I. Mathematical detour #2: characterizing fluctuations

II. Mathematical detour #3: the relative size of fluctuations compared to the number of members in a distribution

I. Mathematical detour #2: characterizing fluctuations

A fluctuation is any case when a member of a distribution does not take the value of the mean.

We sometimes want to characterize the typical fluctuation in order to know how likely any particular member is to deviate from the mean (i.e. deviate from what is expected).

σ^2 is a useful characterization because every fluctuation contributes to it; the positive (above the mean) and negative (below the mean) do not cancel each other out, so no information is lost.

$\sigma = \sqrt{\sigma^2}$ is equally useful.

We will now show that $\sigma = \sqrt{Npq}$, where

$N =$ total #events (members) in the distribution

$p =$ probability that any particular event meets the criteria being measured

$q =$ probability that any particular event fails the criterion.

Recall that by definition, $\sigma^2 = \overline{(\Delta u)^2} = \sum_i P(u_i)(u_i - \bar{u})^2$.

Call the $u_i = n$ ($n = 0, 1, 2, \ldots, N$) so we can use the usual notation for the binomial distribution. Then:

$$\sigma^2 = \overline{(\Delta n)^2} = \overline{(n - \bar{n})^2} = \overline{n^2 - 2n\bar{n} + \bar{n}^2}$$

$$= \overline{n^2} - \overline{2n\bar{n}} + \overline{\bar{n}^2}$$

$$= \text{TermA - TermB + TermC}$$

TermB: Recall $\overline{cf} = c\bar{f}$. Here, $c = 2\bar{n}$.

TermC: Recall $\bar{c} = c$. Here $c = \bar{n}^2$.

$$\sigma^2 = \overline{n^2} - 2\bar{n} \cdot \bar{n} + \bar{n}^2 = \overline{n^2} - \bar{n}^2$$

Calculate $\overline{n^2} = \sum_n n^2 P_N(n)$.   Plug in the binomial distribution.

$$= \sum_n n^2 \left[\frac{N!}{n!(N-n)!} p^n q^{N-n} \right]$$

To do this sum, notice

$$np^n = p\frac{\partial\left(p^n\right)}{\partial p}.$$

Similarly,

$$n^2 p^n = n\left(p\frac{\partial}{\partial p}\right)p^n$$

$$= \left(p\frac{\partial}{\partial p}\right)np^n$$

$$= \left(p\frac{\partial}{\partial p}\right)p\frac{\partial\left(p^n\right)}{\partial p}$$

$$= \left(p\frac{\partial}{\partial p}\right)^2 p^n$$

So we can replace n^2 by $\left(p\dfrac{\partial}{\partial p}\right)^2$ if it precedes p^n.

Return now to the calculation....

$$\overline{n^2} = \sum_n n^2 \left[\frac{N!}{n!(N-n)!} p^n q^{N-n} \right]. \qquad \text{Replace the } n^2.$$

$$= \sum_n \left(p \frac{\partial}{\partial p} \right)^2 \left[\frac{N!}{n!(N-n)!} p^n q^{N-n} \right]$$

$$= \left(p \frac{\partial}{\partial p} \right)^2 \sum_n \left[\frac{N!}{n!(N-n)!} p^n q^{N-n} \right]$$

$$= \left(p \frac{\partial}{\partial p} \right)^2 (p+q)^N$$

$$= \left(p \frac{\partial}{\partial p} \right) \left(p \frac{\partial}{\partial p} \right) (p+q)^N$$

$$= \left(p \frac{\partial}{\partial p} \right) pN(p+q)^{N-1}$$

$$= pN \frac{\partial}{\partial p} \left\{ p(p+q)^{N-1} \right\}$$

$$= pN \left\{ p(N-1)(p+q)^{N-2} + (p+q)^{N-1} \right\}. \qquad \text{Recall } p+q=1.$$

$$= pN \left\{ p(N-1) \cdot 1 + 1 \right\}$$

So $\overline{n^2} = pN(pN - p + 1)$.

Since $p + q = 1,\ -p + 1 = q$

$$= pN(pN + q)$$

$$\overline{n^2} = (pN)^2 + pNq \qquad \text{"Eq 1"}$$

Now we must show that $pN = \overline{n}$, which is the average number of successes among N events.

$$\overline{n} = \sum_n nP(n)$$

Plug in the binomial P(n)

$$\overline{n} = \sum_n n\left[\frac{N!}{n!(N-n)!}\right]p^n q^{N-n}$$

Replace $np^n \rightarrow p\dfrac{\partial}{\partial p}p^n$

$$\bar{n} = \sum_n \left[\frac{N!}{n!(N-n)!} \right] p \frac{\partial}{\partial p} p^n q^{N-n}$$

$$\bar{n} = p \frac{\partial}{\partial p} \sum_n \left[\frac{N!}{n!(N-n)!} \right] p^n q^{N-n}$$

$$\bar{n} = p \frac{\partial}{\partial p} (p+q)^N$$

$$\bar{n} = pN(p+q)^{N-1} \qquad \text{But } (p+q) = 1$$

$$\bar{n} = pN$$

Plug this into Eq 1 to get:

$$\overline{n^2} = \bar{n}^2 + pNq$$

$$\underbrace{\overline{n^2} - \bar{n}^2}_{\Downarrow} = pNq$$

$$\sigma^2 = pNq$$

$$\sigma = \sqrt{pNq} \qquad \text{This predicts/characterizes the size of a typical fluctuation}$$

II. Mathematical detour #3: relative size of fluctuations compared to number of members in the distribution

Recall $\sigma = \sqrt{Npq}$

and $\bar{n} = Np$

So $\dfrac{\sigma}{\bar{n}} = \dfrac{\sqrt{Npq}}{Np} = \sqrt{\dfrac{q}{p}} \cdot \dfrac{1}{\sqrt{N}}$

Thus $\dfrac{\sigma}{\bar{n}} \propto \dfrac{1}{\sqrt{N}}$.

So the more members there are, the smaller the characteristic fluctuation is, relative to the mean.

Example: Suppose

N = #air molecules in a room, 10^{28}

$\bar{n}$ = average #molecules in the front half of the room, $\dfrac{10^{28}}{2}$

Then a characteristic fluctuation we might observe, if we check a large number of identical rooms, is $\sigma = \sqrt{Npq} = \sqrt{10^{28} \cdot \dfrac{1}{2} \cdot \dfrac{1}{2}} = \dfrac{10^{14}}{2}$

The relative size $\dfrac{\sigma}{\bar{n}} = \dfrac{10^{14}/2}{10^{28}/2} = 10^{-14}$.

That is: the number of molecules in the front half is generally VERY close to its mean for large N. If one molecule drifts to the back, there are relatively many more ways, many more molecules to effect a compensation for that fluctuation.

Now compare this to the case in which N is small. Then each molecule's position (front or back of room) carries relatively larger weight in the characteristic fluctuation:

If N=100

Then $\bar{n}(\text{front half}) = \dfrac{100}{2} = 50$

$\sigma = \sqrt{Npq} = \sqrt{100 \cdot \dfrac{1}{2} \cdot \dfrac{1}{2}} = 5$

$\dfrac{\sigma}{\bar{n}} = \dfrac{5}{50} = 0.1$

I. Mathematical detour #4: the Gaussian distribution

Please read Stowe Chapter 10.

I. Mathematical detour #4: the Gaussian distribution

Recall the binomial distribution:

$$P_N(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

This is the probability of n successes out of N trials, if the probability
of success per trial is p and the probability of failure per trial is q.
The binomial distribution is true in general, for any choices of n, N, p, $(q=1-p)$.

Our goal here: find an approximation for it when
i) N is very large
ii) We only care if the approximation matches
the true distribution in the region of the mean.
The approximation is called a Gaussian distribution

In figure: histo = binomial,
green curve = the Gaussian (note, too wide
and skewed left)
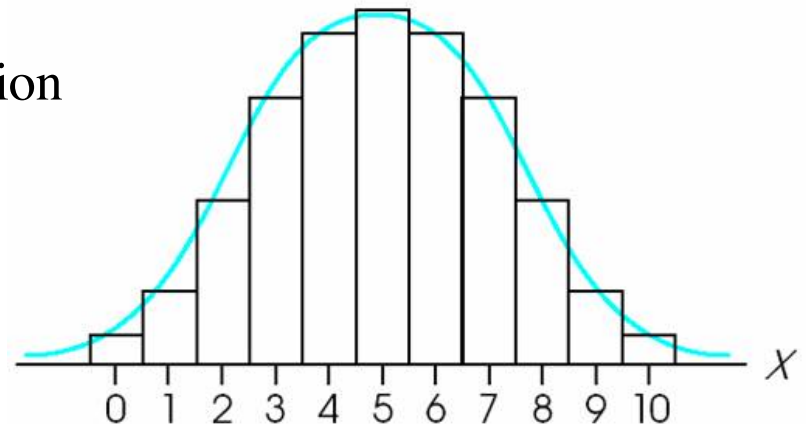
We want an approximation for the shape of $P_N(n) = \dfrac{N!}{n!(N-n)!} p^n q^{N-n}$.

Consider the natural log: $\ln[P_N(n)] = \ln\left[\dfrac{N!}{n!(N-n)!} p^n q^{N-n}\right]$.

Define $\tilde{n} = $ the n for which P is max. Note, this is the max, not necessarily the mean.

So by definition, $\dfrac{dP}{dn} = \dfrac{d(\ln P)}{dn} = 0$ @$n = \tilde{n}$.

Because we only want to match the distribution near the mean, consider small deviations η about the mean, so consider n's for which $n = \tilde{n} + \eta$.

Expand lnP in a Taylor series. (We convert to ln, and then unconvert later, as a trick to ensure that the series converges. See slide 126 for details.)

$$\ln P(n) = \ln P(\tilde{n}) + \left.\frac{d\ln P}{dn}\right|_{n=\tilde{n}} \cdot \eta + \frac{1}{2}\left.\frac{d^2\ln P}{dn^2}\right|_{n=\tilde{n}} \cdot \eta^2 + \dots$$

Define coefficients $B_k \equiv \left.\dfrac{d^k \ln P}{dn^k}\right|_{n=\tilde{n}}$.

$$\ln P(n) = \ln P(\tilde{n}) + B_1 \cdot \eta + \frac{1}{2}B_2 \cdot \eta^2 + \frac{1}{6}B_3\eta^3 \dots$$

Notice:

1) $B_1 = 0$ $\qquad \left(\dfrac{d \ln P}{dn} \bigg|_{n=\tilde{n}} = 0, \text{ the first derivative of a function is zero at its max} \right)$

2) B_2 is intrinsically negative, because this is an inflexion point.

So call it $\text{B}_2 = -\left| \text{B}_2 \right|$ to emphasize this.

Thus:

$$\ln P(n) = \ln P(\tilde{n}) - \frac{1}{2}\left| B_2 \right| \cdot \eta^2 + .\frac{1}{6} B_3 \eta^3 ...$$

Take the exp of both sides:

$$\exp \ln P(n) = P(n) = \exp \left[\ln P(\tilde{n}) - \frac{1}{2}\left| B_2 \right| \cdot \eta^2 + .\frac{1}{6} B_3 \eta^3 ... \right]$$

$$P(n) = \underbrace{e^{\ln P(\tilde{n})}} \, e^{-\frac{1}{2}\left| B_2 \right| \cdot \eta^2} \, \underbrace{e^{\frac{1}{6} B_3 \eta^3 ...}}$$

$\qquad$ call this "$\tilde{P}$" $\qquad$ neglect this for "small η"

$$P(n) \approx \tilde{P} e^{-\frac{1}{2}\left| B_2 \right| \cdot \eta^2} \qquad\qquad \text{'Eq A.' This is the approximation we seek.}$$

Now work out B_2. We need to find B_1, then take its derivative:

$$B_1 = \frac{d\ln P}{dn}\bigg|_{n=\tilde{n}} = \frac{d}{dn}\left[\ln\left(\frac{N!\,p^n q^{N-n}}{n!(N-n)!}\right)\right]_{n=\tilde{n}} \qquad \text{"Eq 0"}$$

$$= \frac{d}{dn}\Big[\ln N! - \ln n! - \ln(N-n)! + n\ln p + (N-n)\ln q\Big]_{n=\tilde{n}}$$

$$\frac{d}{dn}\big(\ln N!\big) = 0$$

$$\frac{d}{dn}\big(n\ln p\big) = \ln p$$

$$\frac{d}{dn}\big[(N-n)\ln q\big] = -\ln q$$

How to compute $\dfrac{d(\ln n!)}{dn}$: If n is a large integer $(n \gg 1)$, $\ln n!$ can be considered an almost continuous function of n, since $\ln n!$ changes only by a small fraction of itself if n is changed by a small integer.

Hence: $\dfrac{d(\ln n!)}{dn} \approx \ln(n+1)! - \ln n! = \ln\left(\dfrac{(n+1)!}{n!}\right) = \ln(n+1) \approx \ln n$

Similarly, $\frac{d}{dn}\left[\ln(N-n)!\right] \approx -\ln(N-n)$ for $n \gg 1$

Plug all of these into Eq 0, and recall that $B_1 = 0$.

$B_1 = 0 = \left[0 - \ln n - \left[-\ln(N-n)\right] + \ln p - \ln q\right]_{\text{evaluated at n=ñ}}$

$0 = -\ln\tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q$ 'Eq 1'

Thus $\ln\left[\frac{(N-\tilde{n}) \cdot p}{\tilde{n} \cdot q}\right] = 0$

                      Recall $\ln 1 = 0$, so

$\frac{(N-\tilde{n}) \cdot p}{\tilde{n} \cdot q} = 1$

$(N-\tilde{n}) \cdot p = \tilde{n} \cdot q$

                   Use $p + q = 1$, so $q = 1 - p$

$(N-\tilde{n})p = \tilde{n}(1-p)$

$Np - \tilde{n}p = \tilde{n} - \tilde{n}p$

$Np = \tilde{n}$ 'Eq 2'. We will use this in a moment.

Now find $B_2 = \dfrac{dB_1}{dn}$. Use Eq 1 but NOT evaluated at $n = \tilde{n}$.

$$B_2 = \frac{d}{dn}\Big[-\ln n + \ln(N - n) + \ln p - \ln q\Big]$$

$$B_2 = -\frac{1}{n} - \frac{1}{N - n}.$$ Now evaluate this at $n = \tilde{n}$:

$$B_2 = -\frac{1}{\tilde{n}} - \frac{1}{N - \tilde{n}}$$

Plug in $\tilde{n} = Np$ from Eq 2:

$$B_2 = -\frac{1}{Np} - \frac{1}{N - Np}$$

In the second term, use $p = 1 - q$

$$B_2 = -\frac{1}{Np} - \frac{1}{N - N(1-q)}$$

$$= -\frac{1}{Np} - \frac{1}{Nq}$$

$$= -\frac{1}{N}\left(\frac{1}{p} + \frac{1}{q}\right)$$

$$= -\frac{1}{N}\left(\frac{q+p}{pq}\right) = -\frac{1}{N}\left(\frac{(1-p)+p}{pq}\right) = -\frac{1}{Npq} = -\frac{1}{\sigma^2}$$

Thus, $B_2 = -\dfrac{1}{\sigma^2}$

Now work out $\tilde{P} \equiv P(\tilde{n})$. Use normalization:

$$\sum_{n=1}^{N} P(n) \approx \int P(n)\,dn = \int_{-\infty}^{+\infty} P(\tilde{n}+\eta)\,d\eta = 1$$

Use $P(n) = \tilde{P}e^{-\frac{1}{2}|B_2|\eta^2}$

$$= \tilde{P}\int_{-\infty}^{+\infty} e^{-\frac{1}{2}|B_2|\eta^2}\,d\eta = 1$$

Use $B_2 = -\dfrac{1}{\sigma^2}$

$$\tilde{P}\int_{-\infty}^{+\infty} e^{-\frac{1}{2\sigma^2}\eta^2}\,d\eta = 1$$

This integral resolves to:

$$\tilde{P}\sqrt{2\pi}\sigma = 1.$$

So: $\tilde{P} = \dfrac{1}{\sqrt{2\pi}\sigma}$

Plug everything into Eq A to get the approximation to the binomial distribution for large N, near the mean:

Beginning with Eq A: $\quad P(n) \approx \tilde{P}e^{-\frac{1}{2}|B_2|\eta^2}$

$$\tilde{P} = \frac{1}{\sqrt{2\pi}\sigma}$$

$$n = \tilde{n} + \eta, \text{ so } \eta = n - \tilde{n}$$

$$\text{and } B_2 = -\frac{1}{\sigma^2}$$

$$P(n) = \frac{1}{\sqrt{2\pi}\sigma}e^{-\frac{1}{2\sigma^2}(n-\tilde{n})^2}$$

From Eq 2, $\tilde{n} \approx Np$.

But $Np = \bar{n}$, exactly.

So for this approximation, $\tilde{n} = \bar{n}$ ("peak = mean")

Then,

$$P(n) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{1}{2\sigma^2}(n-\bar{n})^2\right]. \qquad \text{The Gaussian distribution}$$

Why we used $\ln P$ instead of P:

Consider some $f = (1+y)^{-N}$, for small y

Expand in a Taylor series:

$$f = 1 - Ny + \frac{1}{2}N(N+1)y^2 - \ldots$$

When N is large, Ny can be ≥ 1, depending on y, so convergence is not guaranteed.

Choose instead $\ln f = \ln\left[(1+y)^{-N}\right] = -N\ln(1+y)$.

Expand this ln in a Taylor series:

$$\ln f = -N\left(y - \frac{y^2}{2} + \ldots\right)$$

Take exp of both sides:

$$\exp\ln f = f = \exp\left[-N\left(y - \frac{y^2}{2} + \ldots\right)\right]$$

which converges for any N as long as $y \leq 1$.

I. Energy of a system in equilibrium with a heat reservoir

II. Heat capacity

Please read Stowe Chapter 11 and Chapter 12 Sections A, B, and F

I. Energy of a system in equilibrium with a heat reservoir

Consider a system A_1 with average internal energy $\bar{E}_1$. It is in equilibrium with a heat reservoir.

A heat reservoir is a second system (A_2) that is large relative to A_1, so a small change in its internal energy E_2 does not significantly affect its temperature T_2. Thus:

$$\frac{\partial}{\partial E_2}\left(\frac{1}{T_2}\right) = 0$$

Energy is conserved between the 2 systems, so $\Delta E_1 = -\Delta E_2$

$$\frac{\partial}{\partial E_1}\left(\frac{1}{T_2}\right) = 0$$

E_1 is the energy of system A_1. E_1 can differ from the mean $\bar{E}_1$ by ΔE_1.

We now show that the probability density that A_1 has any particular value of E_1 is given by:

$$P(E_1) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left[-\left(\Delta E_1^2\right)/\sigma^2\right]$$

where $\quad \sigma = \sqrt{\frac{2}{\mathbb{N}}}\bar{E}_1, \qquad \mathbb{N} = \#\text{dof}$

The message: for a macroscopic system, $\mathbb{N}$ is huge, so

$\sigma \propto \dfrac{1}{\sqrt{\mathbb{N}}}$ is very small, and

$P(E_1) \propto \exp\left[-\left(\Delta E_1^2\right)/\sigma^2\right]$ is very small

unless $\Delta E_1 = E_1 - \bar{E}_1 = 0.$

Consequently, for a macroscopic system:

i) one practically never observes deviations from the mean, and

ii) any observed fluctuations follow a Gaussian distribution.

The proof:

Recall if $\Omega_0 = $ #accessible states of the combined system $(A_1 + A_2)$, then

$$P(E_1) = const \cdot \Omega_0(E_1) \qquad\qquad\qquad \text{'Eq 1'}$$

Recall entropy of the combined system is $S_0 = k \ln \Omega_0$,

so $\Omega_0 = e^{S_0/k}$.   Plug this into Eq 1.

$$P(E_1) = const \cdot e^{S_0(E_1)/k}. \qquad\qquad\qquad \text{'Eq 1a'}$$

Consider the case when $E_1 = \bar{E}_1 + \Delta E_1$; i.e., it varies by a small amount ΔE_1

from the mean $\bar{E}_1$. See how S_0 reflects the ΔE_1 :

$$S_0(E_1) = S_0(\bar{E}_1 + \Delta E_1)$$

Expand in a Taylor Series:

$$= S_0(\bar{E}_1) + \left.\frac{\partial S_0}{\partial E_1}\right|_{\bar{E}_1} \cdot \Delta E_1 + \frac{1}{2}\left.\frac{\partial^2 S_0}{\partial E_1^2}\right|_{\bar{E}_1} \cdot (\Delta E_1)^2 + ...$$

Recall $\left.\dfrac{\partial S_0}{\partial E_1}\right|_{\bar{E}_1} = 0:$ the entropy is maximized at equilibrium

$$= S_0(\bar{E}_1) + \frac{1}{2}\left.\frac{\partial^2 S_0}{\partial E_1^2}\right|_{\bar{E}_1} \cdot (\Delta E_1)^2 + ...$$

Use $S_0 = S_1 + S_2$

$$S_0\left(E_1\right) = S_0\left(\bar{E}_1\right) + \frac{1}{2}\left.\frac{\partial^2\left(S_1 + S_2\right)}{\partial E_1^2}\right|_{\bar{E}_1} \cdot \left(\Delta E_1\right)^2 + \dots \qquad \text{'Eq 2'}$$

Focus on this term

$$\left.\frac{\partial^2\left(S_1 + S_2\right)}{\partial E_1^2}\right|_{\bar{E}_1} = \frac{\partial}{\partial E_1}\left(\frac{\partial\left(S_1 + S_2\right)}{\partial E_1}\right) = \frac{\partial}{\partial E_1}\left[\frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_1}\right]$$

Use conservation of energy: $\dfrac{\partial}{\partial E_1} = -\dfrac{\partial}{\partial E_2}$

$$= \frac{\partial}{\partial E_1}\left[\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right]$$

Recall $\dfrac{1}{T} = \dfrac{\partial S}{\partial E}$

$$= \frac{\partial}{\partial E_1}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Recall for a reservoir, $\dfrac{\partial}{\partial E_1}\left(\dfrac{1}{T_2}\right) = 0$

$$= \frac{\partial}{\partial E_1}\left(\frac{1}{T_1}\right)$$

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$$\text{Use } E = \frac{1}{2}\mathbb{N}kT, \text{ so } \frac{1}{T_1} = \frac{\mathbb{N}k}{2E_1}$$

$$\left.\frac{\partial^2\left(S_1+S_2\right)}{\partial E_1^2}\right|_{\bar{E}_1} = \frac{\partial}{\partial E_1}\left(\frac{\mathbb{N}k}{2E_1}\right) = -\frac{\mathbb{N}k}{2E_1^2}$$

Plug this into Eq 2:

$$S_0\left(E_1\right) = S_0\left(\bar{E}_1\right) - \frac{1}{2}\cdot\left.\frac{\mathbb{N}k}{2E_1^2}\right|_{\bar{E}_1}\cdot\left(\Delta E_1\right)^2 + \ldots$$

$$= S_0\left(\bar{E}_1\right) - \frac{1}{2}\cdot\frac{\mathbb{N}k}{2\bar{E}_1^2}\cdot\left(\Delta E_1\right)^2$$

Plug this into Eq 1a:

$$P\left(E_1\right) = const\cdot e^{S_0(E_1)/k} = const\cdot\exp\left[\frac{S_0\left(\bar{E}_1\right)}{k} - \frac{\mathbb{N}\left(\Delta E_1\right)^2}{4\bar{E}_1^2}\right]$$

$$= \underbrace{const\cdot\exp\left[\frac{S_0\left(\bar{E}_1\right)}{k}\right]}\cdot\exp\left[-\frac{\mathbb{N}\left(\Delta E_1\right)^2}{4\bar{E}_1^2}\right]$$

call this const'

Note $\sigma = \sqrt{\dfrac{2}{\mathbb{N}}\bar{E}_1}$, so $\dfrac{\mathbb{N}}{2\bar{E}_1^2} = \dfrac{1}{\sigma^2}$

$$P(E_1) = const' \cdot \exp\left[\frac{-(\Delta E_1)^2}{2\sigma^2}\right]$$

The probability that the system A_1 has energy in the range between E_1 and $E_1 + dE_1$ is

$$P(E_1)dE_1 = const' \cdot \exp\left[\frac{-(\Delta E_1)^2}{2\sigma^2}\right]dE_1$$

Normalize this to find $const'$:

$$\int_{-\infty}^{+\infty} P(E_1)dE_1 \equiv 1 = const' \cdot \int \exp\left[\frac{-(\Delta E_1)^2}{2\sigma^2}\right]dE_1$$

Conclude:

$$const' = \frac{1}{\sqrt{2\pi}\sigma}$$

Finally,

$$P(E_1)dE_1 = \frac{1}{\sqrt{2\pi}\sigma} \cdot \exp\left[\frac{-(\Delta E_1)^2}{2\sigma^2}\right]dE_1 \quad \text{for } \sigma = \sqrt{\frac{2}{\mathbb{N}}}\bar{E}_1$$

II. Heat capacity

It is an intrinsic property of substances that some can absorb more heat (dQ) than others per unit change in temperature dT.

This is because while dT reflects change in thermal energy (modes whose $E \propto q^2$), various substances can convert dQ into forms of E that are NOT proportional to q^2, in which cases that energy is not detected as temperature change.

This property depends upon the chemical structure of the substance.

Define: heat capacity $\left(\text{at constant "}y\text{"}\right) : C_y \equiv \left.\dfrac{\partial Q}{\partial T}\right|_y$

where "y" could be pressure, volume, other macroscopic observables.

Notice that C_y is sensitive to the size of the system (i.e, total amount of material).

More useful definitions for making comparisons between substances

(Note lower and upper case fonts):

Define: molar heat capacity @ constant "y" : $c_y = \dfrac{C_y}{\# \, moles}$.

Define: specific heat @ constant "y" : $c'_y = \dfrac{C_y}{mass}$

The equation $C = \dfrac{dQ}{dT}$ is useful if you need to find change of entropy:

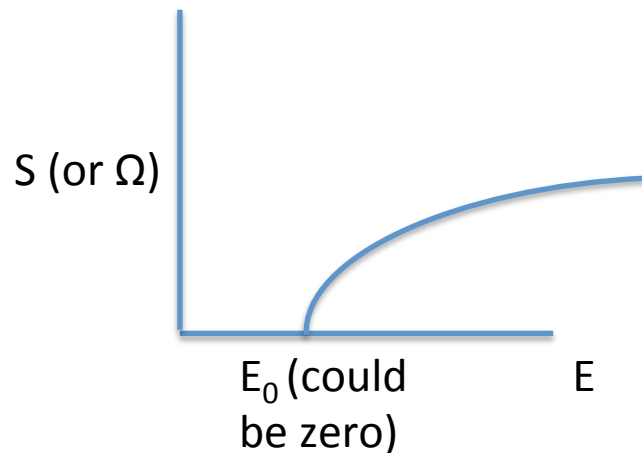$$\Delta S = \int dS = \int \frac{dQ}{T} = \int \frac{CdT}{T} = C \int \frac{dT}{T} \,.$$

I. The Third Law

II. Measuring macroscopic parameters

III. The relationship between volume and #accessible states

IV. Other kinds of work

V. Coefficients of expansion and compressibility

I. The Third Law

Recall $S = k \ln \Omega$ and $\Omega \propto E^{\mathbb{N}/2}$.

So $S \propto \ln\left(E^{\mathbb{N}/2}\right) = \dfrac{\mathbb{N}}{2}\ln E$.

So $S \propto \ln E$. Plot this again (recall slide 102):

S (or Ω) on vertical axis; E on horizontal axis; curve beginning at E_0 (could be zero).

By the nature of the ln function, as $E \to 0$, $S \to S_{min}$.

And because $E = \dfrac{1}{2}\mathbb{N}kT$, as $E \to 0$, $T \to 0$, so

as $T \to 0$, $S \to S_{min}$.

Does S_{min} always equal zero?

Recall again that $S = k\ln\Omega$ (Ω = #states)

so $S_{min} = k\ln\Omega_{min}$.

If there is one unique ground state, then $\Omega_{min} = 1$.

$\ln 1 = 0$, so
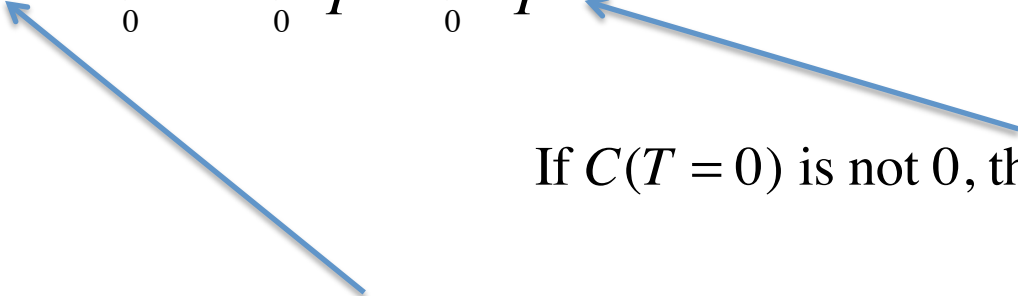
if there is one unique ground state, then $S_{min} = 0$.

If the ground state is degenerate (there are $n > 1$ states with the same minimum energy), then $S_{min} = k\ln n \neq 0$.

Notice that once the energy becomes very low (the limit $E \to 0$), the details of the system (system parameters V, pressure, $\vec{B}$,...) are irrelevant.

This is the Third Law: as T (or E) $\to 0$, $S \to S_{min}$, regardless of the values of the system parameters.

The limit of the temperature at which $S = S_{min}$ is called absolute zero.

Note: for some non-zero temperature T_0,

$$S(T_0) = \int\limits_0^{T_0} dS = \int\limits_0^{T_0} \frac{dQ}{T} = \int\limits_0^{T_0} \frac{CdT}{T}$$

If $C(T = 0)$ is not 0, this integral will diverge as $\ln(0)$

But we know that $S(T_0)$ is
a finite, never infinite, quantity,
because of its alternative definition
as $S = k \ln \Omega$.

So purely for mathematical consistency, we must have $C(T \to 0) \to 0$.
This has been experimentally demonstrated, and we will see later that

$$C_V \approx \left(\frac{E}{V} \right)^2 \exp(-E/T) \quad \text{as } T \to 0.$$

What does it mean for $C(T \to 0) \to 0$?

Recall that $C = \dfrac{dQ}{dT}$. As $T \to 0$, the system is settling into its ground state; it is impossible for it to reach a lower state, so it is impossible for it to give up any more dQ.

II. Measuring macroscopic parameters

Recall:

(i) internal energy: $dE = dQ - dW + \mu dN$

(ii) entropy $dS = \dfrac{dQ}{T}$, so $dQ = TdS$

(iii) we can express all kinds of work symbolically as $dW = pdV$

"p" stands in for a generalized force, not only pressure

"dV" stands in for a generalized length, not only volume

Thus $W = \int \vec{F} \cdot d\vec{\ell}$

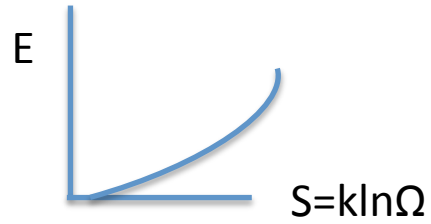So: $dE = TdS - pdV + \mu dN$ 'Eq 1'

Now for a moment treat dE as just a formal mathematical object
that depends on other objects named S, V, and N. Then:

$$dE = \left.\frac{\partial E}{\partial S}\right|_{V,N} dS + \left.\frac{\partial E}{\partial V}\right|_{S,N} dV + \left.\frac{\partial E}{\partial N}\right|_{S,V} dN \qquad \text{'Eq 2'}$$
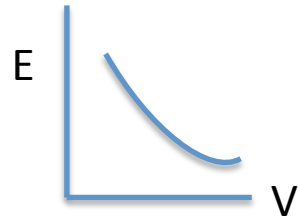
Compare Eq 1 and Eq 2. If therir LHS's are equal, then their RHS's must be equal:

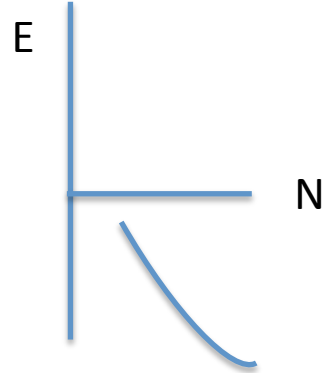# Measure this in the lab from slopes of these curves:

$$T = \left.\frac{\partial E}{\partial S}\right|_{V,N}$$

$$p = -\left.\frac{\partial E}{\partial V}\right|_{S,N}$$

$$\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V}$$

E

S=klnΩ

E

V

E

N

III. The relationship between volume and # accessible states

So far we only know $\Omega = \Omega(E, \mathbb{N}) = const \cdot E^{\mathbb{N}/2}$
$$\text{energy}, \#\text{dof}$$

Our goal now: find $\Omega = \Omega(V)$.

That is: suppose we change the volume of a container but permit no other changes ($\Delta E = \Delta N = 0$). How will the Ω of the contained system be affected?

Begin with $dE = TdS - pdV + \mu dN$.

Rewrite as:

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

So $p = T\left.\dfrac{\partial S}{\partial V}\right|_{E,N}$

Plug in $S = k\ln\Omega$:

$$p = T\frac{\partial(S = k\ln\Omega)}{\partial V} = kT\frac{\partial\ln\Omega}{\partial V} \to kT\frac{\Delta(\ln\Omega)}{\Delta V}.$$

Rewrite:

$$\frac{p\Delta V}{kT} = \Delta\left(\ln\Omega\right) = \ln\Omega_2 - \ln\Omega_1 = \ln\left(\frac{\Omega_2}{\Omega_1}\right)$$

Exponentiate:

$$\exp\left(\frac{p\Delta V}{kT}\right) = \frac{\Omega_2}{\Omega_1} \qquad\qquad \text{'Eq 1'}$$

Conclusion: if you change the volume by ΔV, the #states increases by a factor $\sim e^{\Delta V}$.

In general, $dS = \dfrac{1}{T}dE + \dfrac{p}{T}dV - \dfrac{\mu}{T}dN$

If $\Delta E = \Delta N = 0$ $(dE = dN = 0)$ this reduces to

$$\Delta S = \frac{p}{T}\Delta V$$

$$\frac{\Delta Q}{T} = \frac{p}{T}\Delta V$$

Plug this into Eq 1 to get:

$$\frac{\Omega_2}{\Omega_1} = \exp\left(\frac{\Delta Q}{kT}\right)\Bigg|_{\Delta E = \Delta N = 0}$$

IV. Other kinds of work

Suppose a system's energy E depends on n external parameters x_i (such as volume, N, $\vec{B}$, etc.)

Let the system be in state "r".

So $E_r = E_r\left(x_1, x_2, \ldots, x_n\right)$

If the x_i change from $x_\alpha \rightarrow x_\alpha + dx_\alpha$, then the energy changes from $E_r \rightarrow E_r + dE_r$, where

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

Take the negative of both sides:

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

This is the work done BY the system.

This is the generalized force associated with ("conjugate to") parameter α.

Some external parameters and their generalized forces:

    position dx   Force F

    volume dV   pressure p

    electrostatic potential dU   - charge -q

    magnetic field $\vec{B}$ magnetic moment $\vec{m}$

We can use these pairs in place of any 'pdV" in this course.

V. Coefficients of expansion and compressibility

Begin with definitions of terms that relate change of volume ΔV to change of temperature ΔT and change of pressure Δp.

For volume V, define: $\left.\dfrac{1}{V}\dfrac{\partial V}{\partial T}\right|_{p} \equiv \beta$ "coefficient of volume expansion"

Thus: $\Delta V = \beta V \Delta T$

Typical values of β lie in the range $10^{-6} - 10^{-3}$ per Kelvin.

For length X, define: $\left.\dfrac{1}{X}\dfrac{\partial X}{\partial T}\right|_{p} = \alpha$ "coefficient of linear expansion"

Thus: $\Delta X = \alpha X \Delta T$

To find the relationship between α and β:

Suppose a system experiences a ΔT that causes a ΔV:

$V \rightarrow V' = V + \Delta V$

Compute this 2 ways:

Way 1:

$V' = V + \Delta V$

$\quad = V + \beta V \Delta T$

$\quad = V(1 + \beta \Delta T)$

Way 2:

$V' = X'Y'Z' = (X + \Delta X)(Y + \Delta Y)(Z + \Delta Z)$

$\quad = (X + \alpha X \Delta T)(Y + \alpha Y \Delta T)(Z + \alpha Z \Delta T)$

$\quad = XYZ(1 + \alpha \Delta T)^3$

compare, and conclude:

$(1 + \beta \Delta T) = (1 + \alpha \Delta T)^3 = 1 + 3\alpha\Delta T + 3(\alpha\Delta T)^2 + (\alpha\Delta T)^3$

For small ΔT, neglect $(\Delta T)^2$, $(\Delta T)^3$. Then:

$1 + \beta\Delta T \approx 1 + 3\alpha\Delta T$, so

$\beta \approx 3\alpha$.

Note: we assumed here that $\alpha_1 = \alpha_2 = \alpha_3 \equiv \alpha$. There are materials for which the α_i are not equal: "non-isotropic solids."

Define: $\left. -\dfrac{1}{V}\dfrac{\partial V}{\partial p}\right|_{T} \equiv \kappa$ "isothermal compressibility"

Thus: $\Delta V = -V\kappa\Delta p$

And define the reciprocal:

$\left. -V\dfrac{\partial p}{\partial V}\right|_{T} = \dfrac{1}{\kappa} \equiv B$ "bulk modulus"

I. How to measure chemical potential μ

II. Describing equilibrium mathematically

III. The directions of heat flow, volume change, and particle transport between systems approaching equilibrium

IV. The relationship between number of states Ω and number of particles N

Please read Stowe Chapter 13 including Appendix 13A.

I. How to measure chemical potential μ

Recall the First Law:

$\Delta E = \Delta Q - \Delta W + \mu \Delta N$

Rewrite:

$\Delta Q = \Delta E + \Delta W - \mu \Delta N$

So $\mu = -\dfrac{\Delta Q}{\Delta N}\bigg|_{\substack{W=const \\ \rightarrow V=const}} - \dfrac{\Delta E}{\Delta N}$

Take ΔN molecules of known energy E. For them, $\dfrac{\Delta E}{\Delta N}$ is known. Add them to a solution. Don't let the volume change. Measure the amount of heat, $-\Delta Q$, released by the solution. This gives μ.

II. Describing equilibrium mathematically

Recall thermodynamics equilibrium requires 3 simultaneous conditions:

1. thermal equilibrium
2. mechanical equilibrium
3. chemical equilibrium

Show mathematically that all 3 conditions must hold.

Begin with the First Law: $\Delta E = \Delta Q - \Delta W + \mu \Delta N$

Recall $\Delta S = \dfrac{\Delta Q}{T}$, so $\Delta Q = T \Delta S$.

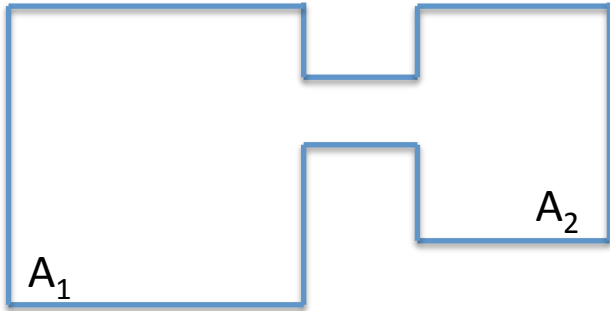Plug in $\Delta Q = T \Delta S$ and $\Delta W = p \Delta V$.

$\Delta E = T \Delta S - p \Delta V + \mu \Delta N$.

Rewrite:

$\Delta S = \dfrac{1}{T} \Delta E + \dfrac{p}{T} \Delta V - \dfrac{\mu}{T} \Delta N$ for any system.

Now consider 2 specific systems in contact with each other:

$A_1 + A_2 = A_0$ which has entropy S_0.

The systems can exchange particles (ΔN)

heat (ΔQ)

volume (ΔV)

But the total number N must be conserved: $\Delta N_1 = -\Delta N_2$

and the total energy E must be conserved: $\Delta E_1 = -\Delta E_2$

and the total volume V must be conserved: $\Delta V_1 = -\Delta V_2$

Suppose the system is in equilibrium. According to the Second Law:

$$\Delta S_0 = 0$$

$$\Delta S_1 + \Delta S_2 = 0$$

$$\Delta S_0 = \frac{1}{T_1}\Delta E_1 + \frac{p_1}{T_1}\Delta V_1 - \frac{\mu_1}{T_1}\Delta N_1 + \frac{1}{T_2}\Delta E_2 + \frac{p_2}{T_2}\Delta V_2 - \frac{\mu_2}{T_2}\Delta N_2 = 0$$

$$\Delta S_0 = \frac{1}{T_1}\Delta E_1 + \frac{p_1}{T_1}\Delta V_1 - \frac{\mu_1}{T_1}\Delta N_1 + \frac{1}{T_2}\left(-\Delta E_1\right) + \frac{p_2}{T_2}\left(-\Delta V_1\right) - \frac{\mu_2}{T_2}\left(-\Delta N_1\right) = 0$$

$$\Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta E_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta N_1 = 0 \text{ at equilibrium} \qquad \text{'Eq 1'}$$

Since E_1, V_1, and N_1 are independent variables, they can change independently, so each term must separately $= 0$.

At equilibrium:

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = 0 \quad \Rightarrow \quad T_1 = T_2 \qquad \text{thermal}$$

$$\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) = 0 \quad \Rightarrow \quad p_1 = p_2 \qquad \text{mechanical}$$

$$\left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) = 0 \quad \Rightarrow \quad \mu_1 = \mu_2 \qquad \text{chemical}$$

III. The directions of heat flow, volume change, and particle transfer between systems approaching equilibrium

The issue: if 2 systems are in contact, but not yet in equilibrium,

1- heat will flow out of the one at higher temperature, into the one at lower temperature.
2- particles will flow out of the one with higher μ, into the one with lower μ.
3- the volume of the one with higher pressure will grow at the expense of the volume of the one at lower pressure.

We already showed the first. Now we show 2 and 3.

Recall Eq 1:

$$\Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta E_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta N_1 > 0 \quad \text{approaching equilibrium}$$

From the First Law, substitute $\Delta E = \Delta Q - p\Delta V + \mu\Delta N$

$$\Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)(\Delta Q_1 - p_1\Delta V_1 + \mu_1\Delta N_1) + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta N_1 > 0$$

Expand the first term:

$$\Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta Q_1 - \frac{p_1\Delta V_1}{T_1} + \frac{p_1\Delta V_1}{T_2} + \frac{\mu_1\Delta N_1}{T_1} - \frac{\mu_1\Delta N_1}{T_2} + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta N_1 > 0$$

$$\Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta Q_1 + \frac{1}{T_2}(p_1 - p_2)\Delta V_1 - \frac{1}{T_2}(\mu_1 - \mu_2)\Delta N_1 > 0$$

Again Q_1, V_1, N_1 are independent, so the inequality will only be guaranteed if each term is separately > 0.

Conclude: as a system approaches equilibrium $(\Delta S_0 > 0)$, it must have simultaneously:

1) $\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)\Delta Q_1 > 0$

If $T_2 > T_1$, $\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right) > 0$, then ΔQ_1 must be > 0. Heat flows into System 1

2) $\dfrac{1}{T_2}(p_1 - p_2)\Delta V_1 > 0$

If $p_1 > p_2$, ΔV_1 must be > 0; if System 1 has higher pressure, it gains volume.

3) $-\dfrac{1}{T_2}(\mu_1 - \mu_2)\Delta N_1 > 0$

$\dfrac{1}{T_2}(\mu_1 - \mu_2)\Delta N_1 < 0$; If $\mu_1 > \mu_2$, ΔN_1 must be < 0. If System 1 has higher μ, it loses particles.

IV. Relationship between # states Ω and # particles N

We already know that $\Omega \propto E^{\mathbb{N}/2}$ where $\mathbb{N}$ = dof and E = energy

We already know that $\dfrac{\Omega_2}{\Omega_1} = e^{p\Delta V/kT}$ where $\Delta V = V_2 - V_1$

Goal: We now show that $\dfrac{\Omega_2}{\Omega_1} = e^{-\mu\Delta N/kT}$ where $\Delta N = N_2 - N_1$

Recall the First Law: $dE = dQ - dW + \mu dN$

Plug in $dQ = TdS$

Plug in $dW = pdV$

$dE = TdS - pdV + \mu dN$

Rewrite:

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN \qquad \text{'Physics Equation'}$$

Compare this to:

$$dS = \left.\frac{\partial S}{\partial E}\right|_{V,N} dE + \left.\frac{\partial S}{\partial V}\right|_{E,N} dV + \left.\frac{\partial S}{\partial N}\right|_{E,V} dN \qquad \text{'Math Equation'}$$

Notice: $-\dfrac{\mu}{T} = \left.\dfrac{\partial S}{\partial N}\right|_{E,V}$

Thus: $-\mu = T\left.\dfrac{\partial S}{\partial N}\right|_{E,V}$

Plug in $S = k\ln\Omega$.

$$-\mu = T\left.\frac{\partial k\ln\Omega}{\partial N}\right|_{E,V}$$

Consider a small change ΔN in the number of particles in a system.

The equation above tells us that

$$\Delta\left(\ln\Omega\right) = -\frac{\mu}{kT}\Delta N$$

$$\ln\Omega_2 - \ln\Omega_1 = -\frac{\mu}{kT}\Delta N$$

$$\ln\left(\frac{\Omega_2}{\Omega_1}\right) = -\frac{\mu}{kT}\Delta N$$

Exponentiate both sides:

$$\frac{\Omega_2}{\Omega_1} = e^{-\frac{\mu}{kT}\Delta N}$$

I. Equations of state

II. The equation of state of an ideal gas

III. The equation of state of a real gas

IV. Facts about heat capacities

Please read Stowe Chapter 14.

I. Equations of state

Recall the First Law: $dE = dQ - dW + \mu dN$.

Consider a diffusionless process, $dN = 0$.

Recall $dQ = TdS$

Recall dW stands for all possible mechanical processes involving generalized forces $\dfrac{\partial E}{\partial x_\alpha}$ that are conjugate to parameters x_α. Suppose there are n such processes.

Name the generalized forces $\dfrac{\partial E}{\partial x_\alpha} \equiv F_\alpha$. One example is pressure. Its conjugate x_α is volume.

Rewrite the First Law as:

$$dE = TdS - \sum_{\alpha=1}^{n} \left(\frac{\partial E}{\partial x_\alpha} \right) dx_\alpha$$

Substitute and divide by T; solve for dS:

$$dS = \frac{1}{T} dE + \frac{1}{T} \sum_{\alpha=1}^{n} F_\alpha dx_\alpha$$

2 Conclusions:

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V,N}$$ We already have this.

$$F_\alpha = T \frac{\partial S}{\partial x_\alpha}\bigg|_{E}$$ We will now focus on this.

Definition:

An equation such as this one, that connects a system's temperature T with a generalized parameter x_α (such as volume, $\vec{B}$, or length) and with its generalized force F_α (such as pressure, $\vec{m}$, or mechanical force F) is called **an equation of state** for the system.

The equation is customized to the particular system through the relation $S = k \ln \Omega$, because Ω is system-specific.

II. Equation of state for an ideal gas

Conditions required of an ideal gas:

i) The gas molecules themselves are pointlike: they occupy no volume.

ii) The molecules have no internal structure: no vibrational degrees of freedom.

iii) The molecules do not interact with each other.

iv) There is no external field: all the energy is kinetic.

We want to solve $F_\alpha = T \dfrac{dS}{dx_\alpha}$ for N gas molecules in volume V.

The "V" is the x_α.

Recall $S = k \ln \Omega$.

So our goal: to find an expression for $\Omega(V)$.

Recall $\Omega_{\text{N particles}} = \prod_{i=1}^{N} \Omega_i$ for $\Omega_i = \#\,$states of a free particle

Recall for each particle, $\Omega_i \propto \dfrac{V_r V_p}{h^3}$ (slide 46)

and for each particle, $V_p \propto E^{\mathbb{N}/2}$ where $\mathbb{N} = \#\,$dof   (slide 68)

Here for each particle, $\mathbb{N} = \#\,$dof $= 3$ (p_x, p_y, p_z)

so for N molecules in 3 dimensions,

so $\Omega_N \propto V_r^N E^{3N/2}$. Now replace $V_r \rightarrow V$

So:

$$S = k \ln \Omega \propto k \ln \left[V^N E^{3N/2} \right] = k \left[\ln \left\{ E^{3N/2} \right\} + N \ln V \right]$$

$$\frac{\partial S}{\partial x_\alpha} = \frac{\partial S}{\partial V} = kN \cdot \frac{1}{V}$$

Also $F_\alpha = p$

Plug these into $F_\alpha = T \dfrac{dS}{dx_\alpha}$:

$$p = T \cdot kN \cdot \frac{1}{V}$$

$pV = NkT$ The equation of state for an ideal gas, "the Ideal Gas Law"

III. Equation of state for a real gas

Conditions for a real gas:

i) The gas molecules are not pointlike: altogether 1 mole occupies a volume b

ii) The molecules still have no internal dof's

iii) The molecules do interact with each other. They are electrically neutral but

polarize, so they have a weak attraction.

iv) There is still no external field.

Begin with the Ideal Gas Law: $pV = NkT$

Divide both sides by #moles present. Recall 1 mole $= 6.023 \times 10^{23}$ molecules.

$$p \frac{V}{moles} = \frac{Nk}{moles} T$$

Define $v \equiv \dfrac{V}{mole}$

Define $R \equiv \dfrac{Nk}{mole}$ "The universal gas constant" $= 8.31 J / K\text{-}mole$

$pv = RT$

Now correct this to reflect the physical conditions:

1) The true volume available to a mole is not v but actually $v - b$.

2) The true pressure is not p but $p + \dfrac{a}{v^2}$.

Motivate (2):

Consider a sphere of gas.

Any molecule in the interior is surrounded by molecules on all sides,

so it feels attracted approximately equally in all directions $\Rightarrow$ no net attraction.

Any molecule on the surface is attracted inward, because there are no

molecules outside it to balance the pull.

So $p_{observed} = p_{actual} - p_{\text{due to unbalanced attractions}}$

$p_{\text{due to unbalanced attractions}} \propto$

$\left(\dfrac{\#\text{molecules}}{\text{unit volume}} \text{ on surface, attracted inward} \right) \cdot \left(\dfrac{\#\text{molecules}}{\text{unit volume}} \text{ on next "layer" in, doing the attracting} \right)$

$p_{\text{due to unbalanced attractions}} \propto \left(\dfrac{N}{V} \right) \cdot \left(\dfrac{N}{V} \right)$

So $p_{actual} = p_{observed} + p_{\text{due to unbalanced attractions}} = p + \dfrac{\text{constant}}{v^2}$

Plug the corrections in, to get:

$$\left(p + \frac{a}{v^2} \right)(v - b) = RT$$

The equation of state for a real gas, the van der Waals equation of state