" A vague discomfort at the thought of the chemical potential is still characteristic of a physics education. This intellectual gap is is due to the obscurity of the writings o f J.Willard Gibbs who discovered and understood the matter 100 years ago."

C.Kittel; Preface to his book : Introduction to Solid State Physics

Lets first remind ourselves of the definition of the chemical potential μ. We start with *a* system of energy E and Volume V and several kinds of species labeled by i. The number of each kind is N_i . The entropy if the system is *a* fuction of the following variables $S = S(E, V, N_i)$ we can then write

$$dS = \left(\frac{dS}{dE}\right)_{V,N} dE + \left(\frac{dS}{dV}\right)_{E,N} dV + \sum_i \left(\frac{dS}{dN_i}\right)_{E,V,N} dN_i$$

where keeping N constant means that you keep all N ' s constant except N_i . Now if we remember that $dS = \frac{dQ}{T} = \frac{dE+pdV}{T}$ when the number of particles is kept constant we can identify

$$\left(\frac{dS}{dE}\right)_{V,N} = \frac{1}{T} \quad \text{and} \quad \left(\frac{dS}{dV}\right)_{E,N} = \frac{p}{T}$$

and we will define the chemical potential $\mu_i = -T\left(\frac{dS}{dN_i}\right)_{E,V,N}$

so $dS = \frac{dE}{T} + \frac{p}{T} dV - \sum_i \frac{\mu_i}{T} dN_i$

We can rewrite this as $dE = TdS - pdV + \sum_i \mu_i \, dN_i$

Now lets assume we have a process where S, V,

and N are kept constant then we can also write $\mu_i = \left(\frac{dE}{dN_i}\right)_{S,V,N}$

The Helmholtz free energy is defined as $F = E - TS$

$dF = d(E - TS) = dE - TdS - SdT =$

$$TdS - pdV + \sum_i \mu_i \, dN_i - TdS - SdT = -SdT - pdV + \sum_i \mu_i \, dN_i$$

If we have a process where T, V, N are kept constant then $\mu_i = \left(\frac{dF}{dN_i}\right)_{T,V,N}$

Here you can see that the idea that the chemical potential is the energy needed to create a particle is consistent with the definition.

Finally the Gibbs Free energy is defined as $G = F + pV$

$dG =$

$$-SdT - pdV + \sum_i \mu_i \, dN_i + pdV + Vdp = -SdT + VdP + \sum_i \mu_i \, dN_i$$

If we have a process where T, p, N are kept constant then $\mu_i = \left(\frac{dG}{dN_i}\right)_{T,p,N}$

Now lets treat a problem where we only have two types of molecules for the moment (like ice and water) which transform into each other 1 to 1 at some sort of phase transition. I will loosten this requirment up later. We keep the energy constant and the volume constant and maximize the entroy to find the equilibrim conditions. So we have as constraints

$$E_1 + E_2 = E = \text{Constant},\ V_1 + V_2 = V = \text{Constant},$$
$$N_1 + N_2 = N = \text{Constant}$$

and we maximize S =

$$S\,(E_1, V_1, N_1, E_2, V_2, N_2)$$ **So lets do this.**

$$dS = dS_1 + dS_2 = 0$$

and using what we found for dS above

$$dS = \left(\frac{1}{T_1}\,dE_1 + \frac{p_1}{T_1}\,dV_1 - \frac{\mu_1}{T_1}\,dN_1\right) + \left(\frac{1}{T_2}\,dE_2 + \frac{p_2}{T_2}\,dV_2 - \frac{\mu_2}{T_2}\,dN_2\right) = 0$$

we use the constraints in diferential form

$$dE_1 + dE_2 = dE = 0,\ dV_1 + dV_2 = dV = 0,$$
$$dN_1 + dN_2 = dN = 0$$

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)dN_1 = 0$$

Since this must be true for arbitrary dE, dV, dN we get

$$\frac{1}{T_1} - \frac{1}{T_2} = 0;\ \frac{p_1}{T_1} - \frac{p_2}{T_2} = 0;\ \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} = 0$$ **and finally we get**

$$T_1 = T_2;\ p_1 = p_2;\ \mu_1 = \mu_2;$$

Its clear that the temperatures and pressures must be equal. What helps , is to think about the chemical potentials as

$\mu_1\,(T, p) = \mu_2\,(T, p)$.

Now lets go to the problem we are interested in. I will now have a reaction u + d $\longleftrightarrow \pi$ (its a funny pion)

I will write it as $-u - d + \pi = 0$.

We will write a general chemical equation in the form

$\sum_{i=1}^{3} b_i B_i = 0$ **where we have the various species denoted by B_i – in this case the b_i ' s are -1 -1 and 1, and the B_i' s are u,d,π**

We will hold the volume and energy constant. The numbers of the species N_i cannot vary arbitrarily because we have to end up conserving the quarks whether they are free or bound up in a pion. The constraint equation (instead of $N_1 + N_2 = N =$ constant) is $dN_i = \lambda b_i$

where λ is a constant of proportionality. We will once again maximize the entropy to find the equilibrium conditions i.e. set $dS = 0$. Again use the equation from above

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

$\sum_i \mu_i dN_i = 0$ **since $dV = 0$ and $dE = 0$**

Now using the constraint eqn we get $\sum_i \mu_i \lambda b_i = 0$

and finally we get the condition for chemical equilibrium

$$\sum_i b_i \mu_i = 0$$

Now suppose we had made assumed that T and V are constant, then we would have used the condition that F is minimum and gotten the same eqn. The chemical potential are functions of the particular variables describing the system. For instance $\mu_i = \mu_i (E, V, N_j)$ if E anv V are chosen as the independent variables etc.

So now we see that for baryons $\mu_b = 3 \mu_q$

How do we use all of this? If one knows the Free energy F (T, V, N_i), we assume that a transition occurs between the species. To find the equilibrium conditions we minimize the free energy

$$dF = \sum \mu_i b_i = 0$$

where $\mu_i = \left(\frac{dF}{dN_i}\right)_{T,V,,N}$ **The task is then to find the free energy and hence the chemical potentials of the system**

Now I will attempt to do this for an ideal gas, i.e. lets assume that the u, d quarks and pions behave as an ideal gas. Now let the possible states of a particles be labeled by s_k and ϵ_k be the energy in this state

$$E = \epsilon_1(s_1) + \epsilon_2(s_2) + \epsilon_3(s_3) + \epsilon_4(s_4) + \epsilon_5(s_5) + \ldots$$

to the total number of particles.

We can write the partition function as Z ' =

$$\sum_{s_1, s_2, s_3,} \exp\{-\beta[\epsilon_1(s_1) + \epsilon_2(s_2) + \epsilon_3(s_3) + \epsilon_4(s_4) + \epsilon_5(s_5) + \ldots]\} =$$

$$\left(\sum_{s_1} e^{-\beta\epsilon_1(s_1)}\right)\left(\sum_{s_2} e^{-\beta\epsilon_2(s_2)}\right)\left(\sum_{s_3} e^{-\beta\epsilon_3(s_3)}\right)\ldots$$

In the following

1 = u, 2 = d, 3 = π

There will be N_i factors for all species of types 1, 2, 3 and we define the partition function for a single particle

$$\zeta_i = \sum_s e^{-\beta\epsilon(s)}$$

So Z ' = $\zeta_1^{N_1}\zeta_2^{N_2}\zeta_3^{N_3}$ **Now we need to fix things up for indistiguishability**

$$Z = \frac{\zeta_1^{N_1}\zeta_2^{N_2}\zeta_3^{N_3}}{N_1!\,N_2!\,N_3!} = Z_1 Z_2 Z_3 \text{ where } Z_i = \frac{\zeta_i^{N_i}}{N_i!} \text{ and } \ln Z = \sum_i \ln Z_i,$$

This last eqn is an important relation since it states that the partition functions are just the sum of the partition functions of

the various species and the thermodynamic functions (E, F, G)

are simply addative. This of course assumes that the molecules

are weakly interacting. All this stuff is classical and will for

quantum mechanics correspond to Maxwell Boltzmann statistics

which is probably ok for the temperatures we will be dealing with

Now lets calculate the chemical potential from the free energy

$$F = -kT\ln Z = -kT \sum_i (N_i \ln\zeta_i - \ln N_i!) = -kT \sum_i N_i (\ln\zeta_i - \ln N_i + 1)$$

where I have used Stirlings formula ln n! =

n ln n − n − another useful formula is

$$\frac{d \ln (N!)}{dN} = \ln N$$

$$\mu_j = \left(\frac{dF}{dN_j}\right)_{T,V,N} = -kT (\ln\zeta_j - \ln N_j) = -kT \ln \frac{\zeta_j}{N_j}$$

Lets now get the equilibrium constant from chemistry and then I

will figure out what that constant is for some quarks and hadrons

If you forgot what an equilibrium constant is

(and the law of mass action) suppose you make water

$$-2\,H_2 - O_2 + 2\,H_2\,O = 0$$

then we can know how much we have of each

if we know the equilibrium constant K defined as

$$K_N (T, V) = \frac{N_{H_2 O}}{N_{H_2}{}^2\, N_{O_2}}$$

The free energy change is

$$dF = \sum \mu_i b_i = -kT \sum b_i (\ln\zeta_i - \ln N_i) = dF_0 + kT \sum b_i \ln N_i$$

where $dF_0 = -kT \sum b_i \ln\zeta_i$

dF_0 **is the "standard free−energy change of the reaction" which depends on T and V but not on** N_i **. It iss an intensive variable. We want to set** $dF = 0$ **so we get**

$$\frac{-dF_0}{kT} = \sum b_i \ln N_i = \ln (N_i^{b_1} N_2^{b_2} N_3^{b_3} \ldots)$$

and finally we can define the equilibrium constant $K_N(T, V)$ **as**

$K_N(T, V) =$

$$\exp\left(-\frac{dF_0}{kT}\right) = N_i^{b_1} N_2^{b_2} N_3^{b_3} \ldots = \exp\left(\sum b_i \ln\zeta_i\right) = \zeta_1^{b_1} \zeta_2^{b_2} \zeta_3^{b_3} \ldots$$

recall $\zeta_i = \sum_s e^{-\beta\epsilon(s)}$ **and the** b_i **are the numbers in the constraint eqn.**

So for our case

$$K_N(T, V) = \frac{N_\pi}{N_u N_d}$$

Now Lets try to calculate ζ_i **and hence**

get an expression for the chemical potential

$$\mu_j = -kT \ln \frac{\zeta_j}{N_j}$$

OK, so do do this we need to evaluate $\zeta_i = \sum_{r_i} e^{-\beta \epsilon_{r_i}}$

where r_i **enumerates the states of molecule type i. We will assume a non − relativistic single particle to eneumerate the states. I will try to do the relativistic case later. In the classical case fixing it up for Quantum mechanics which worries about the uncertainty prinicple to bring in** $\hbar$

This will be

$$\zeta_i = \frac{1}{h^3} \int_{-\infty}^{\infty} d^3 r \int_{-\infty}^{\infty} \exp\left(\frac{-\beta\,(p_{ix}{}^2 + p_{iy}{}^2 + p_{iz}{}^2)}{2\,m}\right) d\,p_x\, d\,p_y\, d\,p_z =$$

$$\frac{V}{h^3}\left(\int_{-\infty}^{\infty} \exp\left(\frac{\beta p^2}{2\,m}\right) d\,p\right)^3$$

However see Reif pp 353 − 360 where this is done by the standard particle in a box method where one makes an equivalent box in phase space and sums over $n_{x,y,z}$ **by finding the volume in n − space. We find**

$$\zeta_j = \frac{V}{(2\,\pi\,\hbar)^3}\left(\frac{2\,\pi m_j}{\beta}\right)^{3/2} = \frac{V}{\hbar^3}\,(2\,\pi m_j\,kT)^{3/2}$$

So now lets put it all together :

define $n_j = \frac{N_j}{V}$

$$\mu_j =$$

$$-kT\,\ln\left[\frac{1}{\hbar^3\,n_j}\,(2\,\pi m_j\,kT)^{3/2}\right]$$ **for j = up or down for the two quarks**

$$\mu_\pi = -kT\,\ln\left[\frac{1}{\hbar^3\,n_\pi}\,(2\,\pi m_\pi\,kT)^{3/2}\right]$$

Now I am going to do this relativistically since we would now like to create pairs. Really I need to reevaluate

$\zeta_i = \sum_{r_i} e^{-\beta \epsilon_{r_i}} = \sum_{r_i} e^{-\beta \sqrt{p_{r_i}{}^2 c^2 + m^2 c^4}}$ **which is a pain. I found the answer on the web. But I will cheat and just add the rest mass into the chemical potential. For the pion I will also add an extra factor ϵ_0 which represents the "binding energy" for the pion. There will be a requirement on this. I will leave out c^2 and the masses of the quarks will be m_q**

$$\mu_j = -kT \ln\left[\frac{1}{\hbar^3 n_j} (2\pi m_q kT)^{3/2}\right] + m_q$$

$$\mu_\pi = -kT \ln\left[\frac{1}{\hbar^3 n_\pi} (2\pi m_\pi kT)^{3/2}\right] + m_\pi + \epsilon_0$$

Now I am going to assume that we are at T_C where we have the requirement from before now written out explicitely that

$\sum \mu_i b_i = 0 = -\mu_u - \mu_d + \mu_\pi$ **so** $\mu_\pi = \mu_u + \mu_d$

I ignore the spins of the quarks, colors etc

$$2\, kT \ln\left[\frac{1}{\hbar^3 n_q} (2\pi m_q kT)^{3/2}\right] - 2 m_q =$$

$$kT \ln\left[\frac{1}{\hbar^3 n_\pi} (2\pi m_\pi kT)^{3/2}\right] - m_\pi - \epsilon_0$$

$$\frac{1}{\hbar^3}\left(\frac{2\pi}{\beta}\right)^{\frac{3}{2}} \frac{m_q{}^3}{n_q{}^2} e^{-2\beta m_q} = \frac{m_\pi{}^{3/2}}{n_\pi} e^{-\beta m_\pi} e^{-\beta \epsilon_0}$$

or solving for the equlilibrium constant

$$\frac{n_q{}^2}{n_\pi} = \left(\frac{2\pi}{\beta \hbar^2}\right)^{3/2} \left(\frac{m_q{}^2}{m_\pi}\right)^{3/2} e^{\beta (m_\pi - 2 m_q + \epsilon_0)}$$

Where now you see the relationship between the masses, the number densities and the "biniding energy". This really does not make sense, but I think what it is telling us is that the ideal gas approximation is lousy near T_C and that there is some potential that is not taken into consideration which is driving the quarks together to make pions.

We can solve for the equilibrium constant with some assumptions about the quark masses. Lets also assume that m_π, m_q and ϵ_0 are functions of the temperature then are.

$$\frac{n_q^2}{n_\pi} = \left(\frac{2\pi}{\beta\hbar^2}\right)^{3/2} e^{\beta(m_\pi - 2m_q + \epsilon_0)} = aT^{3/2} e^{b(T)/T}$$

As long as $b(T) = (m_\pi - 2m_q + \epsilon_0) < 0$ this makes some sense. If T gets bigger then there are more quarks, if T gets smaller then there are more pions.

If it becomes positive, then the formula is funny in that it gets large for T either small or large. (we might be able to do something to fix this case us if the masses have a jump at T_C)

The problem of course is that below T_C there should be no quarks and presumably above T_C there should be no pions, but this doesnt hold true for this eqn. The problem is that in a phase transition, the free energy should have a singurity, and of course, the energy for the ideal gas doesnt have this. Note that for a first order phase transition, the first derivative of the Free energy has a discontinuity

of is ill defined. Ror a second order phase transition,

the second derivative of F has a discontinuity or is ill defined.

Also, where are the gluons? In any case,

if the free energy, or the partition function has a singularity,

then μ will have a jump. (I will comment on the relationship

between this fact and μ across a phase transition in a next.)

$$\sum_i b_i \mu_i = 0$$

is the reqirement. In our case where we assume that 2

quarks makes a pion then we will require $\mu_q + \mu_{\overline{q}} = \mu_\pi$

Now the chemical potential $\mu_j = \left(\frac{dF}{dN_j}\right)_{T,V,N}$

can be a function of Temperature. Since
the first derivative of F will have a
discontinuity at the phase transition,
μ will have a jump. Now lets suppose we have
a different system, like ice and water. Then
our equation for chemical potential is
$\mu_{water} = \mu_{ice}$ across the phase transition. Nevertheless,
the μ' s do change. Just like the fact that $T_{water} = T_{ice}$
for a system in equlibrium,
but the T' s are changing as we bring
a system through the phase transition.

The final resolution of the problem

of the masses and and chemical potential is

1. the chemical potentials do have to be equal if there is

only one species that changes phase (like water) ,

but if there are several (our case), then its the equation $\sum_{i} b_i \mu_i = 0$

As long as these eqations are obeyed then the system is in equilibrium but the chemical potentials can change. In our case, I believe they jump due to the change in mass.

2. The chemical potential tells us how hard it is to make a particle. When we are near Tc its complicated and involves a lot more than the masses – it also involves whatever potentials that are in the system – that is what confinement and chiral symmetry breaking are about. What someone has to do is to give us the right Hamiltonian at Tc so we can calculate the correct energy to put into the partition function.

So lets try to make a model. Remember

$$\sum_{i=1}^{3} b_i B_i = 0$$

where we have the various species denoted by B_i –

$$\sum_i b_i \mu_i = 0 \text{ for chemical equilibrium}$$

I change my notation a bit.

$$\mu_j = -kT \ln\left[\frac{1}{\hbar^3 n_j} (2\pi M_q kT)^{3/2}\right] + M_q(T)$$

$$\mu_\pi = -kT \ln\left[\frac{1}{\hbar^3 n_\pi} (2\pi M_\pi kT)^{3/2}\right] + M_\pi(T) + \epsilon_0(T)$$

$$\frac{n_q^2}{n_\pi} = \left(\frac{2\pi}{\beta\hbar^2}\right)^{3/2} \left(\frac{M_q^2}{M_\pi}\right)^{3/2} e^{\beta(M_\pi+\epsilon_0-2M_q)}$$

Let the values of $M_\pi(T)$ and $M_q(T)$ be the temperature dependent values of the masses and $\epsilon_0(T)$ the binding energy of the pion. Now lets just take the dressed quark masses that Fries et al use.

Below Tc we know $M_q(T > T_c) = M_q = 260$ MeV

Above T_c $M_q(T > T_c) = 5$ MeV

Below T_c $M_\pi = 135$ MeV

Above T_c $M_\pi = ? = x$

Below T_c $\epsilon_0 = ? = 385$ (which I calculate below)

Above T_c $\epsilon_0 = 0$ (the pions have no binding energy)

For ease let set the binding energy below Tc

$M_\pi - 2M_q + \epsilon_0 = 0$ so $\epsilon_0 = 2M_q - M_\pi = 2(260) - 135 = 385$

So then now we can solve for M_π above T_c by requireing n_q^2 / n_π just below T_c to be the same as just above T_c

Now from above, so that the equations make sense and we will use the chemical eqilibirum condition on to find x and $\epsilon_0(T)$ start below T_c . I will use 170 MeV for T_c

$$\left(\frac{2\pi}{\beta\hbar^2}\right)^{3/2}\left(\frac{M_q{}^2}{M_\pi}\right)^{3/2} e^{\beta\,(M_\pi+\epsilon_0-2\,M_q)} = \left(\frac{2\pi}{\beta\hbar^2}\right)^{3/2}\left(\frac{M_q{}^2}{M_\pi}\right)^{3/2} e^{\beta\,(M_\pi+\epsilon_0-2\,M_q)}$$

$$\frac{3}{2}\,(2\,\ln M_q - \ln M_\pi) + \beta\,(M_\pi + \epsilon_0 - 2\,M_q) = \frac{3}{2}\,(2\,\ln M_q - \ln M_\pi) + \beta\,(M_\pi + \epsilon_0 - 2\,M_q)$$

$$\frac{3}{2}\,(2\,\ln 260 - \ln 135) + \frac{(135 + 385 - 2 * 260)}{170} = \frac{3}{2}\,(2\,\ln 5 - \ln x) + \frac{x - 2 * 5}{170}$$

$$9.32 = 4.828 - \frac{3}{2}\,\ln x + \frac{x}{170} - .0588$$

$$4.5508 = \frac{x}{170} - \frac{3}{2}\,\ln x$$

$$773.636 = x - 225\,\ln x$$

$x = 40$ MeV ??