Briefly review the criteria for a heat reservoir (also called a thermostat). It is a system with a large number of energy levels distributed "quasi-continuously" so that one can speak of the density of energy levels $\sigma(E)\,dE$.

One has two requirements: The reservoir is supposed to have a total energy $E_0$. It gets connected to a small system whose energy levels are small. The first requirement is that

$$\frac{\sigma(E_0 + \Delta E)}{\sigma(E_0)} = e^{f_0 \Delta E}$$

is a good approximation for $\Delta E$ an energy level of the small system. Thus

$$\frac{d}{dE} \log \sigma \bigg|_{E_0} = f_0$$

and we want $\log(\sigma)$ to be linear to a good approximation around $E = E_0$.

The second requirement is that the actual behavior of the reservoir at energy $E_0$ should be very close to its thermal behavior. This means that in the partition function

$$Z(\beta) = \int e^{-\beta_0 E} \sigma(E)\,dE$$

the measure should peak near $E = E_0$ so that a steepest descent calculation is good.

$$Z(\beta) = \frac{Z(\beta_0)}{Z(\beta_0)} = e^{-\beta_0 E + \log \sigma} e^{\frac{1}{2} \frac{d^2}{dE^2} \log \sigma(E)} (E-E_0)^2 + \cdots$$

$$\frac{Z(\beta)}{Z(\beta_0)} = \frac{\int e^{-\beta_0 E} e^{-\beta_0 E + \log \sigma} \,dE}{\int e^{-\beta_0 E + \log \sigma} \,dE} \approx e^{-\Delta \beta E_0} \int e^{-(\Delta \beta)(E-E_0) - \frac{1}{2} (E-E_0)^2} \,dE$$
\[ \frac{Z(\beta)}{Z(\beta_0)} = e^{-(\Delta \beta) E_0 + \frac{1}{2} a (\Delta \beta)^2} \]

Now the steepest descent calculation is apt to be accurate when \( a \) is large. But this would mean that \( \log \sigma(E) \) is not very linear near \( E_0 \). So the two requirements are slightly inconsistent, as it appears.

Consider for example \( N \) copies of the same system with partition fn.

\[ Z(\beta) = \int e^{-\beta E \sigma(E)} dE. \]

Then

\[ Z_N(\beta) = Z(\beta)^N = \int e^{-\beta E \sigma_N(E)} dE \]

is the partition function for the ensemble (Notice: the thermal behavior of the ensemble is always easy to compute)

\[ \text{Let's compute } \sigma_N \text{ by steepest descent around } E_0 = N E_0 \]

where

\[ \varepsilon_0 = -\frac{\partial}{\partial \beta} \log Z(\beta) \bigg|_{\beta_0}. \]

\[ \sigma_N(E) = \frac{\int e^{\beta E - N \varepsilon_0} \beta^N d\beta}{\int e^{\beta E_0 + \log Z(\beta) N} d\beta} \]

\[ \frac{\sigma_N(E)}{\sigma_N(N E_0)} = \frac{\int e^{\beta E - N \varepsilon_0} \beta^N d\beta}{\int e^{\beta E_0 + \log Z(\beta) N} d\beta} \]

\[ \beta \varepsilon_0 + \log Z = \beta_0 \varepsilon_0 + \log Z(\beta_0) + \frac{1}{2} \frac{d^2}{d \beta_0^2} \log Z(\beta_0) \bigg|_{\beta_0} (\beta - \beta_0)^2 + \ldots \]

\[ \frac{\sigma_N(E)}{\sigma_N(N E_0)} = \frac{\int e^{\beta_0 (E - N \varepsilon_0) + (\beta - \beta_0) (E - N \varepsilon_0) + \frac{N}{2} \tilde{a} (\beta - \beta_0)^2} \beta^N d\beta}{\int e^{\frac{N \tilde{a}}{2} (\beta - \beta_0)^2} d\beta} = e^{\beta_0 (E - N \varepsilon_0) - \frac{1}{2N \tilde{a}^2} (E - N \varepsilon_0)^2} \]
Thus \[
\frac{\sigma_N(E)}{\sigma_N(N\varepsilon_0)} = e^{\beta_0 \Delta E - \frac{1}{2N\tilde{a}}(\Delta E)^2}
\]

where \(\Delta E = E - N\varepsilon_0\) and \(\tilde{a} = \frac{d^2}{d\beta^2} \log Z(\beta) \bigg|_{\beta_0}\)

Therefore one sees that for large \(N\), the quadratic part becomes negligible (for \(\log \sigma_N(E)\)). On the other hand, if one looks at the partition function

\[
Z_N(\beta) = Z(\beta)^N = \int e^{-\beta_0 E} \sigma_N(E) dE
\]

and asks about the relative distribution of measure, one should write

\[
\int e^{-\beta_0 E} \sigma_N(E) dE = N \int e^{-\beta_0 N\varepsilon} \sigma_N(N\varepsilon) d\varepsilon
\]

and notice that

\[
\frac{e^{-\beta N\varepsilon} \sigma_N(N\varepsilon)}{e^{-\beta N\varepsilon_0} \sigma_N(N\varepsilon_0)} = e^{-\frac{1}{2N\tilde{a}}(N(\varepsilon - \varepsilon_0))^2}
\]

so one does get the required concentration of the measure \(e^{-\beta_0 E} \sigma_N(E) dE\) near \(E = N\varepsilon_0\).

Let's go over thermo-potentials. Consider a heat engine executing a Carnot cycle between the temperatures \(T_1\) and \(T_2\).

\[
\text{efficiency } = \frac{\text{work done}}{\text{heat in}} = \frac{Q_1 - Q_2}{Q_1}
\]

The 2nd law of Kelvin definition of temperature says \(\frac{Q_1 - Q_2}{Q_1} \leq \frac{T_1 - T_2}{T_1}\).
hence \( 1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1} \), \( \frac{T_2}{T_1} \leq \frac{Q_2}{Q_1} \)

or \( \frac{Q_1}{T_1} \leq \frac{Q_2}{T_2} \) (can remember by looking at the case \( T_1 > T_2 \), \( Q_1 = Q_2 \))

For a general cycle, one breaks it up into little Carnot cycles to get the inequality of Clausius:

\[ \int \frac{dQ}{T} \leq 0 \]

with equality for a reversible engine. (dQ is not the differential of a function; it is also not the differential \( dU + pdV \) for irreversible changes. If I use \( dQ = dU + pdV \), then the above integral is zero.)

The entropy \( S \) satisfies \( ds = \frac{dU + pdV}{T} \) and hence for a reversible change from A to B we have

\[ \int_{A}^{B} \frac{dQ}{T} = S_B - S_A \]

and in general Clausius inequality gives

\[ \int_{A}^{B} \frac{dQ}{T} \leq S_B - S_A \]

Consider constant temperature changes

\[ \int_{A}^{B} dQ \leq TS_B - TS_A \]

Heat put into engine.
Example of an irreversible change: Joule experiment. Initially the gas is on one side with pressure \( p \), volume \( V \), temp. \( T \) and \( pV = nRT \).

The stopcock is opened and it is found that the temperature stays the same. Of course \( p \rightarrow p/2 \) because \( V \rightarrow 2V \). The process is irreversible because suppose we allowed the expansion to go slowly against a piston from \( V \) to \( 2V \). Then work is done so heat has to be added. In Joule expansion no work is done and no heat is added.

Let's compute the Clausius inequality in this case.

\[
S_B - S_A = \int \frac{dQ}{T} = \int \frac{pdV}{T} = \int nR \frac{dV}{V} = nR \log \left( \frac{V_B}{V_A} \right)
\]

Thus the entropy increase is \( nR \log \left( \frac{V_B}{V_A} \right) \) but the work done is 0.

Return to isothermal change where

\[
\int_{A}^{B} dQ \leq TS_B - TS_A
\]

heat in = \( U_B - U_A \) + work done. Therefore

\[
\text{work done} \leq F_A - F_B \quad F = U - TS
\]
If we have a change at constant pressure and temperature, then

\[ \text{work done} = p(V_B - V_A) \]

and so we get the inequality

\[ \phi_A \geq \phi_B \]

where \( \phi = U - TS + pV \)

for a change at constant temperature and pressure.
June 20, 1980

To see if I can get the Sackur-Tetrode formula \( Z \) from the vapor pressure of a crystalline solid. Assume the solid occupies zero volume and that it satisfies Einstein's model in that all the modes have the same frequency. Let \( n_s \) be the number of solid molecules. For a single oscillator

\[
Z = \frac{e^{-\beta \frac{1}{2} \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \quad U = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \approx \frac{1}{\beta} = kT
\]

\[
F = -\frac{1}{\beta} \log Z = \frac{1}{2} \hbar \omega + \frac{1}{\beta} \log (1 - e^{-\beta \hbar \omega})
\]

Thus

\[
F_0 = 3n_s \left( \frac{1}{2} \hbar \omega + kT \log (1 - e^{-\frac{\hbar \omega}{kT}}) \right)
\]

and since the volume is zero

\[
\phi_s = F_0 + pV = F_s
\]

Next look at the gas which is assumed to be ideal.

Thus

\[
U = \frac{3}{2} NkT \quad pV = NkT \quad H = U + pV = \frac{5}{2} NkT
\]

\[
T dS = dU + p dV = \frac{3}{2} Nk dT + d(pV) - V dp
\]

\[
dS = \frac{5}{2} Nk \frac{dT}{T} - Nk \frac{kT}{p} dp
\]

\[
S = Nk \log \left( \frac{T^{5/2}}{p} \right) + S_0(N)
\]

\[
\phi_g = H - TS = \frac{5}{2} NkT - NkT \log \left( \frac{T^{5/2}}{p} \right) - TS_0(N)
\]

At equilibrium with \( n_s \) solid molecules and \( n_g \) gas molecules we have \( \phi_s = \phi_g \) or

\[
3n_s \left( \frac{1}{2} \hbar \omega + kT \log (1 - e^{-\frac{\hbar \omega}{kT}}) \right) = \frac{5}{2} n_g kT - n_g kT \log \left( \frac{T^{5/2}}{p} \right) - TS_0(n_g)
\]
If you are given \( p, T \) and the total number of molecules, then this equation tells you how many gas + solid molecules there are, provided \( S_0(n) \) is known. Now I want there to be a \( p, T \) at which the solid + gas can interchange freely, which means that this equation should hold for all \( n_s, n_g \) with \( n_s + n_g = N \) constant. This seems to be impossible for this model. In effect \( S_0(n_g) \) has to be linear in \( n_g \), and
\[
-T S_0(n_g) = 3 N \left( \frac{1}{2} \hbar \omega + kT \log (1-e^{-\frac{\hbar \omega}{kT}}) \right)
\]
depends on \( N \).

So if we want a model which will exhibit vapor and gas in equilibrium we have to do something else. The basic problem is whether it is possible to have an equation \( \phi_s = \phi_g \) for all \( n_s, n_g \) with \( n_s + n_g = N \),
\[
\phi_s = \frac{n_s \phi_s}{N-n_g} = \frac{n_g \phi_g}{N-n_g}
\]
This relation can hold only if \( \phi_s = \phi_g = 0 \).
Yesterday I ran into difficulty with a solid + vapor in equilibrium. Possibly the difficulty is due to treating the number of molecules in the wrong way. One has to treat \( N \) "macroscopically," maybe, which means you form a grand ensemble and choose \( \mu \) appropriately, so I should go over chemical potential.

Recall the basic formulas:

\[
dU = TdS - pdV \\
dF = -SdT - pdV \\
d\phi = -SdT + Vdp \\
F = U - TS \\
\phi = U - TS + pV
\]

which hold provided the number of molecules of different types remains fixed. Suppose more generally we have different constituents, types of molecules, in our system and that the numbers \( n_i \) of these can change. Then one defines the chemical potential \( \mu_i \) by

\[
d\phi = -SdT + Vdp + \sum \mu_i dn_i
\]

i.e.

\[
\mu_i = \left( \frac{\partial \phi}{\partial n_i} \right)_{T, p}
\]

It follows that

\[
dF = -SdT - pdV + \sum \mu_i dn_i
\]

or

\[
\mu_i = \left( \frac{\partial F}{\partial n_i} \right)_{T, V}
\]

I need to get some feeling for this notion of chemical potential. Suppose we have a gas made up of \( \mathbf{N} \) particles in a box of volume \( V \). Suppose the \( \mathbf{N} \) particles repel each other. Then adding an
extra particle increases the energy, and \( \mu \) should be a positive quantity, so that lowering energy means fewer particles.

Make this quantitative: suppose the \( N \) particle gas described by partition function \( Z(T,V,N) \). Think of the system running through all the different energy states with the appropriate frequency. Then the internal or average energy is the appropriate average

\[
U = \langle E_x \rangle = -\left( \frac{\partial}{\partial \beta} \log Z \right)_{T,V,N}
\]

Now \( \mu \) is going to be like \( p \) in that you figure out how the energy changes without changing the probability distribution. One computes \( \frac{\partial E}{\partial N} \) for each occurring state and then averages. Thus

\[
\mu = \langle \frac{\partial E}{\partial N} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial N} \log Z(T,V,N)
\]

\[
= \left( \frac{\partial F}{\partial N} \right)_{T,V}
\]

(Check out the formulas: \( F = -\frac{1}{\beta} \log Z = -kT \log Z(T,V,N) \)

\[
U = -\frac{\partial}{\partial \beta} \log Z \quad p = \frac{k}{\beta} \frac{\partial}{\partial V} \log Z = -\frac{\partial F}{\partial V}
\]

\[
\mu = \frac{\partial F}{\partial N}
\]

\[
-\frac{\partial F}{\partial T} = \frac{\partial}{\partial T} (kT \log Z) = k \log Z + kT \left( \frac{\partial}{\partial T} \log Z \right) \frac{\partial}{\partial T} (\beta)
\]

\[
= k(\log Z + U\beta) = S
\]

so

\[
dF = -SdT -pdV + \mu dN
\]

Also

\[
du = d(F + TS) = TdS - pdV + \mu dN
\]
\[ \Delta Q = dU + pdV - \mu dN \]

and

\[ dU = \Delta Q - pdV + \mu dN \]

so that each particle adds extra energy \( \mu \).

The above is for fixed \( N \) and is not yet "macroscopic." To one forms the grand partition function

\[ Z_G(T, V, \mu) = \sum_N Z(T, V, \mu) e^{(\beta \mu) N} \]

which is a kind of Laplace transform with respect \( N \).

Assume this has a dominant term at \( N \), then

\[ \frac{\partial}{\partial N} \left( \log Z(N) + \beta \mu N \right) = \frac{\partial}{\partial N} \log Z + \beta \mu = 0 \]

or

\[ \mu = -\frac{\partial}{\partial N} \left( -\frac{\log Z(T, V, N)}{\beta} \right) = \frac{\partial F}{\partial N} \]

so that \( \mu \) is indeed the chemical potential at \( N \).

Approximating by dominant term gives

\[ Z_G \approx Z(N) e^{(\beta \mu) N} \]

\[ -\frac{\log Z_G}{\beta} \approx -\frac{\log Z(N)}{\beta} + \mu N \]

so that

\[ \Omega(T, V, \mu) = -\frac{1}{\beta} \log Z_G(T, V, \mu) \]

is the thermodynamic potential, then

\[ \Omega = F - \mu N = F - N \frac{\partial F}{\partial N} \]

is the Legendre transform of \( F(T, V, N) \) with \( N \).

New viewpoint: Let us start by being given \( \sigma(E, V, N) = \) number of states with energy \( E \), volume \( V \),
and \( N \) particles. Following Boltzmann we define
\[
S(E, V, N) = k \log \sigma(E, V, N)
\]
which immediately presents \( S \) as a function of \( E, V, N \) which are its natural variables. Then \( T, p, \mu \) can be defined by the fundamental relation
\[
TdS = dE + pdV - \mu dN
\]
The above is only reasonable "macroscopically." One normally Laplace transforms with respect to \( E \) or with respect to \( E, N \).

\[
Z(T, V, N) = \sum_E e^{-\frac{E}{kT}} \sigma(E, V, N)
\]

\[
Z_G(T, V, \mu) = \sum_{N, E} e^{\beta \mu N} e^{-\beta E} \sigma(E, V, N)
\]

Assume \( Z(T, V, N) = \sum_E e^{-\beta E} \sigma(E, V, N) \) has a dominant term when \( \frac{\partial}{\partial E} \log \sigma = \beta \). Then
\[
\log(Z) \approx -\beta E + \log \sigma
\]
is the Legendre transform of \( -\log \sigma(E, V, N) \) wrt \( E \). Thus we have
\[
-\frac{\partial}{\partial \beta} \log Z = E
\]
and
\[
S = k(\beta E + \log Z) = k \log \sigma
\]
The Laplace transform method, i.e. using \( S \) defined in terms of \( Z \) is somehow always correct even when (*) isn't.

Question: Why isn't Laplace transform wrt \( V \) used?
vapor pressure of a crystal: \( N \) atoms total, \( n \) in gas and \( N-n \) in solid. The problem is to compute the probability of \( n \) gas atoms. One has the partition fn.

\[
\sum \sum e^{-\beta E_a}
\]

and \( p_n \) is proportional to \( \sum e^{-\beta E_a} \) states with \( n \) gas molecules.

The picture used by Stern (I guess - see Fermi or Tolman books) is to assume that there is only one possible state for the solid having a given number of atoms, and that it has zero energy. Then there are two ways of getting the partition function:

1) distinguishable atoms. The \( N \) atoms have to be divided into solid + gas. This gives combinatorial factor:

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

different ways to assemble the unique solid state with \( (N-n) \) atoms.

Supposing the gas molecules have potential energy \( -\omega \) relative to the solid, and masses \( m \), the 1-gas molecule partition \( p_n \) is

\[
Z_1 = \int e^{-\beta \left( \frac{p^2}{2m} + \omega \right)} \frac{d^3p}{p^3} = e^{-\beta \omega} V \beta^{-\frac{3}{2}} (\frac{m 2\pi}{\hbar^2})^{\frac{3}{2}}
\]

The grand partition function is then
\[ Z = \sum_{n=1}^{N} \frac{N!}{n!} \left( e^{-\beta \omega} \sqrt{\beta} \left( \frac{2\pi m}{\hbar^2} \right)^{3/2} \right)^n \]

2) indistinguishable atoms. In this case the combinatorial factor is missing, but \( (Z_i)^n \) has to replaced by \( Z_i^n / n! \) for the gas atoms. However, still one is assuming only one solid configuration. Then
\[ Z = \sum_{n=1}^{N} \frac{1}{n!} \left( e^{-\beta \omega} \sqrt{\beta} \left( \frac{2\pi m}{\hbar^2} \right)^{3/2} \right)^n \]

Here is a good picture of the way the system looks:

![Diagram of solid and gas phases]

Note: The above model simply gives the grand partition function for an ideal gas with chemical potential \( \mu = -\omega \).

So now we can compute the expected value of \( n \) by maximizing probability:
\[ P_n \sim \frac{1}{n!} Z_i \]
\[ \log P_n = n \left[ e^{-\beta \omega} \sqrt{\beta} \left( \frac{2\pi m}{\hbar^2} \right)^{3/2} \right] - (n \log n - n) + \text{const} \]
\[ 0 = \frac{d}{dn} \log P_n = e^{-\beta \omega} \sqrt{\beta} \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} - \log n \]
\[ n = e^{\frac{-\omega}{kT}} \sqrt{\beta} \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} \]
Alternatively, we can use the partition function \( Z_0 \) directly to get the expected value of \( n \):

\[
\frac{1}{\beta} \frac{\partial}{\partial \beta} \log Z_0 = -\frac{1}{\beta} \frac{\partial}{\partial \beta} \left( e^{-\beta \omega} \sqrt{\beta^{-3/2} \left( \frac{2\pi m}{\hbar^2} \right)^{3/2}} \right)
\]

to get the same formula. (This is exact only as \( N \to \infty \).

For an ideal gas we have:

\[
\frac{p}{\beta} = e^{-\beta \omega} \sqrt{\beta^{-3/2} \left( \frac{2\pi m}{\hbar^2} \right)^{3/2}}
\]

\[
p = e^{-\beta \omega} \beta^{-3/2} \left( \frac{2\pi m}{\hbar^2} \right)^{3/2}
\]

or

\[
p = e^{-\frac{\omega}{kT}} (kT)^{3/2} \left( \frac{2\pi m}{\hbar^2} \right)^{3/2}
\]

This could be obtained more simply from:

\[
p = \frac{1}{\beta} \frac{\partial}{\partial \beta} \log Z_0
\]

Note: When the method of maximum probability is applied to

\[
Z_0 = \sum_{n=0}^{\infty} \frac{1}{n!} (e^{\beta \mu Z_1})^n = e^{\left( e^{\beta \mu Z_1} \right)}
\]

one gets:

\[
\log p_n = n \log (e^{\beta \mu Z_1}) - \log (n!) - \log (Z_0)
\]

\[
0 = \frac{d}{dn} \log p_n = \log (e^{\beta \mu Z_1}) - \log n
\]

or

\[
n = e^{\beta \mu Z_1}
\]

This is the same if one puts

\[
n = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_0
\]

This we have an example where maximum probability is exact.
Next problem to examine is where there is a fixed number \(N\) of atoms. Here we have to pay attention to the fact that the partition function is summed for \(0 \leq n \leq N\). If we use the maximum probability method then we don't see this cutoff until \(n = N\). Assuming \(N\) is large, the dominant term method ought to be pretty accurate.

Example: Consider \(e^n = \sum_{k=0}^{\infty} \frac{n^k}{k!}\) where \(n\) is large. The dominant term occurs when

\[
\frac{d}{dk} (k \log n - k!) = \log n - \log k = 0 \quad k = n
\]

Approximating the sum by its dominant term yields

\[
e^n \approx \frac{n^n}{n!} \quad \text{or} \quad n! \approx n^n e^{-n},
\]

which is OK by Stirling's formula.

So let's consider the partition function for the crystal-vapor system with \(N\) atoms.

\[
Z = \sum_{n=0}^{N} \frac{1}{n!} \left( e^{-\beta \mu_w} \beta^{-\frac{3}{2}} \left( \frac{2 \pi m \beta^{3/2}}{h^2} \right)^{3/2} \right)^n
\]

Let's use the dominant term method to compute the equation of state. \(T, V\) are the independent variables. The dominant term in the above series was computed above and gave

\[
n = V \beta^{-3/2} e^{-\beta \mu_w} \chi
\]

provided \(n \leq N\); otherwise the dominant term is \(n = N\). Let's fix the temperature and begin to increase \(V\). Then the number of gas atoms increases linearly with \(V\) until the solid is completely evaporated.
What is the pressure \( \bar{p} \) when \( n \leq N \)? In general

\[
p = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z
\]

It is clear that \( \frac{\partial}{\partial V} \) takes \( V^n \) to \( n V^{n-1} \), so that when one has the dominant term at \( n \):

\[
p = \frac{1}{\beta} \frac{n}{V} \quad \text{or} \quad \rho V = n k T
\]

which is the ideal gas law. From another viewpoint if the dominant term occurs for \( n \leq N \), then

\[
Z \sim e^{-\beta \omega V \beta^{-3/2} \omega} \implies \frac{1}{\beta} \frac{\partial}{\partial V} \log Z = \frac{1}{\beta} e^{-\beta \omega V \beta^{-3/2} \omega}
\]

which leads to the same result. Note

\[
p = \frac{1}{\beta} \frac{n}{V} = e^{-\beta \omega \beta^{-5/2} \omega}
\]

is the equation for the vapor pressure in terms of \( T \). This is constant as \( V \) goes from 0 to

\[
V = N \sqrt[3]{\beta^{-3/2} e^{-\beta \omega \omega}}
\]

As \( V \) increases beyond this point the dominant term in the partition function is the \( N \)-th, so

\[
Z \sim \frac{1}{N!} (e^{-\beta \omega V \beta^{-3/2} \omega})^N
\]

which is the partition function for \( N \)-molecules of an ideal monatomic gas, except for the factor \( e^{-\beta \omega \omega N} \) which contributes only a constant to the internal energy.

**Question:** Can one make the above approximations exact by making \( N \) "macroscopic"? Somehow let the parameters \( N, V \) go to infinity.
Consider the frozen solid which has a state of zero energy having \( N \) atoms for each \( N > 0 \). Thus
\[
Z(T, V, N) = 1 \quad \text{for all } N.
\]

Review the grand formalism: One puts
\[
Z_\mu(T, V, \mu) = \sum_{N > 0} (e^{\beta \mu})^N Z(T, V, N)
\]
If one is in a good situation, where the dominant term method works, then
\[
\log Z_\mu(\mu) = N(\beta \mu) + \log Z(N)
\]
where \( N \) is such that
\[
\beta \mu + \frac{2}{\beta} \frac{\partial}{\partial N} \log Z(N) = 0
\]
or
\[
\mu = -\frac{1}{\beta} \frac{\partial}{\partial N} \log Z(N) = \frac{2}{\beta} \left( -\frac{\log Z(N)}{\beta} \right)
\]
It follows that \( \frac{1}{\beta} \log Z_\mu(\mu) \) is the Legendre transform of \( \log Z(N) \)
so that
\[
\beta \frac{\partial}{\partial \mu} \log Z_\mu(\mu) = N
\]
In general one uses this formula relating \( \mu \) and \( N \) when the dominant term method doesn't work.
For example with \( Z(N) = 1 \) for all \( N \) we have
\[
Z_\mu(\mu) = \sum_{N > 0} (e^{\beta \mu})^N = \frac{1}{1-e^{\beta \mu}}
\]
and
\[
N = -\frac{1}{\beta} \frac{\partial}{\partial \mu} \log (1-e^{\beta \mu}) = \frac{e^{\beta \mu}}{1-e^{\beta \mu}} = \frac{1}{e^{\beta \mu}-1}
\]
Of course \( \mu \) has to be \( < 0 \) in order that this have any meaning. There is no resistance to adding more particles to the solid, so that in order to get a finite number
The partition function, when \( N \) atoms are present is
\[
\sum_{m=0}^{\infty} z(T/V/n) = \sum_{n=0}^{N} \left( \frac{e^{-\beta E_{m}}}{n!} \right) \]

\( z(T/V/n,m) = \frac{1}{n!} (e^{-\beta E_{m}})^{n} \)

\( Z(T/V,m) \) is the partition function for a single gas molecule:
\[
Z(T/V,m) = \frac{1}{n!} \left( \frac{Z(T/V)}{e^{-\beta E_{m}}} \right)^{n} \]

\( Z(T/V) \) is the partition function for the whole of gas.

The key point is to compute the grand partition function for the solid + gas.

We saw yesterday that we had the solid molecules and in gas molecules and that's what k so means. However, the larger \( N \) is, the less the tendency to grow is.

Notice: For \( T > 0 \)

The red box means to grow bigger -

\[
\mu = \frac{1}{kT} \ln \left( \frac{N!}{\Lambda} \right) \approx \frac{-kT}{N} \]

\( \Lambda \) = usual of the solid is \( \Lambda \), in fact

If particles we have to provide them with energy to keep them away. This we see that the chemical potential.

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Hence the grand partition function is

\[ Z_G(T, V, \mu) = \sum_N e^{\beta \mu N} \sum_{m+n=N} \frac{(e^{-\beta \mu} Z_1)^n}{n!} \]

\[ = \sum_{m, n} e^{\beta \mu (m+n)} \frac{(e^{-\beta \mu} Z_1)^n}{n!} \]

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

\[ Z_G = \frac{1}{1-e^{\beta \mu}} e^{\beta \mu (\mu - \omega)} Z_1 \]

\[ \log Z_G = -\log(1-e^{\beta \mu}) + e^{\beta (\mu - \omega)} Z_1 \]

Then \( \mu \) is to be determined so that

\[ N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G = \frac{e^{\beta \mu}}{1-e^{\beta \mu}} + e^{\beta (\mu - \omega)} V \beta^{-3/2} \lambda \]

Also

\[ p = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z_G = \frac{1}{\beta} e^{\beta (\mu - \omega)} \beta^{-3/2} \lambda = \frac{n}{\beta V} \]

so the vapor behaves like an ideal monatomic gas.

Suppose \( \beta, V, n \) fixed and we let \( n \) vary. We can solve

\[ N = \frac{1}{e^{\beta \mu} - 1} + n \]

for \( \mu \). Then we can determine \( V \).

\[ \lambda \sim \frac{kT}{n-n} \]
We see that because of the $\mu$ dependence in
\[ n = e^{\beta(\mu - \omega)} V \beta^{-\frac{3}{2}} \alpha \]
the volume $V$ is not a linear function of $n$. Consequently from $p = \frac{n}{\beta V}$ one sees that the pressure is not really constant as we vaporize the solid.

It would be nice to be able to plot in a $pV$ diagram an isothermal curve. Let's rewrite our basic equations in terms of $z = e^{\beta \mu}$ and the constants $\beta, \gamma = e^{-\beta \omega} \beta^{-\frac{3}{2}} \alpha$.

Then
\[ p = \frac{z}{\beta} \gamma \]
\[ N = \frac{z}{1 - z} + 2V \gamma \]

These are parametric equations for the isothermal curve.

\[ z = \frac{\beta}{\gamma} p \]
\[ \gamma z \frac{V}{N} = 1 - \frac{1}{N} \frac{z}{1 - z} \]
\[ \frac{V}{N} = \frac{1}{\gamma z} - \frac{1}{N} \frac{1}{\gamma (1 - z)} = \frac{1}{\beta p} - \frac{1}{N} \frac{1}{\gamma - \beta p} \]

Picture:

\[ p \]
\[ p = \frac{z}{\beta} \]
\[ \gamma z \frac{V}{N} = 1 - \frac{1}{N} \frac{z}{1 - z} \]
\[ \frac{V}{N} = \frac{1}{\gamma z} - \frac{1}{N} \frac{1}{\gamma (1 - z)} = \frac{1}{\beta p} - \frac{1}{N} \frac{1}{\gamma - \beta p} \]
\[ V/N \]
\[ pV = NkT \]
When these curves are put together one gets the isothermal \( p \)

\[
p = \frac{x}{\beta} = e^{-\beta x \beta^{-\frac{1}{2}}} = e^{-\frac{N}{kT} + \frac{3}{2} (\frac{\hbar^2}{2m})^{\frac{3}{2}}}
\]

and the larger \( N \) is the flatter the isothermal curve becomes at the beginning. As \( N \to \infty \) one gets
June 24, 1980

chemical potential approach. Ideal gas:

Method 1: \( Z(T, V, N) = \frac{1}{n!} (V \beta^{-\frac{3}{2} \alpha})^n \quad \alpha = \left( \frac{2\pi m}{h^2} \right)^{3/2} \)

\[
F = -\frac{1}{\beta} \log Z(N) = -\frac{1}{\beta} \left( n \log (V \beta^{-\frac{3}{2} \alpha}) - n \log n + n \right)
\]

\[
= -\frac{n}{\beta} \left( \log \left( \frac{V \beta^{-\frac{3}{2} \alpha}}{n} \right) + 1 \right)
\]

\[
P = -\frac{\partial F}{\partial V} = \frac{n}{\beta} \frac{1}{V} \quad \text{as usual.} \quad \therefore \frac{V}{n} = \frac{1}{\beta P}
\]

\[F = -\frac{n}{\beta} \left( \log \left( \frac{\beta^{-\frac{3}{2} \alpha}}{P} \right) + 1 \right)
\]

and so \( \phi = F + PV = F + \frac{n}{\beta} \alpha \)

\[
\phi = -\frac{n}{\beta} \log \left( \frac{\beta^{-\frac{3}{2} \alpha}}{P} \right) \quad \text{Gibbs potential for ideal monatomic gas}
\]

Recall \( \begin{cases} dU = TdS - pdV + \mu dn \\ dF = -SdT - pdV + \mu dn \\ d\phi = -SdT + Vdp + \mu dn \end{cases} \)

hence the chemical potential is given by

\[
\mu = \left( \frac{\partial \phi}{\partial n} \right)_{T,P} = -\frac{1}{\beta} \log \left( \frac{\beta^{-\frac{3}{2} \alpha}}{P} \right)
\]

Method 2: \( Z_0(T, V, \mu) = \sum_n e^{\mu n} Z(T, V, n) \). When the dominant term method works in this sum we have

\[
\log Z_0(\mu) = \beta \mu n + \log Z(n) \quad \text{where}
\]

\[n \text{ is such that } \mu = -\frac{1}{\beta} \left( \frac{\partial}{\partial n} \log Z(n) \right)_{T,V}
\]
June 25, 1980

Let's review the chemical potential approach to equilibrium between the solid and gas. First we need the chemical potential of the ideal gas.

Method I based upon \( Z(T, V, n) \), the \( n \)-particle partition function:
\[
Z(T, V, n) = \frac{1}{n!} \left( V \beta^{-3/2} \alpha \right)^n \quad \alpha = \frac{(2\pi m)^{3/2}}{h^3}
\]
The free energy is
\[
F = -\frac{1}{\beta} \log Z
\]
and one has
\[
dF = -SDT - p dV + \mu dn.
\]

Hence
\[
\mu = \left( \frac{\partial F}{\partial n} \right)_{T, V} = \frac{\partial}{\partial n} \left( -\frac{1}{\beta} \left( n \log (V \beta^{-3/2} \alpha) - n \log n + n \right) \right)
\]
\[
= -\frac{1}{\beta} \log (V \beta^{-3/2} \alpha) + \frac{\log n}{\beta}
\]
\[
\mu = -\frac{1}{\beta} \log \left( \frac{V \beta^{-3/2} \alpha}{n} \right) \quad \text{as a fn. of } T, V, n
\]

Also
\[
p = -\frac{\partial F}{\partial V} = \frac{n}{\beta} V \quad \text{or} \quad \frac{V}{n} = \frac{1}{\beta p}
\]

So
\[
\mu = -\frac{1}{\beta} \log (\beta^{-5/2} \alpha / p) \quad \text{as a fn. of } T, p, n.
\]

If the gas atoms have extra potential energy \( \omega \) then
\[
\mu = \omega - \frac{1}{\beta} \log (\beta^{-5/2} \alpha / p)
\]

Notice also that if we form the Gibbs free energy
\[
\phi = F + pV = -\frac{n}{\beta} \log \left( \frac{V \beta^{-3/2} \alpha}{n} \right) - \frac{V}{\beta} + \frac{\omega}{\beta}
\]
\[
\phi = -\frac{n}{\beta} \log \left( \frac{\beta^{-5/2} \chi}{\rho} \right)
\]

Then
\[
\mu = \left( \frac{\partial \phi}{\partial n} \right)_{T, \rho} = -\frac{1}{\beta} \log \left( \frac{\beta^{-5/2} \chi}{\rho} \right) \quad \text{as it should be.}
\]

Method 2 based upon grand partition fn.
\[
Z_6(T, V, \mu) = \sum_n e^{\beta \mu n} Z(T, V, n)
\]

When dominant term method works, we have
\[
\log Z_6 \approx \beta \mu n + \log Z \quad \text{where } \beta \mu + \frac{\partial}{\partial n} \log Z = 0
\]

and hence we get the formula
\[
\frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_6 = n
\]

\[
F(T, V, n) = -\frac{1}{\beta} \log Z(T, V, n)
\]

\[
F(T, V, n) = -\frac{1}{\beta} \log Z_6(T, V, \mu) + \mu n
\]

where
\[
n = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_6(T, V, \mu)
\]

These formulas are used even when dominant term method doesn't work.

For ideal gas, \( Z_6(T, V, \mu) = e^{\beta \mu V} \beta^{-3/2} \chi \)

so
\[
n = e^{\beta \mu V} \beta^{-3/2} \chi
\]

and
\[
\rho = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_6 = e^{\beta \mu} \beta^{-3/2} \chi
\]

Next consider the solid where \( Z(T, V, n) = 1 \) for all \( n \). In this case we have to use the grand partition fn.
\[
Z_6(T, V, \mu) = \sum e^{\beta \mu n} = \frac{1}{1 - e^{\beta \mu}}
\]
Then
\[ n \frac{\partial}{\partial \mu} \log \left( \frac{1}{1 - e^{\beta \mu}} \right) = \frac{e^{\beta \mu}}{1 - e^{\beta \mu}} \]

\[ n = \frac{c e^{\beta \mu}}{1 - e^{\beta \mu}} \quad c \begin{array}{l}
\end{array} = \frac{n}{n+1} \quad \mu = \frac{1}{\beta} \log \left( \frac{n}{n+1} \right) \]

Equilibrium between solid and vapor at constant \( T, V \) is achieved when the Helmholtz free energy
\[ F_s + F_g \]

is minimum.

Equilibrium at constant \( T, p \) is achieved when the Gibbs free energy
\[ \phi_s + \phi_g \]

is minimum.

These must be minimized as \( n_s, n_g \) vary subject to \( n_s + n_g = N \). Thus (when \( dT = dp = 0 \)) at equilibrium
\[ d(\phi_s + \phi_g) = \mu_s dn_s + \mu_g dn_g = 0 \]
\[ dN = dn_s + dn_g = 0 \]

which means that
\[ \mu_s = \mu_g \]
determines \( n_s, n_g \).

This is the same condition whether we work at constant \( T, V \) or constant \( T, p \).

In the solid-vapor system
\[ \mu_s = \frac{1}{\beta} \log \frac{n_s}{n_s + 1} \]
\[ \mu_g = \omega - \frac{1}{\beta} \log \left( \frac{\beta^{\frac{5}{2}} \lambda}{p} \right) = -\frac{1}{\beta} \log \left( \frac{e^{-\beta \omega} \beta^{-\frac{3}{2}} \lambda}{\beta p} \right) \]
\[ n_s = \mu_s = \mu_g \] means

\[ n_{s+1} = 1 + \frac{1}{n_s} = \frac{x}{\beta p} \]

\[ n_s = \frac{\beta p}{y - \beta p} \]

equilibrium

condition

since \( n_s = N - n_g = N - pV\beta \), we get

\[ N - pV\beta = \frac{\beta p}{y - \beta p} \]

\[ \frac{N}{\beta p} - V = \frac{1}{y - \beta p} \]

or

\[ \frac{V}{N} = \frac{1}{\beta p} - \frac{1}{Ny - \beta p} \]

which is the equation of state derived before.
The goal is to understand solid ↔ vapor when the solid is described by the Einstein or Debye model. Take the Einstein model where

\[ Z(T, \beta, n) = \left( \frac{e^{\beta \frac{1}{2} k_B T}}{1 - e^{-\beta k_B T}} \right)^n Z_1 \]

Then

\[ F = -\frac{1}{\beta} \log Z = -\frac{3n}{\beta} \log Z_1 \]

and

\[ \mu = \frac{\partial F}{\partial n} = -\frac{3}{\beta} \log Z_1 \quad \text{is independent of } n. \]

But if we form

\[ Z_G(T, \beta, \mu) = \sum e^{\beta \mu n} Z(T, \beta, n) = \frac{1}{1 - e^{\beta \mu} Z_1^3} \]

Then

\[ n = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G = \frac{e^{\beta \mu} Z_1^3}{1 - e^{\beta \mu} Z_1^3} \]

\[ e^{\beta \mu} Z_1^3 = \frac{n}{n+1} \]

\[ \therefore \mu = -\frac{3}{\beta} \log Z_1 + \frac{1}{\beta} \log \left( \frac{n}{n+1} \right) \quad \text{depends on } n \]

However these two formulas agree in the limit as \( n \to \infty \).

In some sense the second formula is the more correct one.

---

Compare equilibrium condition \( \mu_s = \mu_g \) with the use of the grand partition fn. for the system.

\[ Z_G = \sum_{m,n} Z_s^T(T, V, m) Z_g(T, V, n) e^{\beta \mu (m+n)} \]
Clearly $Z_G = Z_s Z_g$. The condition that $N$ atoms total be present is

\[ N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_s + \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_g \]

I've already seen how this leads to an equation of state. Now if one defines $\mu_s$ as a function of $n_s$ via

\[ n_s = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_s(\mu_s) \]

and similarly define $\mu_g$ as a function of $n_g$, then (10) is equivalent to

\[ N = n_s + n_g \quad \text{and} \quad \mu_s = \mu_g. \]

So (10) and $\mu_s = \mu_g$ lead to the same equation of state.

Recall equation of equilibrium:

\[ \mu_s = -\frac{3}{\beta} \log Z_s + \frac{1}{\beta} \log \frac{n_s}{n_s+1} = \mu_g = -\frac{1}{\beta} \log \left( \frac{\beta}{\gamma} \right) \]

where $\gamma = e^{\beta s \xi} \beta^{-3/2}$. Thus

\[ 1 + \frac{1}{n_s} = \frac{n_s+1}{n_s} = \frac{\gamma}{\beta \beta Z_s^3} \]

\[ n_s = \frac{\beta \beta Z_s^3}{\gamma - \beta \beta Z_s^3} = N - n_g = N - pV/\beta \]

\[ \frac{V}{N} = \frac{1}{\beta} - \frac{1}{N} \frac{Z_s^3}{\gamma - \beta \beta Z_s^3} \]

Same except that $V$ is replaced by $V Z_s^{-3}$.
Note that the vapor pressure is given by
\[ p = \frac{\delta}{\beta} Z_1^{-3} = e^{-\beta \omega} \beta^{-\frac{3}{2}} \alpha Z_1^{-3} \]
where \[ Z_1 = \frac{e^{-\beta \omega}}{1 - e^{-\beta \omega}}. \]
Notice that this is what we obtain if we use
\[ \mu_s = -\frac{3}{\beta} \log Z_1 = \mu_g = -\frac{1}{\beta} \log \left( \frac{\delta}{\beta} \right) \]
based on \( Z(T_m) \)

and so we see that \( \mu_s \) as computed from \( Z(T_m) \) is correct in the large \( n_s \) limit.
Equilibrium for ideal gas reactions. Suppose we have a container with $T, V$ fixed in which there are three gas molecules of types $A, B, C$ which can react according to the scheme

$$A + B \leftrightarrow C.$$ 

We want to determine the equilibrium concentrations of these were no reaction, then our container would hold $n_A, n_B, n_C$ molecules and the partition function would be

$$Z(T, V, n_A, n_B, n_C) = \frac{(Z_i^A)^{n_A}}{n_A!} \frac{(Z_i^B)^{n_B}}{n_B!} \frac{(Z_i^C)^{n_C}}{n_C!} \tag{1}$$

where $Z_i^A$ is the partition function for a single $A$ molecule:

$$Z_i^A = V \beta^{-3/2} \sqrt{A} \quad \alpha_A = \frac{(2\pi m_A)^{3/2}}{h^3}$$

if $A$ were monatomic (better - only translational degrees of freedom). Actually, because of the interaction, the numbers $n_A, n_B, n_C$ can vary so that

$$n_A + n_C = \text{const} \quad \text{say } N_A$$

$$n_B + n_C = \text{const} \quad \text{say } N_B$$

and so the partition function is

$$Z(T, V, N_A, N_B) = \sum_{\substack{n_A + n_C = N_A \\ n_B + n_C = N_B}} Z(T, V, n_A, n_B, n_C) \tag{2}$$

Also in going from $C$ to $A + B$ some internal energy (represented by electronic energy = molecular orbitals) changes.
Thus in the 1-particle partition function there belongs an potential energy term \( e^{-x} \) where \( x \) is the ground state energy. This is a first approximation where we assume the higher molecular orbitals are not excited. Later one can add things like rotational, vibrational, and electronic energy to the 1-molecule partition functions.

Returning to (2) lets first determine the equilibrium condition by the dominant term method:

\[
\frac{\partial}{\partial n_c} \log Z(T, V, n_A, n_B, n_C) = 0
\]

where \( n_A, n_B \) are regarded as functions of \( n_C \). What this amounts to is to take the free energy

\[
F(T, V, n_A, n_B, n_C) = -\frac{1}{\beta} \log Z(T, V, n_A, n_B, n_C)
\]

\[
= F_A(T, V, n_A) + F_B(T, V, n_B) + F_C(T, V, n_C)
\]

and then require \( dF \) to be zero while \( dT = dV = 0 \)

and \( dn_A + dn_C = dn_B + dn_C = 0 \). Thus

\[
0 = dF = \mu_A \, dn_A + \mu_B \, dn_B + \mu_c \, dn_C
\]

\[
= (-\mu_A - \mu_B + \mu_c) \, dn_C
\]

and so the equilibrium condition is

\[
\mu_A + \mu_B = \mu_c
\]

where

\[
\mu_A = \left( \frac{\partial F_A}{\partial n_A} \right)_{TV}
\]

etc.
Next consider a reaction
\[ aA + bB \leftrightarrow cC + dD. \]

Look at the vector \((n_A, n_B, n_C, n_D)\). This can change by a multiple of \((a, b, -c, -d)\) so that
\[ d(n_A, ..., n_D) \] proportional to \((a, b, -c, -d)\).

Thus the equilibrium condition
\[ 0 = dF = \mu_A \, dn_A + ... + \mu_D \, dn_D \]
becomes
\[ \mu_A \, a + \mu_B \, b - \mu_C \, c - \mu_D \, d = 0 \]
or
\[ \frac{a}{\mu_A} + \frac{b}{\mu_B} = \frac{c}{\mu_C} + \frac{d}{\mu_D} \]

---

Return to \( A + B \leftrightarrow C \). Suppose
\[ Z_1^A = V \beta^{-3/2} \alpha_A \, e^{-\beta \omega_A} \]
\[ \alpha_A = \frac{(2\pi m A)^{3/2}}{\hbar^3} \]

Then
\[ F(T, V, n_A) = -\frac{1}{\beta} \log \frac{(Z_1^A)^n_A}{n_A!} \]
\[ = -\frac{n_A}{\beta} \left( \log \left(V \beta^{-3/2} \alpha_A \, e^{-\beta \omega_A}\right) - \log n_A + 1 \right) \]
\[ \mu_A = -\frac{1}{\beta} \log \left(\frac{V \beta^{-3/2} \alpha_A \, e^{-\beta \omega_A}}{n_A}\right) \]
\[ = \frac{1}{\beta} \log \left(\frac{n_A}{V \beta^{-3/2} \alpha_A \, e^{-\beta \omega_A}}\right) \]

So the condition \( \mu_A + \mu_B = \mu_C \) becomes
\[
\frac{(n_A/V)(n_B/V)}{(n_C/V)} = \frac{\alpha_A \alpha_B}{\alpha_C} \beta^{-3/2} e^{-\beta(\omega_A + \omega_B - \omega_C)}
\]

Suppose we work at constant pressure and temperature. Then we want to use

\[
\mu_A = \frac{1}{\beta} \log \left( P_A \beta^{5/2} \alpha_A e^{-\beta \omega_A} \right)
\]

which leads to the formula

\[
\frac{P_A P_B}{P_C} = \beta^{-5/2} \frac{\alpha_A \alpha_B}{\alpha_C} \beta(\omega_A + \omega_B - \omega_C)
\]

for equilibrium. Chemists like to write this as follows.

The free energy for the \( A \)-gas is

\[
\phi_A = \frac{N_A}{\beta} \log \left( P_A \beta^{5/2} \alpha_A e^{-\beta \omega_A} \right)
\]

so \( \mu_A \) is just the Gibbs free energy per molecule. At constant temperature \( T \) one has

\[
\mu_A = \frac{1}{\beta} \log (P_A) + \text{const}
\]

So that if \( \mu_A^0 \) = chemical potential at \( P_A = 1 \) we have

\[
\mu_A - \mu_A^0 = \frac{1}{\beta} \log (P_A)
\]

Thus

\[
\log \left( \frac{P_A P_B}{P_C} \right) = -\beta \left( \mu_A^0 + \mu_B^0 - \mu_C^0 \right)
\]

free energy change per molecule at the temp. \( T \) from standard.