frac{-(-\beta) e^{-\beta\epsilon_S}}{1 - e^{-\beta\epsilon_S}} \\ &= \frac{e^{-\beta\epsilon_S}}{1 - e^{-\beta\epsilon_S}} \\ &= \frac{1}{e^{\beta\epsilon_S} - 1} \end{aligned}$$

9.4 Bose-Einstein statistics

The partition function for BE:

$$Z = \sum_R = e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

where $\sum_r n_r = N$ so $Z(N')$ has a rapidly increasing with N' which is a variable.

$Z(N')e^{-\alpha N'}$ has a sharp maximum, so if we choose α, this maximum happens at $N = N'$. First we define a Grand Partition function

$$\mathcal{Z} \equiv \sum_{N'} Z(N')e^{-\alpha N'}$$

so

$$\begin{aligned}
\mathcal{Z} &= \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)} e^{-\alpha(n_1 + n_2 + \dots)} \\
&= \sum_{n_1=0}^{\infty} e^{-\beta(n_1\epsilon_1) - \alpha n_1} \sum_{n_2=0}^{\infty} e^{-\beta(n_2\epsilon_2) - \alpha n_2} \dots \\
&= \frac{1}{1 - e^{-\beta\epsilon_1}e^{-\alpha}} \frac{1}{1 - e^{-\beta\epsilon_2}e^{-\alpha}} \dots
\end{aligned}$$

where

$$\ln \mathcal{Z} = -\sum_r \ln\left(1 - e^{-(\alpha + \beta e_r)}\right)$$

And using the taylor series approximation $\ln Z = \alpha N + \ln \mathcal{Z}$, and the maximum condition

$$\left.\frac{\partial \ln\left(Z(N')e^{-\alpha N'}\right)}{\partial N'}\right|_{N'=N} = 0$$

and

$$\frac{\partial}{\partial N} \ln Z - \alpha = 0 \implies \alpha = \alpha(N)$$

So we get

$$N + \frac{\partial \ln \mathcal{Z}}{\partial \alpha} = 0 \implies \frac{\partial \ln Z(N)}{\partial \alpha} = 0$$

Worksheet From BE

$$\ln(Z) = -\beta\mu N - \sum_R \ln\left(1 - e^{-\beta(\epsilon_r - \mu)}\right)$$

1. Determine $\bar{n}_S$ for BE

$$\begin{aligned}
\bar{n}_S &= \frac{1}{e^{\beta(\epsilon_S - \mu)} - 1} \\
&= \frac{1}{\beta} \frac{-\beta e^{-\beta(\epsilon_S - \mu)}}{1 - e^{-\beta(\epsilon_S - \mu)}} \\
&= \frac{e^{-\beta(\epsilon_S - \mu)}}{1 - e^{-\beta(\epsilon_S - \mu)}} \\
&= \frac{1}{e^{\beta(\epsilon_S - \mu)} - 1}
\end{aligned}$$

2. Partition function for Fermions (Fermi-Dirac statistics): Since each n_r can be 0 or 1, the partition function is

$$\begin{aligned}\mathcal{Z} &= \sum_{n_1=0}^{1} e^{-\beta n_1 \epsilon_1 - \alpha n_1} \sum_{n_2=0}^{1} e^{-\beta n_2 \epsilon_2 - \alpha n_2} \dots \\ &= \left(1 + e^{-\beta\epsilon_1 - \alpha}\right)\left(1 + e^{-\beta\epsilon_2 - \alpha}\right) \dots\end{aligned}$$

so

$$\ln \mathcal{Z} = \sum_r \ln\left(1 + e^{-\beta\epsilon_r - \alpha}\right)$$

Thus the partition function is

$$\begin{aligned}\ln Z &= \alpha N + \ln \mathcal{Z} \\ &= \alpha N + \sum_r \ln\left(1 + e^{-\beta\epsilon_r - \alpha}\right)\end{aligned}$$

1.

$$
\begin{aligned}
W(n) &= \sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2}\cdots\sum_{m=1}^{2} w_i w_j w_k \dots w_m \\
&= \sum_{i=1}^{2} w_i \sum_{j=1}^{2} w_j \sum_{k=1}^{2} w_k \cdots \sum_{m=1}^{2} w_m \\
&= (w_1 + w_2)(w_1 + w_2)(w_1 + w_2)\dots(w_1 + w_2) \\
&= (w_1 + w_2)^N
\end{aligned}
$$

since there are N factors from $i \to m$. Using binomial theorem:

$$
\begin{aligned}
(w_1 + w_2)^N &= \sum_{n=0}^{N} \binom{N}{n} w_1^n w_2^{N-n} \\
&= \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} w_1^n w_2^{N-n}
\end{aligned}
$$

where the term involving w_1^n is simply

$$
W(n) = \frac{N!}{n!(N-n)!} w_1^n w_2^{N-n}
$$

2. N_0 molecules in container of volume V_0. N molecules in subvolume V.

(a) Probability that any given molecule is in the subvolume V:

The probability of *one single* molecule being in the subvolume is $p = \frac{V}{V_0}$, and $q = 1 - p$ for the opposite case. Then for any given molecule, we use the binomial theorem:

$$P(n) = \frac{N_0!}{N!(N_0 - N)!}\left(\frac{V}{V_0}\right)^N \left(1 - \frac{V}{V_0}\right)^{N_0 - N}$$

(b) the mean # of molecules in V for a binomial distribution is simply [From Information Theory, Mackay eq 1.7]

$$\bar{N} = N_0 p = N_0 \frac{V}{V_0}$$

(c) The relative dispersion:

$$\begin{aligned}
\frac{\overline{(N - \bar{N})^2}}{\bar{N}^2} &= \frac{\overline{N^2 - 2N\bar{N} + \bar{N}^2}}{\bar{N}^2} \\
&= \frac{\overline{N^2} - 2\bar{N}^2 + \bar{N}^2}{\bar{N}^2} \\
&= \frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2}
\end{aligned}$$

where the top term is the variance/dispersion $\overline{N^2} - \bar{N}^2 = N_0 pq$, so

$$\begin{aligned}
&= \frac{N_0 pq}{\bar{N}^2} \\
&= \frac{N_0 \frac{V}{V_0}\left(1 - \frac{V}{V_0}\right)}{(N_0 \frac{V}{V_0})\bar{N}} \\
\text{relative dispersion} &= \frac{1 - \frac{V}{V_0}}{\bar{N}}
\end{aligned}$$

(d) When $V \ll V_0$, $\frac{V}{V_0} \approx 0$, so

$$\text{relative dispersion} \approx \frac{1}{\bar{N}} \to \infty$$

(e) When $V \to V_0$:

$$\begin{aligned}
\overline{(N - \bar{N})^2} &= N_0 pq \approx N_0 \frac{V_0}{V_0}\left(1 - \frac{V_0}{V_0}\right) \\
&= 0
\end{aligned}$$

which agrees with part (c) since

$$\text{relative dispersion} \to \frac{1 - \frac{V_0}{V_0}}{\bar{N}} = 0$$

3. N antennas with em radiation of wavelength λ and velocity c. Antennas are on the x-axis separated λ apart. Observer on x-axis measures intensity I from one antenna.

(a) Total intensity of all antennas:

All of the antennas are in phase, so the amplitudes add up i.e.

$$E_T = NE$$

and since intensity is proportional to the square of the amplitude $I \propto E^2$, the total intensity is

$$I_T = N^2 I$$

(b) For completely random phases (but same freq), the total amplitude as a vector is

$$E_T = \sum_{i=1}^{N} \mathbf{E}_i$$

so the mean square amplitude is [from Reif eq (1.9.9)]

$$\begin{aligned} \overline{E_T^2} &= \overline{\sum_{i=1}^{N} \mathbf{E}_i \cdot \sum_{j=1}^{N} \mathbf{E}_j} \\ &= \sum_{i=0}^{N} \overline{E^2} + \sum_{i \neq j} \sum \overline{\mathbf{E}_i \cdot \mathbf{E}_j} \\ &= NE^2 \end{aligned}$$

where the (second) cross terms add up to zero since the phases are random— there are just as many positive and negative values. So the mean intensity is

$$\bar{I}_T \propto \overline{E_T^2} = NI$$

4. N particles of spin 1/2. Magnetic moment μ which points parallel or antiparallel in an applied field H. Energy E in the field is then $E = -(n_1 - n_2)\mu H$ where n_1 is parallel and n_2 is antiparallel.

(a) In the energy range $[E, E + \delta E]$ the total # of states $\Omega(E)$ in the range:

A single particle can have spin $\pm\mu H$, so in the range of δE there are $\delta E/2\mu H$ different states. So the total number of states for a large number N is

$$\Omega(E) = \binom{N}{n_1}\frac{\delta E}{2\mu H} = \frac{N!}{n_1!n_2!}\frac{\delta E}{2\mu H}$$

And using $n_1 + n_2 = N$ or $n_2 = N - n_1$ and $n_1 = N - n_2$ we can get

$$\begin{aligned} E &= -(n_1 - n_2)\mu H \\ \frac{E}{\mu H} &= -(n_1 - (N - n_1)) = -2n_1 + N \\ \implies n_1 &= \frac{1}{2}\left(N - \frac{E}{\mu H}\right), \quad n_2 = \frac{1}{2}\left(N + \frac{E}{\mu H}\right) \end{aligned}$$

So the total number of states is

$$\Omega(E) = \frac{N!}{\left[\frac{1}{2}\left(N - \frac{E}{\mu H}\right)\right]!\left[\frac{1}{2}\left(N + \frac{E}{\mu H}\right)\right]!}\frac{\delta E}{2\mu H}$$

(b) Using Stirling's approximation ($\ln N! \approx N\ln N - N$):

$$\ln\Omega(E) \approx N\ln N - N - [n_1\ln n_1 - n_1] - [n_2\ln n_2 - n_2] + \ln\frac{\delta E}{2\mu H}$$

simplifying some terms:

$$\begin{aligned} -[n_1\ln n_1 - n_1] - [n_2\ln n_2 - n_2] &= -n_1\ln n_1 - n_2\ln n_1 + n_1 + n_2 \\ \text{where} \quad n_1 + n_2 &= \frac{1}{2}\left(N - \frac{E}{\mu H}\right) + \frac{1}{2}\left(N + \frac{E}{\mu H}\right) = N \end{aligned}$$

so we can cancel out a term:

$$\ln\Omega(E) = N\ln N - n_1\ln n_1 - n_2\ln n_2 + \ln\frac{\delta E}{2\mu H}$$

(c) A Gaussian approximation to part (a): From (a)

$$\begin{aligned} \Omega(E) &= \frac{N!}{n_1!n_2!}\frac{\delta E}{2\mu H} \\ &= \frac{N!}{n_1!(N - n_1)!}\frac{\delta E}{2\mu H} \\ &= W(n_1)\frac{\delta E}{2\mu H}, \qquad W(n_1) = \frac{N!}{n_1!(N - n_1)!} \end{aligned}$$

Using $n_1 \equiv \bar{n}_1 + \xi$ the Taylor expansion gives [From lecture notes...]

$$\begin{aligned} \ln W(n_1) &\approx \ln W(\bar{n}_1) + \frac{1}{2}B_2\xi^2 \\ \implies W(n_1) &= W(\bar{n}_1)e^{-\frac{1}{2}B_2\xi^2} \end{aligned}$$

where

$$\begin{aligned} B_2 &= \frac{1}{Npq} \quad \text{using} \quad p = \frac{1}{2},\ q = \frac{1}{2} \\ B_2 &= \frac{4}{N} \end{aligned}$$

and using $\bar{n}_1 = N/2$

$$\xi = n_1 - \bar{n}_1 = \frac{1}{2}\left(N - \frac{E}{\mu H}\right) - \frac{N}{2}$$
$$\implies \xi^2 = \left(\frac{E}{2\mu H}\right)^2$$

To find $W(\bar{n}_1)$ we must satisfy the normalization condtion: the integral of $W(n_1)$ over all n_1 must equal the total number of possible spins 2^N (like N coin flips) i.e.

$$\int_{-\infty}^{\infty} W(n_1)\,\mathrm{d}n_1 = 2^N$$
$$\int_{-\infty}^{\infty} W(\bar{n}_1)e^{-\frac{1}{2}B_2\xi^2}\,\mathrm{d}n_1 = 2^N$$

and since [From Randy Harris Modern Physics Front Page]

$$\int_{-\infty}^{\infty} e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$
$$\implies W(\bar{n}_1) = \frac{2^N}{\sqrt{2\pi/B_2}} = \frac{2^N}{\sqrt{\pi N/2}}$$

So the Gaussian approximation is

$$W(n_1) = \frac{2^N}{\sqrt{\pi N/2}}e^{-\frac{1}{2}B_2\xi^2}$$
$$= \frac{2^N}{\sqrt{\frac{\pi N}{2}}}e^{-\frac{2}{N}\left(\frac{E}{2\mu H}\right)^2}$$

Finally, we get the total number of states from $\Omega(E) = W(n_1)\frac{\delta E}{2\mu H}$:

$$\boxed{\Omega(E) = \frac{2^N}{\sqrt{\frac{\pi N}{2}}}e^{-\frac{2}{N}\left(\frac{E}{2\mu H}\right)^2}\frac{\delta E}{2\mu H}}$$

5. $Adx + Bdy \equiv dF$

(a) Show that $\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}$:
Since dF is an exact differential

$$\frac{\partial F}{\partial x} = A, \quad \frac{\partial F}{\partial y} = B$$

so

$$\frac{\partial A}{\partial y} = \frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right) = \frac{\partial B}{\partial x}$$

(b) Show that $\int dF$ on any closed path in xy plane is zero:
For an exact differential

$$\int_a^b dF = F(b) - F(a)$$

so for a closed path $a \to b$ then back $b \to a$:

$$\int_a^b dF + \int_b^a dF = F(b) - F(a) + F(a) - F(b) = 0$$

6. From $A \to B$ the mean pressure is

$$\bar{p} = \alpha V^{-5/3}$$

(a) Work done when system expanded to final volume, heat added to maintain pressure ($V = 1 \to 8$), $\bar{p} = 32$. Heat extracted to reduce pressure to 10^6 dynes cm^{-2}:

First finding α at macrostate B:

$$\alpha = \bar{p}V^{5/3} = 1 * 8^{5/3} = 32$$

so the work done is

$$\begin{aligned} W_a = \int đW &= \int_{V_i}^{V_f} \bar{p}\,\mathrm{d}V \\ &= 32V\Big|_1^8 \\ &= 224 \times 10^9\,\text{dynes cm} \end{aligned}$$

From wikipedia, 1 dynes $= 10^{-5}$ N, so the units of work is

$$10^6\,\text{dynes cm}^{-2} \times 10^3\,\text{cm}^3 = 10^9\,\text{dynes cm} * \frac{10^{-5}\,\text{N}}{1\,\text{dynes}} * \frac{1\,\text{m}}{10^2\,\text{cm}} = 100\,\text{J}$$

so

$$W_a = 22\,400\,\text{J}$$

To find the net heat absorbed we use the first law of thermodynamics:

$$\Delta E = Q - W \implies Q = \Delta E + W$$

where from macro state A to B

$$\begin{aligned} \Delta E = \int dE &= -\int \bar{p}\,\mathrm{d}V \\ &= -32\int_1^8 V^{-5/3}\,\mathrm{d}V \\ &= 32\frac{3}{2}V^{-2/3}\Big|_1^8 \\ &= 48(8^{-2/3} - 1) \\ &= -36 \times 10^9\,\text{dynes cm} = -3600\,\text{J} \end{aligned}$$

Finally the net heat absorbed is

$$Q = \Delta E + W = -3600\,\text{J} + 22\,400\,\text{J} = 18\,800\,\text{J}$$

(b) Volume increase and heat added to cause linear decrease in pressure:

New pressure equation is in the form $p = mV + b$, where the slope $m = \frac{-31}{7}$ and the intercept is at

$$32 = \frac{-31}{7} + b \implies b = \frac{255}{7}$$

thus

$$p = \frac{-31}{7}V + \frac{255}{7}$$

The work done is

$$W_b = \int_1^8 p\,\mathrm{d}V = \int_1^8 \left(\frac{-31}{7}V + \frac{255}{7}\right)\mathrm{d}V$$
$$= -\frac{31}{14}V^2 + \frac{255}{7}V\Big|_1^8$$
$$= 11\,550\,\mathrm{J}$$

and using the energy change found in part (a)

$$Q = \Delta E + W = -3600\,\mathrm{J} + 11\,550\,\mathrm{J} = 7950\,\mathrm{J}$$

(c) Part (a) but in reverse:

First the pressure is reduced to 1×10^6 dynes/cm^2, then expanding the volume from $V = 1 \to 8$ amounts to work

$$W_c = \int_1^8 p\,\mathrm{d}V = \int_1^8 1\,\mathrm{d}V$$
$$= 700\,\mathrm{J}$$

and the net heat absorbed is

$$Q = \Delta E + W = -3600\,\mathrm{J} + 700\,\mathrm{J} = -2900\,\mathrm{J}$$

7. 3D particle in a box with energy level

$$E = \frac{\hbar^2}{2m}\pi^2\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

(a) Force by particle on wall perpendicular to x axis:

$$đW = -dE = -\frac{\partial E}{\partial L_x}\,\mathrm{d}L_x = F_x\,\mathrm{d}L_x$$

where F_x is the generalized force on the wall perpendicular to the x axis. This holds true as long as $đQ = 0$.

(b) Pressure on the wall, and the mean pressure:

The unit area for the pressure on the wall perpendicular to the x axis is $a = L_yL_z$, so the pressure is

$$p_x = \frac{F_x}{a} = -\frac{1}{L_yL_z}\frac{\partial E}{\partial L_x}$$

where

$$\frac{\partial E}{\partial L_x} = \frac{\hbar^2}{2m}\pi^2 n_x^2 \frac{\partial}{\partial L_x}\left(\frac{1}{L_x^2}\right) = -\frac{\hbar^2}{m}\pi^2\frac{n_x^2}{L_x^3}$$

so

$$p_x = \frac{\hbar^2}{mV}\pi^2\frac{n_x^2}{L_x^2}$$

where $V = L_xL_yL_z$ is the volume. The mean pressure is then

$$\bar{p} = \frac{\hbar^2}{mV}\pi^2\overline{\frac{n_x^2}{L_x^2}}$$

Since $\overline{n_x^2} = \overline{n_y^2} = \overline{n_z^2}$ and $L_x = L_y = L_z$ by *symmetry* we can rewrite the mean energy as

$$\bar{E} = \frac{\hbar^2}{2m}\pi^2\left(\overline{\frac{n_x^2}{L_x^2}} + \overline{\frac{n_y^2}{L_y^2}} + \overline{\frac{n_z^2}{L_z^2}}\right) = \frac{\hbar^2}{2m}\pi^2\left(\overline{\frac{3n_x^2}{L_x^2}}\right)$$

$$\implies \frac{2}{3}\bar{E} = \frac{\hbar^2}{m}\pi^2\overline{\frac{n_x^2}{L_x^2}}$$

Thus we can substitute $\bar{E}$ into the mean pressure equation:

$$\bar{p} = \frac{2}{3}\frac{\bar{E}}{V}$$

8.

(a) yes

(b) I will try... should I reference equations from the main textbook as well?

1.

(a) Given

$$\Omega(E, E+\delta E) = \frac{N!}{(N/2 - E/(2\mu H))!(N/2 + E/(2\mu H))!}\frac{\delta E}{2\mu H}$$

and using $\beta = \frac{\partial \ln \Omega}{\partial E}$ & stirling approx $\ln N! = N\ln N - N$, so taking the log of the DoS:

$$\begin{aligned}
\ln\Omega(E) &= \ln N! - \ln(N/2 - E/(2\mu H))! - \ln(N/2 + E/(2\mu H))! + \ln\frac{\delta E}{2\mu H} \\
&= \ln N! - (N/2 - E/(2\mu H))\ln(N/2 - E/(2\mu H)) + (N/2 - \cancel{E/(2\mu H)}) \\
&\quad - (N/2 + E/(2\mu H))\ln(N/2 + E/(2\mu H)) + (N/2 + \cancel{E/(2\mu H)}) + \ln\frac{\delta E}{2\mu H} \\
&= \ln N! + N - (N/2 - E/(2\mu H))\ln(N/2 - E/(2\mu H)) \\
&\quad - (N/2 + E/(2\mu H))\ln(N/2 + E/(2\mu H)) + \ln\frac{\delta E}{2\mu H}
\end{aligned}$$

Finally taking the partial derivative

$$\begin{aligned}
\frac{\partial \ln\Omega}{\partial E} &= \frac{1}{2\mu H}\ln(N/2 - E/(2\mu H)) - \cancel{\frac{N/2 - E/(2\mu H)}{N/2 - E/(2\mu H)}}\left(-\frac{1}{2\mu H}\right) \\
&\quad - \frac{1}{2\mu H}\ln(N/2 + E/(2\mu H)) - \frac{1}{2\mu H} \\
\beta &= \frac{1}{2\mu H}\left[\ln(N/2 - E/(2\mu H)) - \ln(N/2 + E/(2\mu H))\right] \\
&= \frac{1}{2\mu H}\ln\left(\frac{N/2 - E/(2\mu H)}{N/2 + E/(2\mu H)}\right) \\
&= \frac{1}{2\mu H}\ln\left(\frac{N/2}{N/2}\frac{1 - E/(N\mu H)}{1 + E/(N\mu H)}\right) \\
&= \frac{1}{2\mu H}\ln\left(\frac{1 - E/(N\mu H)}{1 + E/(N\mu H)}\right)
\end{aligned}$$

or using the inverse hyperbolic tangent

$$\operatorname{arctanh}(x) = \frac{1}{2}\ln\left(\frac{1+x}{1-x}\right)$$

So we set $x = -E/(N\mu H)$

$$\beta = \frac{1}{\mu H}\operatorname{arctanh}(-E/(N\mu H))$$

Thus using $\beta = 1/kT$ and the odd function $\tanh(-x) = -\tanh(x)$

$$\begin{aligned}
\frac{\mu H}{kT} &= \operatorname{arctanh}(-\frac{E}{N\mu H}) \\
\implies \tanh\left(\frac{\mu H}{kT}\right) &= -\frac{E}{N\mu H}
\end{aligned}$$

and finally

$$\boxed{E = -N\mu H\tanh\left(\frac{\mu H}{kT}\right)}$$

(b) For $T = -T_0 < 0$ the sign of the hyperbolic tangent is negative

$$E = -N\mu H \tanh\left(-\frac{\mu H}{kT_0}\right) = N\mu H \tanh\left(\frac{\mu H}{kT_0}\right)$$

$\implies \boxed{E > 0}$

(c) The total magnetic moment is proportional to the difference of parallel and antiparallel spins

$$M = \mu(n_1 - n_2) = \mu(n_1 - (N - n_1)) = \mu(2n_1 - N)$$

and from the previous HW 1 we know that

$$n_1 = \frac{1}{2}\left(N - \frac{E}{\mu H}\right)$$

thus

$$M = \mu\left[(N - \frac{E}{\mu H}) - N\right] = -\frac{E}{H}$$

and therefore

$$\boxed{M(H,T) = N\mu \tanh\left(\frac{\mu H}{kT}\right)}$$

2.

(a) Once again the numnber of ways is

$$\Omega(N, n_+) = \frac{N!}{n_+!(N-n_+)!}$$

And the total length is

$$\ell = (n_+ - n_-)d = (2n_+ - N)d \implies n_+ = \frac{1}{2}(N + \ell/d)$$

so

$$\boxed{\Omega(\ell) = \frac{N!}{\left[\frac{1}{2}(N+\ell/d)\right]!\left[\frac{1}{2}(N-\ell/d)\right]!}}$$

(b) And using

$$x = \frac{\ell}{Nd} \implies \ell = xNd$$

we can equate the two expressions above:

$$xNd = (2n_+ - N)d \implies xN = 2n_+ - N \implies n_+ = \frac{N}{2}(1+x)$$

So

$$\Omega = \frac{N!}{\frac{N}{2}(1+x)!(N - \frac{N}{2}(1+x))!} = \frac{N!}{\left[\frac{N}{2}(1+x)\right]!\left[\frac{N}{2}(1-x)\right]!}$$

and using stirling's approximation

$$\begin{aligned}
\ln\Omega = N\ln N - \cancel{N} &- \frac{N}{2}(1+x)\ln\left(\frac{N}{2}(1+x)\right) + \cancel{\frac{N}{2}(1+x)} \\
&- \frac{N}{2}(1-x)\ln\left(\frac{N}{2}(1-x)\right) + \cancel{\frac{N}{2}(1-x)} \\
= N\ln N &- \frac{N}{2}(1+x)\ln\left(\frac{N}{2}(1+x)\right) - \frac{N}{2}(1-x)\ln\left(\frac{N}{2}(1-x)\right)
\end{aligned}$$

and from

$$\begin{aligned}
-\left(\frac{\partial S}{\partial \ell}\right)_E &= -k\left(\frac{\partial \ln\Omega}{\partial \ell}\right)_E \\
&\implies S = k\ln\Omega
\end{aligned}$$

or

$$\boxed{S = k\left[N\ln N - \frac{N}{2}(1+x)\ln\left(\frac{N}{2}(1+x)\right) - \frac{N}{2}(1-x)\ln\left(\frac{N}{2}(1-x)\right)\right]}$$

(c) Using

$$\frac{\partial S}{\partial \ell} = \frac{S}{\partial x}\frac{\partial x}{\partial \ell} = \frac{\partial S}{\partial x}\frac{1}{Nd}$$

So the force relation is

$$\begin{aligned}
\frac{F}{T} &= -\frac{\partial S}{\partial \ell} = -\frac{\partial S}{\partial x}\frac{\partial x}{\partial \ell} \\
&= -k\Big(0 - \frac{N}{2}\left[\ln\left(\frac{N}{2}(1+x)\right) + \cancel{\frac{1+x}{1+x}\frac{2}{N}}\right] \\
&\qquad - \frac{N}{2}\left[-\ln\left(\frac{N}{2}(1-x)\right) + \cancel{\frac{1-x}{1-x}\frac{2}{N}(-1)}\right]\Big)\frac{\partial x}{\partial \ell} \\
&= k\frac{N}{2}\left(\ln\frac{1+x}{1-x}\right)\frac{\partial x}{\partial \ell}
\end{aligned}$$

and since for small x we can Taylor expand (or see graphically)

$$\ln(1+x) \approx x \quad \ln(1-x) \approx -x \implies \ln\frac{1+x}{1-x} \approx 2x$$

So

$$\frac{F}{T} = \frac{kN}{2}(2x)\frac{1}{Nd} = \frac{kx}{d}$$

and finally $x = \ell/(Nd)$ thus

$$\boxed{F \approx \frac{kT\ell}{Nd^2}}$$

3. From the 2nd law of thermodynamics the total entropy S_T of the thermally isolated system must increase i.e.

$$\Delta S_T = \Delta S + \Delta S' \geq 0$$

and since system A absorbs heat Q from system A' the change in entropy of system A' is

$$\Delta S' = -\frac{Q}{T'}$$

thus

$$\Delta S + \Delta S' = \Delta S - \frac{Q}{T'} \geq 0$$

which implies

$$\boxed{\Delta S \geq \frac{Q}{T'}}$$

4. A glass bulb with air at room temp and 1 atm is placed in to a chamber with helium at 1 atm. Since the glass bulb is only permeable to helium, so over time, the pressure of helium outside the bulb will have to equal the partial pressure of helium inside the bulb. Thus the final pressure inside the bulb after equilibrium is

$$\boxed{P_0 + P_{\text{Helium out}} = 2\,\text{atm}}$$

5. $m_c = 750$ g copper calorimeter can contains $m_w = 200$ g of water in equilibrium at $T_i = 293$ K. $m_{\text{ice}} = 30$ g of ice at $T_{\text{ice}} = 273$ K is placed in the calorimeter and enclosed in a heat-insulating shield.

(a) Given

$$c_w = 4.18\,\text{J/gK} \quad c_c = 0.418\,\text{J/gk}$$

After the ice melts and reaches equilibrium the final temperature of the water and calorimeter must be equal

$$\begin{aligned}\Delta Q &= Q_{ice} + Q_{\text{melted ice}} + Q_{water} + Q_{copper} = 0\\ &= m_{\text{ice}}L_f + m_{\text{ice}}c_w(T_f - T_{\text{ice}}) + m_w c_w(T_f - T_i) + m_c c_c(T_f - T_i)\\ &= 30\,\text{g} \times 333\,\text{J/g} + 30\,\text{g} \times 4.18\,\text{J/gK}(T_f - 273\,\text{K})\\ &+ 200\,\text{g} \times 4.18\,\text{J/gK}(T_f - 293\,\text{K}) + 750\,\text{g} \times 0.418\,\text{J/gK}(T_f - 293\,\text{K})\\ &= 9990 + 125.4(T_f - 273) + 836(T_f - 293) + 313.5(T_f - 293)\\ \implies T_f &= 283\,\text{K}\end{aligned}$$

(b) The total entropy for ice melting at $T = 273$ K is

$$\Delta S_{\text{ice}} = \frac{Q_{\text{ice}}}{T_{\text{ice}}} = \frac{m_{\text{ice}}L_f}{T_{\text{ice}}}$$

and for three other processes

$$\Delta S_a = \int_{T_0}^{T_f} \frac{m_a c_a}{T} dT = mc \ln \frac{T_f}{T_i}$$

so

$$\begin{aligned}\Delta S &= \frac{m_{\text{ice}}L_f}{273} + m_{\text{ice}}c_w \ln \frac{283}{273} + m_w c_w \ln \frac{283}{293} + m_c c_c \ln \frac{283}{293}\\ \Delta S &= 1.19\,\text{J/K}\end{aligned}$$

(c) The work required to bring the water back to $T_i = 293$ K i.e. $\Delta T = T_f - T_i = 293 - 283 = 10$ K

$$\begin{aligned}W &= \Delta Q\\ &= (m_w + m_i)c_w(T_f - T_i) + m_c c_c(T_f - T_i)\\ &= 230(4.18)10 + 750(0.418)10\\ W &= 12\,749\,\text{J}\end{aligned}$$

1. For an idea gas in *two dimensions* confined to an area A, determine the multiplicity $\Omega(E)$: For a 2D particle in a box,

$$E = \frac{p}{2m} = \frac{\hbar^2 k^2}{2m}$$
$$\implies k = \sqrt{\frac{2mE}{\hbar^2}}, \quad dE = \frac{\hbar^2 k dk}{m} \quad \text{or} \quad dk = \frac{m}{\hbar^2 k} dE$$

In $k-$space, the area of a microstate is

$$k_x k_y = \frac{\pi^2}{L^2} = \frac{\pi^2}{A}$$

In the range $k \to k + dk$ the area of the peel is a quarter of the circles circumference times the width of the peel dk:

$$\frac{1}{4}(2\pi k)dk = \frac{\pi k dk}{2}$$

So the multiplicity is

$$\Omega(k)dk = \frac{1}{2}\frac{\pi k dk}{\pi^2/A} = \frac{A}{2\pi} k dk$$
$$\Omega(E)dE = \frac{A}{2\pi}(k)\frac{m}{\hbar^2 k} dE = A\frac{m}{2\pi\hbar^2} dE$$
$$\implies \Omega(E) = A\frac{m}{2\pi\hbar^2}$$

so for N particles we have to care for $N!$ permutations:

$$\boxed{\Omega(E) = \frac{A^N}{N!}\left(\frac{m}{2\pi\hbar^2}\right)^N}$$

2. van der Waals gas

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{1}$$

where $v \equiv V/n$ is the molar volume.

(a) The constant a as units pressure times molar volume squared which captures the long range attractions, or the positive pressure that keep the molecules together. The constant b has units V/n, or molar volume, which expressess the occupied volume of the molecules.

(b) Molar energy (energy of one mol of gas) dependent on volume: To find the dependence of molar energy to volume we start from the first law of thermodynamics

$$dE = TdS - pdV \to \frac{dE}{dV} = T\frac{dS}{dV} - p$$

where we can apply the Maxwell relation

$$\frac{\partial S}{\partial V} = \frac{\partial p}{\partial T}$$

so

$$\frac{dE}{dV} = T\frac{\partial p}{\partial T} - p$$

We can differentiate (1) by $\frac{\mathrm{d}}{\mathrm{d}T}$:

$$(v - b)\frac{dp}{dT} = R \implies \frac{\partial p}{\partial T} = \frac{R}{v - b}$$

Thus

$$\frac{dE}{dV} = T\frac{R}{v - b} - p$$

solving (1) for p

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

and substituting back into the energy equation

$$\begin{aligned}\frac{dE}{dV} &= T\frac{R}{v - b} - \left(\frac{RT}{v - b} - \frac{a}{v^2}\right)\\ &= \boxed{\frac{a}{v^2}}\end{aligned}$$

(c) Show that molar heat capacity is independent of volume: Starting with the relation

$$c_V = \left(\frac{\text{đ}Q}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

and differentiating with respect to volume (with T constant)

$$\begin{aligned}\left(\frac{\partial c_V}{\partial V}\right)_T &= T\left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)\right]\\ &= T\left[\frac{\partial}{\partial T}\frac{\partial S}{\partial V}\right]_V \quad \text{using} \quad \frac{\partial S}{\partial V} = \frac{\partial p}{\partial T}\\ &= T\frac{\partial^2 p}{\partial T^2} = 0\end{aligned}$$

using what we found for p in part (b), So c_V is independent of volume.

(d) Taking temp T and volume v as independent parameters, determine dS in terms of dv and dT:

$$s = s(v, T)$$

so the differential is

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

So using the Maxwell relation and molar heat capacity equations

$$\frac{\partial s}{\partial T} = \frac{c_V}{T} \quad \text{and} \quad \frac{\partial s}{\partial v} = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{v-b}$$

We get

$$\boxed{ds = \frac{c_V}{T}dT + \frac{R}{v-b}dv}$$

3.

(a) Using the ideal gas law for the molar volume $pV = vRT$

$$
\begin{aligned}
p_i V_i^{\gamma} &= p_f V_f^{\gamma} \\
\frac{vRT_i}{V_i} V_i^{\gamma} &= \frac{vRT_f}{V_f} V_f^{\gamma} \\
T_i V_i^{\gamma-1} &= T_f V_f^{\gamma-1}
\end{aligned}
$$

so

$$
\implies \boxed{T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1}}
$$

(b) With constant entropy $\Delta S = 0$:

$$
\begin{aligned}
\Delta S(T, V; v) = v\left(\int_{T_i}^{T_f} \frac{đQ}{T}\right) &= v\left(\int_{T_i}^{T_f} c_V \frac{dT}{T} + \int_{V_i}^{V_f} \frac{R}{V} dV\right) = 0 \\
&= vc_V \ln\left(\frac{T_f}{T_i}\right) + vR\ln\left(\frac{V_f}{V_i}\right) = 0 \\
\implies 0 &= \ln\left[\frac{T_f}{T_i}\left(\frac{V_f}{V_i}\right)^{R/c_V}\right]
\end{aligned}
$$

where $R = c_P - c_V$ so

$$
\frac{R}{c_V} = \frac{c_P - c_V}{c_V} = \gamma - 1
$$

Exponentiating both sides and using the result above:

$$
e^0 = \frac{T_f}{T_i}\left(\frac{V_f}{V_i}\right)^{\gamma-1} \implies \boxed{T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1}}
$$

4. Molar specifc heat at constant volume for a monoatomic ideal gas $c_V = \frac{3}{2}R$. One mole $n = 1$ of gas is subjected to a cyclic quasi-static process:

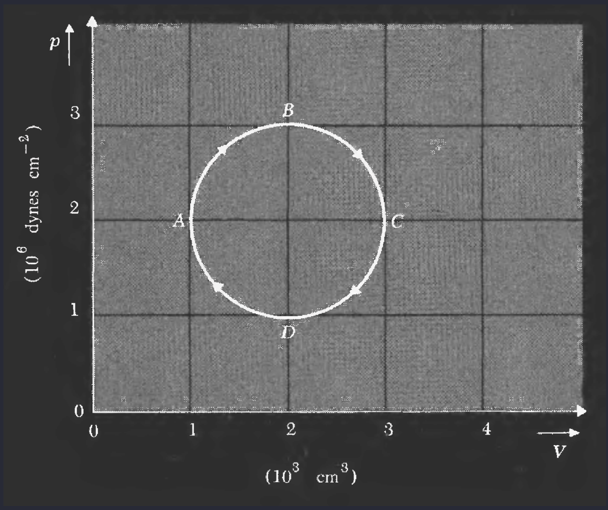

Figure 3.1: Cyclic process pV diagram

(a) The net work in one cycle is the area enclosed by the cycle in the pV diagram i.e. the area of the ellipse $A = \pi pV$:

$$\begin{aligned}W &= \int pdV = \pi \cdot 10^6 \,\text{dynes}\,\text{cm}^{-2} \times 10^3 \,\text{cm}^3 \\ &= \pi \cdot 10^9 \,\text{dyne}\,\text{cm} \times \frac{10^{-7}\,\text{J}}{\text{dyne}\,\text{cm}} \\ &\approx \boxed{314\,\text{J}}\end{aligned}$$

(b) The internal energy difference between state C and A:

$$\begin{aligned}\Delta U &= c_V \delta T \quad \text{using} \quad PV = nRT \implies T = \frac{PV}{R} \\ &= \frac{3}{2}R\left(\frac{P_C V_C}{R} - \frac{P_A V_A}{R}\right) \\ &= \frac{3}{2}(P_C V_C - P_A V_A) \quad P_C = P_A = 2 \times 10^6 \,\text{dynes}\,\text{cm}^{-2} \\ &= \frac{3}{2}(3-1) \times 10^9 \,\text{dyne}\,\text{cm} \\ &= 6 \times 10^9 \,\text{dyne}\,\text{cm} \times \frac{10^{-7}\,\text{J}}{\text{dyne}\,\text{cm}} \\ &\approx \boxed{600\,\text{J}}\end{aligned}$$

(c) The heat absorbed by gas going from A to C via path ABC:

The change in internal energy is the same as (b) and the work done is the area under the curve i.e. semicircle + rectangle area:

$$\begin{aligned}Q &= \Delta U + W \\ &= 600\,\text{J} + [A_{\text{rect}} + A_{\text{semicircle}}] \\ &= 600\,\text{J} + (2 \cdot 210^9 \,\text{dynes}\,\text{cm}) + \frac{1}{2}314\,\text{J} \\ &= 600\,\text{J} + 400\,\text{J} + 157\,\text{J} \\ &= \boxed{1157\,\text{J}}\end{aligned}$$

5. The piston is in equilibrium with the force of gravity + the force due to the atmosphere:

$$F = pA - p_0 A - mg = 0 \implies p = p_0 + \frac{mg}{A}$$

and at equilibrium we can use the adiabatic equation of state $pV^\gamma = \text{constant}$:

$$pV^\gamma = \Big(p_0 + \frac{mg}{A}\Big)V_0^\gamma = \text{constant}$$

where $V = Ax$ for the piston moving in the x direction. So we can rewrite Newton's 2nd law as

$$\begin{aligned} m\ddot{x} &= \frac{1}{x^\gamma}\Big(p_0 + \frac{mg}{A}\Big)\Big(\frac{V_0}{A}\Big)^\gamma A - mg - p_0 A \\ &= \frac{1}{x^\gamma}\Big(p_0 + \frac{mg}{A}\Big)\Big(\frac{V_0}{A}\Big)^\gamma A - \Big(p_0 + \frac{mg}{A}\Big)A \\ &= \Big(p_0 + \frac{mg}{A}\Big)A\Big[\frac{1}{x^\gamma}\Big(\frac{V_0}{A}\Big)^\gamma - 1\Big] \end{aligned}$$

and approximating small $x = x_0 + \delta x = x_0 + \epsilon$ near equilibrium:

$$x = \frac{V_0}{A} + \epsilon$$

We can taylor expand about x_0:

$$\frac{1}{x^\gamma} \approx \frac{1}{(\frac{V_0}{A})^\gamma} - \gamma\frac{\epsilon}{(\frac{V_0}{A})^{\gamma+1}}$$

Substituting back into the equation of motion we now have a function of ϵ:

$$\begin{aligned} m\ddot{\epsilon} &= \Big(p_0 + \frac{mg}{A}\Big)A\Bigg[\frac{(\frac{V_0}{A})^\gamma}{(\frac{V_0}{A})^\gamma} - \gamma\frac{\epsilon(\frac{V_0}{A})^\gamma}{(\frac{V_0}{A})^{\gamma+1}} - 1\Bigg] \\ &= \Big(p_0 + \frac{mg}{A}\Big)A\Big[1 - \gamma\epsilon\frac{A}{V_0} - 1\Big] \\ &= -\Big(p_0 + \frac{mg}{A}\Big)\frac{A^2\gamma}{V_0}\epsilon = -k\epsilon \end{aligned}$$

The solution to the differential equation $m\ddot{\epsilon} = -k\epsilon$ is a simple harmonic oscillator:

$$\epsilon = A\cos(\omega t + \phi)$$

where we know the angular frequency:

$$\omega = 2\pi\nu = \sqrt{\frac{k}{m}} = \sqrt{\frac{(p_0 + \frac{mg}{A})\gamma A^2}{mV_0}}$$

$$\implies \boxed{\gamma = \frac{4\pi^2 m V_0 \nu^2}{p_0 A^2 + mgA}}$$

6. From Reif, the relation between c_p and c_V is

$$c_p - c_V = VT\frac{\alpha^2}{\kappa} \tag{5.7.13}$$

So the quantity on the right is

$$\begin{aligned} VT\frac{\alpha^2}{\kappa} &= 14.72\,\mathrm{cm^3/mol} \times 273\,\mathrm{K} \times \frac{\left(1.81\times10^{-4}\,\mathrm{deg^{-1}}\right)^2}{3.88\times10^{-12}\,\mathrm{cm^2/dyne}} \times \frac{1\times10^{-7}\,\mathrm{J}}{\mathrm{dyne\,cm}} \\ &= 3.39\,\mathrm{J/mol\,deg} \end{aligned}$$

and the specific heat at constant volume is

$$c_V = c_p - VT\frac{\alpha^2}{\kappa} = 28\,\mathrm{J/mol\,deg} - 3.39\,\mathrm{J/mol\,deg} = \boxed{24.6\,\mathrm{J/mol\,deg}}$$

Furthermore, the ratio is

$$\gamma = \frac{c_p}{c_V} = \frac{28}{24.6} = \boxed{1.14}$$

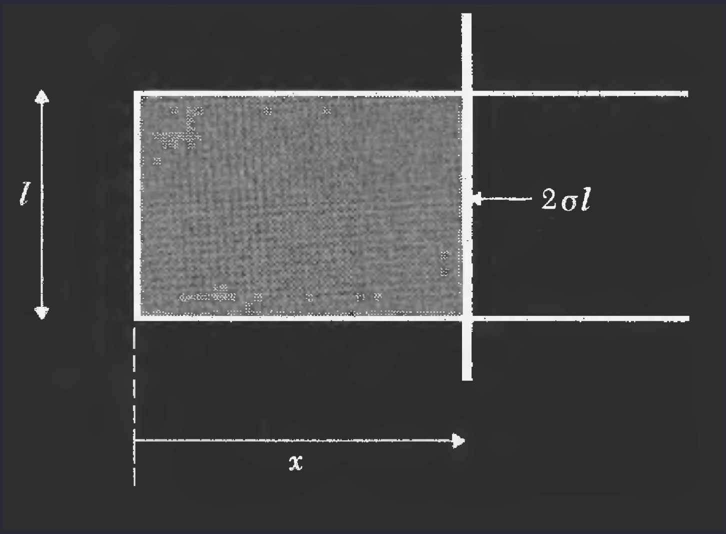

Figure 3.2: Soap film supported by wire frame with force $2\sigma l$.

7. For a soap film in Fig. 3.2, the temperature dependence of the surface tension σ is given by

$$\sigma = \sigma_0 - \alpha T$$

(a) With x as the only external parameter the change dE in terms of heat $đQ$ absorbed and the work done by it dx:

$$đQ = dE + đW, \quad đW = -F dx = -2\sigma l dx$$
$$\implies \boxed{dE = đQ + 2\sigma l\, dx}$$

(b) Calculate the change in mean energy $\Delta E = E(x) - E(0)$ when it is stretched at constant T_0 from $x = 0 \to x$:

$$đQ = TdS = dE + đW = dE - F dx$$
$$\implies dS = \frac{dE}{T} - \frac{F dx}{T} = \frac{dE}{T} - \frac{2\sigma l dx}{T}$$

Using the differential for $S = S(x, T)$ and $E = E(x, T)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_x dT + \left(\frac{\partial S}{\partial x}\right)_T dx, \quad \text{and} \quad dE = \left(\frac{\partial E}{\partial T}\right)_x dT + \left(\frac{\partial E}{\partial x}\right)_T dx$$

Since the film is stretched at constant T_0

$$\frac{\partial S}{\partial T} = 0, \quad \frac{\partial E}{\partial T} = 0$$

so

$$\left(\frac{\partial S}{\partial x}\right)_T dx = \frac{1}{T}\left(\frac{\partial E}{\partial x}\right)_T dx - \frac{2\sigma l}{T} dx$$
$$\implies \left(\frac{\partial E}{\partial x}\right)_T = T\left(\frac{\partial S}{\partial x}\right)_T + 2\sigma l$$

From $TdS = dE - F dx$ we can get the Maxwell relation

$$\frac{\partial S}{\partial x} = -\frac{\partial F}{\partial T} = -2l\frac{\partial \sigma}{\partial T} \quad \text{using} \quad \sigma = \sigma_0 - \alpha T$$
$$\implies \frac{\partial S}{\partial x} = 2l\alpha$$

Finally

$$\left(\frac{\partial E}{\partial x}\right)_T = T\left(\frac{\partial S}{\partial x}\right)_T + 2\sigma l = 2l\alpha T + 2l(\sigma_0 - \alpha T) = 2l\sigma_0$$

so the change in mean energy is

$$\Delta E = \int_0^x \left(\frac{\partial E}{\partial x}\right)_T dx = \boxed{2l\sigma_0 x}$$

(c) Calculate the work $W(0 \to x)$ done in order to stretch the film at constant temp from $x = 0 \to x$:

$$W = -\int_0^x F dx = -\int_0^x 2\sigma l dx = \boxed{-2l\sigma x}$$