ENSEMBLES AND ALL THAT
Physics 664 Statistical Mechanics

Ensembles are mental constructs that contain replicated systems chosen in such a way as to mimic real systems. There are different kinds of ensembles depending on the nature of the systems of interest, but all of which have much in common. We will begin by developing the formalism for the **Canonical Ensemble** because it illustrates the mechanics of the problem at hand and is mathematically the most tractable. However, it may be helpful to first contrast the more elementary but less abstract method often used in introducing statistical thermodynamics for the first time in the typical undergraduate course on the subject. The following table compares the 'System/Ensemble' method of J. Willard Gibbs (1902) with the more elementary 'Particle/System' method of Boltzmann, 1877.

COMPARISON OF THE ENSEMBLE/SYSTEM FORMALISM VS THE SYSTEM/PARTICLE FORMALISM

ENSEMBLE/SYSTEM FORMALISM	SYSTEM/PARTICLE FORMALISM
Stirlings formula is exact as $N_{SYSTEMS} \to \infty$	$N_{PARTICLES} << \infty$ so Stirling's formula is approximate
Systems are macroscopic so labels are okay	Real particles do not come with labels
Systems can be composed of strongly interacting particles	This formalism assumes weak interactions between particles
$S = k \log \Omega(N,V,E)$ follows logically from the mathematics and thermodynamics	$S = k \log \Omega(N,V,E)$ must be postulated (Boltzmann, 1877)
Harder to describe the 'single particle' partition function since the system partition is the natural identity	The single particle partition function is the natural identity

First, some definitions:

System:
A hypothetical enclosure of volume V containing N particles at temperature T that is constructed (mentally) to replicate a real system of interest. The walls of the system are diathermal and closed. The system has an associated energy state spectrum $\{E_i\}$ that is some combination of the constantly fluctuating states of the individual particles making up the system. We make no assumptions at this point regarding the nature of the particles, their state or the nature of how they interact – strongly, weakly or not all. Because the particle energy states making up the system change constantly due to collisions, interactions and the natural time evolution of the particle wave functions, the specific energy state of the system will also change with time. What does not change is the *spectrum* of possible energies available to the system (the system is isothermal), although again, we cannot know those details either. Consequently, fluctuations can occur over time in the mechanical variables like the energy and pressure, but V, N and T remain fixed in our system.

Canonical Ensemble:
Now consider an adiabatically sealed structure (hence isolated) consisting of N_T ($N_T \to \infty$) identical systems of the type described above, and all of which are embedded in a common heat bath and are therefore in thermal equilibrium, i.e., the systems in the ensemble are

isothermal. All systems are defined by exactly the same T, V, N and energy state spectrum, {E_i}. Furthermore, we assume that the thermal interactions between systems do not influence their energy state spectrums. Thus, T, V, N and {E_i} are the same for all N_T systems making up the ensemble. Finally we assume the systems are macroscopic and can be labeled.

Constraints:
Since the ensemble is isolated, it will be characterized by a fixed energy $E_T = \sum n_i E_i$ where E_T = constant. We can also speak of the number of systems, n_i, in the ith **system** energy state where $\sum n_i = N_T$ and E_i is the energy of the ith system state.

SIMPLE EXAMPLE – THE BABY ENSEMBLE

The following table illustrates the case of four systems A, B, C, and D with an available energy state spectrum consisting of with only four energies. For purposes of illustration, we assume nothing about the values of the E_i's, so while $N_T = 4$ we don't specify E_T except to say that it is a constant for the ensemble. We will further assume that our little ensemble is limited to exactly three possible distributions as seen in the first column of the following table. It should be noted however that not specifying the energies is equivalent to assuming that all four energies are the same in which case you can show that the actual number of possible ensemble states for our 'Baby Ensemble' is 256 = $(\text{number of states})^{N_T}$. For now, three distributions or 17 ensemble states is enough to get a feel for the process.

BABY ENSEMBLE

Ensemble States	E1	E2	E3	E4	Ω (n)	$P_{dist} = \dfrac{\Omega(n)}{\Omega_T(n)}$
Dist. 1	ABCD	-	-	-	1	1/17
Dist. 2	AB	C	D	-	12	12/17
	AB	D	C	-		
	AC	B	D	-		
	AC	D	B	-		
	AD	B	C	-		
	AD	C	B	-		
	BD	C	A	-		
	BD	A	C	-		
	BC	A	D	-		
	BC	D	A	-		
	CD	A	B	-		
	CD	B	A	-		
Dist. 3	ABC	-	-	D	4	4/17
	ABD	-	-	C		
	ACD	-	-	B		
	BCD	-	-	A		

Ensemble State:

An ensemble state is realized by specifying the number of systems, or occupation number of every energy state in the ensemble. However there is no way to know which systems are in a specific E_i ... for even one system much less for all $N_T \to \infty$, so our only choice is to assume an *a-priori* approach where we are forced to assume that every system can visit every energy state consistent with our constraints on N_T and E_T.

Thus in our example above, it is not sufficient to say for example, that Dist. 2 has two systems in state E_1 and one system in each of the states E_2 and E_3 because these systems are macroscopic, can be labeled and therefore be realized in 12 equivalent ways. In this case we would say Dist. 2 represents 12 ensemble states or alternatively, Dist. 2 is 12 fold degenerate. Likewise, Dist.1 can be realized in one way and Dist. 3 in four ways. These numbers of systems in each distribution are called the 'occupation' numbers of the distributions, viz, if we write $(n) = \{n_1, n_2, ...\}$ then for Dist. 1: $n_1 = 4$, Dist. 2: $n_1 = 2$, $n_2 = 1$, $n_3 = 1$. For this simple case we can specifically compute the degeneracy of each distribution from the usual combinatorial expression $\Omega(n) = N_T! \Big/ \prod_i n_i!$ (see page 22 of your text) for distinguishable systems. This is how $\Omega(n)$ in Column 6 of the table was calculated. The sum of the degeneracy's over all distributions is then the total degeneracy of the ensemble.

Thus our example ensemble has some 17 possible ensemble states based on three possible distributions, but real ensembles have nearly an infinite number of possible configurations. The question that arises is this: is there a preferred or most probable distribution amongst the huge number of possibilities? In our little ensemble, Dist. 2 is the most likely but for real systems it is impossible to know so we are forced to assume, a priori, the following:

Postulate 1):

All $\Omega_T(\text{ensemble}) = \sum_{\{n\}} \Omega(n)$ ***ensemble states are postulated to be equally probable.***

Ensemble states are generated by specifying how many systems in the ensemble are in each of the (almost infinite) energy states E_1, E_2,.. available to every system and consistent with the constraints on E_T and N_T. Thus, in our example, we must assume all 17 possible states are equally probable.

STATEMENT OF THE PROBLEM:

Our basic goal is to compute P_i which can be thought of in following equivalent ways:

- Probability that a system chosen at random is in the ith energy state E_i, or
- Fraction of the systems in the ith energy state at any time, or
- Fraction of time that a system chosen at random is in the ith energy state

Once we have P_i we can calculate averages of the mechanical variables like pressure and energy from the relationship: $\bar{G} = \sum_i P_i G_i$. This brings us to the second postulate:

Postulate 2):
It is assumed that the time average of any mechanical variable, G[p(t), q(t)]

$$\overline{G}_{time} \equiv G_{obs} = \frac{1}{\tau}\int_{t_0}^{\tau+t_0} G[p(t),q(t)]dt \quad \textbf{where } \tau \textbf{ is large enough to eliminate fluctuations,}$$

is equal to the ensemble average of the same variable, i.e.,

$$\overline{G}_{time} = \overline{G}_{ensemble} = \sum_{states} P_i G_i \quad \textbf{where the sum is over all system states.}$$

What we need then is an expression for calculating P_i for an arbitrary system chosen at random.

CALCULATION OF P_i:

Suppose our ensemble consists of a single distribution and for illustration purposes take Dist. 2 in the example above to represent our ensemble. Calculation of P_i, for all four energy states is straight forward, viz,

P_i for Distribution 2

	$P_i = n_i/N_T$
P_1	2/4
P_2	¼
P_3	¼
P_4	0

where $\Omega(n) = \Omega(n_1 = 2, n_2 = n_3 = 1, n_3 = 0)$. In column 2 we used the intuitive relationship for the probably, $P_i = n_i/N_T$, for a single distribution but this won't work for when we want P_i for an ensemble consisting of many distributions. In that case we must include the degeneracy for each distribution and then sum over all possible sets of occupation numbers. So our next task is to generalize $P_j = n_j/N_T$ to multiple distributions.

We write now for n_j

$$n_j = \left\{ \begin{array}{l} \text{total systems in state j of distribution} \\ \text{n summed over all distributions} \end{array} \right\} = \sum_{\{n\}} \Omega(n)n_j(n)$$

Our probability is then,

$$P_j = \left\{ \begin{array}{l} \text{fraction of systems in state} \\ \text{j for all distributions} \end{array} \right\} = \frac{n_j}{\{\text{total systems in all states of all distributions}\}}$$

$$= \frac{\sum_{\{n\}} \Omega(n)n_j(n)}{\sum_{states}\sum_{\{n\}} \Omega(n)n_j(n)}$$

Example: P_1 for the Baby Ensemble:

$$P_1 = \frac{[1*4+2*12+3*4]}{[1*4+2*12+3*4]+[0+1*12+0]+[0+1*12+0]+[0+0+1*4]} = 10/17$$

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But, for any specific distribution n, we can write,

$$\sum_{states}\sum_{\{n\}}\Omega(n)n_j(n) = \sum_{states}n_j(n)\sum_{\{n\}}\Omega(n) = N_T\sum_{\{n\}}\Omega(n)$$

i.e., $N_T = \sum_{\{states\}}n_j(n)$ since for any particular distribution, the sum of the n_j over all possible energy states must add to the total number of systems in the ensemble, that is, every system in the ensemble must be accounted for when we sum over all states for a fixed distribution.

We finally have our desired recipe for calculating P_j, namely,

$$P_j = \frac{1}{N_T}\frac{\sum_{\{n\}}\Omega(n)\,n_j(n)}{\sum_{\{n\}}\Omega(n)}$$

and which is a completely general result for an arbitrary ensemble.

The sum in the numerator says: pick a j and then look at the first distribution. Multiply the number of systems in that distribution by its degeneracy. Then move onto the next distribution for that same j value. Do this for all distributions for a given j making sure to sum the values for each distribution. Then divide by the denominator which is just the total degeneracy times the number of systems. You then have P_j.

Applying our expression for P_j to our baby-ensemble above, we have:

P_1	[1/(4*17)] * [1*4 + 12*2 + 4*3] = 10/17
P_2	[1/(4*17)] * [12*1] = 3/17
P_3	[1/(4*17)] * [12*1] = 3/17
P_4	[1/(4*17)] * [4*1] = 1/17

Note that the P_i's sum to 1 as they should. We can also compute the average energy of the ensemble if we arbitrarily assign some values to the E_i's, eg, if E_1=5, E_2=10, E_3=15 and E_4=20 then $E_{avg} = \sum_i E_i P_i$ = 145/17 = 8.53.

We mentioned earlier that not specifying the values of the E_i's was tantamount to assuming they were all equal in which case one can show that the total degeneracy is given by

$$\Omega_T = \sum_{\{n\}}\frac{N_T!}{\prod_{n_i} n_i!} = [\text{number of states}]^{N_T}$$

and subject only to the restriction that

$$\sum_{\{n\}} n_i = N_T$$

Thus, our Baby Ensemble really has some $4^4 = 256$ possible energy states – something you might wish to confirm.

You can also apply our general expression for P_j to the previous case where we assumed the ensemble consisted of only distribution 2, to get $P_j = [1/(4*12)] \times [2*12] = \frac{1}{2}$ as before.

METHOD OF THE MOST PROBABLE DISTRIBUTION:
The expression for P_j that we have just derived is a general expression but as it stands is of limited value because the sums are not computable due to the fact that the number of systems is assumed to be infinite. That's the bad news. The good news is that we can take advantage of the bad news. *It is precisely the immensity of the problem that allows us to use the remarkable fact that for sums of this kind, there will always exist a single most probable distribution whose degeneracy is so overwhelmingly much greater than the degeneracy of all other distributions that our problem reduces to determining only one set of distribution numbers in our expression for P_i. First though, we need to justify this extraordinary fact.*

PROOF OF THE MAXIMUM TERM METHOD
We now give a short proof of our assertion that 'only the largest term in the sum need be considered', is true. Following McQuarrie (also see Wikipedia – search on 'Maximum Term Method in Statistical Mechanics) we define S as the sum over the degeneracy, i.e.,

$$S = \sum_{N=1}^{M} T_N = T_1 + T_2 + ... + T_M$$ where T_N is positive for all N and the maximum value of T, i.e.

T_{max}, resides somewhere in the set T_1 to T_M but where is unknowable due to the immensity of the problem. For out purposes, it only matters that there is a maximum term. This enables us to write,

$$T_{max} \leq S \leq MT_{max}$$

which says that S is bounded by the maximum term, and the product of the number of terms M, and the value of the maximum term.

Taking logs of both sides changes nothing in terms of the relative bound so we have,

$$\ln T_{max} \leq \ln S \leq \ln M + \ln T_{max}$$

Now in statistical mechanics we find typically that $T_{max} \sim O(10^M)$ where $M \approx 10^{20}$ or larger, in which case we have,

$$10^{20} \leq \log S \leq 10^{20} + \log M$$

Thus, we find that $\ln S$ is bracketed by $\ln T_{max}$ since log M is negligible, that is,

$$\ln T_{max} \leq \ln S \leq \ln T_{max}$$

and conclude that $\ln S = \ln T_{max}$, that is, the sum itself is equal to its largest value, a result whose importance cannot be overstated.

Another way of viewing this result that emphasizes the nature of the factorial to grow really big in a hurry (in fact the only reason these approximations work at all is because of this property of the factorial) is the expression:

$\underset{M_{max}\to\infty}{\text{limit}} \log \sum_{k=1}^{M_{max}} k! \sim \log M!_{max}$ where, unlike the expression for S above, the sum is

monotonically increasing. Note that again, we are replacing the sum by its largest term. So how good is this approximation? The error for M=10 is 0.7% and for M=150 it's already about 0.001%. Assuming the error for $M \approx 10^{20}$ or greater is vanishingly small we now derive the expression for the probability of the jth system state P_j

$$P_j = \frac{1}{N_T} \frac{\sum\limits_{\{n\}} \Omega(n) n_j(n)}{\sum\limits_{\{n\}} \Omega(n)} \cong \frac{1}{N_T} \frac{\Omega(n*) n_j(n*)}{\Omega(n*)} = \frac{n_j(n*)}{N_T} \equiv \frac{n_j^*}{N_T}$$

where n_j^* is the number of systems in the jth energy state **of the most probable distribution,** and that is precisely what we are after – provided of course that we can figure how to compute the value of n in the most probable distribution.

Our problem now boils down to determining the set of occupation numbers {n*} that correspond to the most probable distribution which is the one with the largest degeneracy. In other words we want to maximize,

$$\Omega(n) = \frac{N_T!}{\prod\limits_i n_i!}$$

subject to the constraints,

$$\sum_i n_i = N_T \text{ and,}$$

$$\sum_i n_i E_i = E_T$$

Once we have the set {n*} we have $P_j = \dfrac{n_j^*}{N_T}$ which is the basis for everything we do from

now on.

Maximizing $\Omega(n) = \dfrac{N_T!}{\prod\limits_i n_i!}$ is done by taking the logs of $\Omega(n)$, using Stirlings approximation,

adding in the constraints on N_T and E_T through the use of Lagrange Multipliers, differentiating and then solving for the general term n_i^* which maximizes Ω. This I leave to you folks (see problem 1-49 of your text).

Our result, after a bit of mucking about is:

$$n_j^* = N_T e^{-\alpha} e^{-\beta E_j}$$

which is the recipe for finding the set of occupation numbers that define the most probable distribution, $\Omega(n^*)$. The Lagrange Multipliers, α and β will be discussed in class and in your text, assuming you bought one.

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$$n_j^* = N_T e^{-\alpha} e^{-\beta E_j}$$

STATISTICAL MECHANICS
Ensemble Homework Problems

1) Consider an ensemble of just 3 systems A, B, and C with three energy states, E_1, E_2, and E_3 available to each system.

	E_1	E_2	E_3	$\Omega(n)$	P_{dist}
Dist 1					
Dist 2					
Dist 3					
Dist 4					
Dist 5					
Dist 6					
Dist 7					
Dist 8					
Dist 9					
Dist 10					
P_j					

Here $\Omega(n)$ = degeneracy of the nth distribution, and P_{dist} its probability in the ensemble. The numbers you are to put into the boxes are the occupation numbers eg, 2,1,0 etc. assuming **no** restrictions on E_{total}. Make sure you can write out all 27 possible ensemble states in terms of A, B and C corresponding to the 10 possible distributions. Then, calculate the total degeneracy, $\Omega_T(n)$, of each distribution and the total degeneracy of the entire ensemble thus verifying the formula:

$$\sum_{all\,distributions} \frac{N_T!}{\prod_{n_i=1}^{s} n_i!} = s^{N_T}$$

where the only restriction is: $\displaystyle\sum_{all\,distributions} n_i = N_T$

and s = number of energy states available to each system (3 systems and 3 energy states in this case). How would you rationalize the right hand side of this formula? Now compute the probability of each ensemble energy state P_1, P_2 and P_3 using:

$$P_j = \frac{1}{N_T} \frac{\sum_{\{n\}} \Omega(n)\, n_j(n)}{\sum_{\{n\}} \Omega(n)}$$

The next problem does assume a restriction on E_T as well as N_T.

2) A little more realistic problem uses the constraints on N_T and E_T. So let $E_1 = E_2 = 2$ and $E_3 = E_4 = 3$ and $E_5 = 4$ where $E_{total} = 12$ and $N_T = 4$. Again, write out all possible occupation numbers for the ensemble distributions. Then calculate the degeneracy for each distribution as before. Finally, calculate the probabilities of all five system states. Using these results, compute the average energy of a system picked at random from the ensemble and confirm that it equals E_T/N_T.

	$E_1=2$	$E_2=2$	$E_3=3$	$E_4=3$	$E_5=4$	$\Omega(n)$	P_{dist}
Dist 1							
Dist 2							
Dist 3							
Dist 4							
Dist 5							
Dist 6							
Dist 7							
Dist 8							
Dist 9							
Dist 10							
Dist 11							
Dist 12							
Dist 13							
Dist 14							
Etc. ??							
P_j							

Using the table compute:

$$\bar{E} = \sum_{states} P_i E_i =$$

$$\bar{E} = E_T / N_T =$$

Question: what would the total degeneracy, Ω_T, of the ensemble be *if all of the E_i's were the same?* _____

What would the average energy be in this case? _____

Evaluation of The Lagrange Multipliers α and β

We have (problem 1-49 in your text):

$$n_j^* = N_T e^{-\alpha} e^{-\beta E_j}$$

Where n_j^* = no. of systems in the jth energy state of the most probable distribution an N_T = total systems,

Evaluation of α

From

$$\sum_j n_j^* = \sum_j N_T e^{-\alpha} e^{-\beta E_j} = N_T \qquad \text{true for every dist., not just } n^*.$$

so

$$e^{-\alpha} = \frac{1}{\sum_j e^{-\beta E_j}} \qquad \text{and}$$

$$n_j^* = \frac{N_T e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \qquad \text{Go to 8.2}$$

Evaluation of β

The usual procedure consists of two parts:

a) Deriving a standard thermodynamic relationship using S.M. and then comparing with that same formula from thermodynamics & identifying the relationship for β. Our author starts with the relationship

$$\bar{E}(N,V,\beta) = \frac{\sum_j E_j(N,V) e^{-\beta E_j(N,V)}}{\sum_j e^{-\beta E_j(N,V)}}$$

And proceeds to derive the expression

$$\left(\frac{\partial \bar{E}}{\partial V}\right)_{N,\beta} + \beta \left(\frac{\partial \bar{P}}{\partial \beta}\right)_{N,V} = -\bar{P} \qquad \bar{P} - avg. \ pressure$$

to be be compared with the thermodynamic formula

$$\left(\frac{\partial E}{\partial V}\right)_{N,T} + \frac{1}{T}\left(\frac{\partial P}{\partial\left(\frac{1}{T}\right)}\right)_{N,V} = -P$$

Then, identifying the SM averages of E & P ie. $\bar{E}$ & $\bar{P}$ w
E & P Thermodynamics, we have:

$$\beta = \frac{constant}{T}$$

which brings us to the next step.

b) Now one must show that the constant is universal for all substances. This is typically done by analyzing an ensemble consisting of 2 or more different substances. In any case we conclude that

$$\beta = \frac{1}{KT} \qquad K = 1.380... \times 10^{-23} \ JK^{-1}$$

where $K \equiv$ Boltzmann constant. See your text for details.

Partition Function for a System

We define the system partition function as

$$Q = \sum_i' e^{-\beta E_i(N,V)} \qquad \beta = \frac{1}{kT}$$

Where the sum is over all energy states accessible to every system in the ensemble that conform to symmetry rules for acceptable wave functions.

Probability Function for the Canonical Ensemble

We now have

$$n_j^* = N_T e^{-\alpha} e^{-\beta E_j} = \frac{N_T e^{-E_j/kT}}{\sum_i e^{-E_i/kT}} \quad \text{OR}$$

$$P_j \equiv \frac{n_j^*}{N_T} = \frac{e^{-\beta E_j(N,V)}}{Q}$$

where P_j is the prob. that a system observed randomly will be in the jth energy state of the ensemble.

Canonical Ensemble Averages

We have:

$$\overline{G}_{system} = \sum_{states}' P_j G_j = \frac{1}{Q} \sum_j' G_j e^{-\beta E_j(N,V)} \quad \text{where}$$

G_j is some mechanical property of each system and now identify

$$\overline{G}_{system} \underset{\substack{2nd \\ postulate}}{\longleftrightarrow} G_{obs} = G_{thermo}$$

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Heat, Work and Entropy

We have:

1) $\bar{E} = \sum E_i P_i$ where

2) $P_j = \dfrac{n_j^*}{N_T} = \dfrac{e^{-\beta E_j}}{Q}$

Now $E_i = E_i(N,V)$ so for fixed N, we have from 1

3) $d\bar{E}_{sm} = \sum E_i dP_i + \boxed{\sum P_j dE_j} = \sum E_i dP_i + \sum P_j \left(\dfrac{\partial E_j}{\partial V}\right)_N dV$

but $P_j = \left(\dfrac{\partial E_j}{\partial V}\right)_N = \boxed{\text{pressure of system in the } j^{th} \text{ energy state}}$

so

4) $d\bar{E}_{sm} = \sum E_i dP_i + \sum P_j P_j dV = \sum E_i dP_i + \boxed{\bar{P}\,dV}$

From 3) and the First Law we can write

$dE_{rev} = dQ_{rev} + dW_{rev} = dQ_{rev} + P\,dV_{sys}$ Thermodynamics

$\longleftrightarrow d\bar{E}_{sm} = \sum E_i dP_i + \underbrace{\boxed{\sum P_j dE_j}}_{\bar{P}\,dV}$ statistical Mech

we have

$dQ_{rev} = \sum E_i dP_i$ ie, heat added causes a change in dP_j or the time a system is in E_j

$dW_{rev} = \sum P_j dE_j$ ie, work done causes a shift in the entire energy level spectrum due to a change in volume.

We can also take logs of both sides of (2) & solve for E_j and sub. into (4) to get:

5) $d\bar{E} = -\dfrac{1}{\beta}\sum_i [\log P_j + \log Q]\,dP_j - \bar{P}\,dV$

Which can be reduced to

$$d\bar{E} = -\frac{1}{\beta} d\left[\sum_j P_j \log P_j\right] - \bar{P}dv \quad \text{since} \quad \sum dP_j = d\sum P_j = \emptyset$$

$$\text{and } d\left[\sum P_j \log P_j\right]$$

$$= \sum \log P_j \, dP_j$$

and since, again

$$d\bar{E} = TdS - Pdv \quad \text{we have the identification,}$$

6) $$TdS = -\frac{1}{\beta} d\left[\sum_j P_j \log P_j\right]$$

<u>which holds</u> <u>for all</u> <u>ensemble types</u>; is of fundamental importance.

<u>Thermodynamic Relationships - Canonical Ensem.</u>

We have from 6) and $\beta = \frac{1}{kT}$

$$dS = -\frac{1}{T\beta} d\left[\sum_j P_j \log P_j\right] = -k \cdot d\left[\sum_j P_j \log P_j\right]$$

OR $$\boxed{S = -k \sum_j P_j \log P_j}$$

Now substitute

$$P_j = \frac{e^{-\beta E_j}}{Q}$$

to get

$$S = \frac{\bar{E}}{T} + k\log Q \iff \frac{\bar{E}}{T} - \frac{A}{T} \quad \text{since } A = E - TS$$

OR $$\boxed{A = -kT \log Q}$$ where $A = A(N,V,T)$; $Q = Q(N,V,T)$

Which gives us finally the characteristic eq'n for the canonical ensemble:

$$dA = -SdT - PdV + \sum_i \mu_i dN_i$$

So we now have:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,n} = kT\left(\frac{\partial \log Q}{\partial T}\right)_{V,N} + k\log Q$$

$$P = kT\left(\frac{\partial \log Q}{\partial V}\right)_{T,N}$$

$$E = kT^2\left(\frac{\partial \log Q}{\partial T}\right)_{V,N}$$

$$\mu_i = -kT\left(\frac{\partial \log Q}{\partial N_i}\right)_{T,V,N}$$

$$A = -kT\log Q$$

We see then that Q serves as the bridge linking the microscopic world to the macroscopic.

Microcanonical Ensemble

Consists of an ensemble of system selected from a canonical ensemble all of which are in the same energy <u>level</u> whose degeneracy is Ω. All the systems are at the same temperature, contain the same no. of particles and have the same volume, ie, N,V,T.

Each selected system is then isolated so there is no interaction between systems in the ensemble.

Since our M.C. ensemble is just a special case of a canonical ensemble the expression for the entropy must hold:

$$S = -k \sum_j P_j \log P_j .$$

and since all systems are constrained to a single energy level E whose degeneracy is Ω then the prob. of the jth <u>energy state</u> P_j is given by:

$$P_j = \frac{1}{\Omega}$$

so

$$S = -k \sum \frac{1}{\Omega} \log \frac{1}{\Omega} = -k \left[\frac{1}{\Omega} \log \frac{1}{\Omega} + \frac{1}{\Omega} \log \frac{1}{\Omega} + \cdots \right]$$

$$= -k \, \Omega \cdot \frac{1}{\Omega} \log \frac{1}{\Omega}$$

$$= -k \log \frac{1}{\Omega} \qquad \text{since there are } \Omega \text{ terms in the sum.}$$

$$= k \log \Omega \qquad \text{introduced by Boltzmann as a postulate.}$$

Comments

1) S increases w increasing degeneracy

2) Since $S = K \log \Omega$ so $\Omega = e^{S/k}$ where $S \approx \overbrace{NK}^{R} = N$ so
we have:

$$\Omega \approx e^{10^{23}} \approx 10^{N}$$

exp. result

for a system of N particles which justifies our
assertion that $T_{max} = \Omega(n^*) \approx 10^{10^{20}}$.

Characteristic Equation

For the M.C.E we have

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

so

$$\frac{1}{KT} = \left(\frac{\partial \log \Omega}{\partial E} \right)_{N,V}$$

$$\frac{P}{KT} = \left(\frac{\partial \log \Omega}{\partial V} \right)_{N,E}$$

$$\frac{\mu}{KT} = -\left(\frac{\partial \log \Omega}{\partial N} \right)_{V,E}$$

$$S = K \log \Omega (N, V, E)$$

Comment

The M.C.E. is of limited value since real systems
are not isolated etc. but as we shall see
due to the nature of fluctuations, all ensembles
are basically microcanonical in nature.

Grand Canonical Ensemble

Thermodynamic System:

Open WRT both energy & particles. Defined by μ, V & T.
Both E & N can fluctuate. Example - 2 phase system.

Representative Ensemble:

Large (infinite) collection of canonical ensembles whose walls are permeable to matter, ie open but rigid. Each system is defined in terms of V, T & μ.

Notation:

N_T — no. of systems in the ensemble $\to \infty$

n_T — TOTAL particles in the ensemble = constant

E_T — TOTAL energy of the ensemble = "

$n_i(N)$ — no. of systems in the ith energy state containing N particles. N varies from $\emptyset$ to $n_T (n_T \to \infty)$

N — no. of particles in a given energy state, can fluctuate.

Distribution:

Since E & N can both fluctuate, then our distribution will look like:

E_1	E_2	E_3	
$n_1(0)$	$n_2(0)$	$n_3(0)$	...
$n_1(1)$	$n_2(1)$	$n_3(1)$	
$n_1(2)$	:	:	

Where $n_i(N)$ means the no. of systems in the ith energy state containing N particles.

Note:

$E_j = E_j(N,V)$, ie, the spectrum depends on the specific value of N, ie $E_j = E_j(\epsilon_1, \epsilon_2, \ldots, \epsilon_N)$ where N can vary.

Proceeding as we did in the case of the Canonical ensemble, we again wish to maximize the degeneracy to find the most probable distribution subject to the three conditions:

$$\sum_N' \sum_j n_j(N) = N_T \qquad \text{TOTAL SYSTEMS. Fix N, sum on j.}$$

$$\sum_N' \sum_j n_j(N) E_j(N,V) = E_T \qquad \text{TOTAL ENERGY}$$

$$\sum_N' \sum_j n_j(N) N = n_T \qquad \text{TOTAL particles in the esemble}$$

The degeneracy is given by:

$$\Omega_T(n) = \frac{N_T!}{\prod_N \prod_j n_j(N)!}$$

Again we fix N & sum j, increment N & sum j etc.
For example, a specific distribution might look like $n_1(0)! \, n_1(1)! \, \ldots \, n_2(0)! \, \ldots \, n_k(j)! \, \ldots$ etc.

Maximizing $\Omega_T(n)$ to get $\Omega_T(n^*)$ subject to our restrictions requires three Lagrange Multipliers. The result is:

$$n^*_{j,N} = N_T e^{-\alpha} e^{-\beta E_j} e^{-\gamma N}$$

Where, like the canonical ensemble, we sum both sides to get e^{α}, ie,

$$\underbrace{n^*_j(N)}_{} = N_T \frac{e^{-\beta E_j(N,V)} e^{-\gamma N}}{\sum_{i,N} e^{-\beta E_i(N,V)} e^{-\gamma N}}$$

No. of systems in the jth energy
state containing N particles
in the most probable distribution

where we can define the Grand Partition Function as (Ξ - Xi - ξ pronounced Ksi in Greek or "A" in English)

$$\Xi \equiv \sum_{i,N} e^{-\beta E_i(N,V)} e^{-\gamma N} \qquad \text{where } \Xi = \Xi(T,V,\mu)$$

$$= \sum_N \left[e^{N\mu/kT} \sum_j e^{-E_j(N,V)/kT} \right] \text{ as } \gamma = -\frac{\mu}{kT}$$

but $Q = \sum_j e^{-E_j(N,V)/kT}$

and $\lambda \equiv e^{\mu/kT}$ — absolute activity

so $$\boxed{GPF = \Xi(T,V,\mu) = \sum_N Q(N,V,T) \lambda^N}$$

By analogy w

$$S = -\kappa \sum_j P_j \log P_j \qquad \text{canonical ensemble}$$

we can show that

1) $$S = -\kappa \sum_{j,N} P_{j,N} \log P_{j,N} \qquad \text{Grand Canonical ensemble}$$

Thermodynamic Relationships:

Substitution of $P_{j,N}(V,T,\mu) = \dfrac{e^{-E_j(N,V)/\kappa T} e^{N\mu/\kappa T}}{\Xi(V,T,\mu)}$

into Eqtn 1, will after some agony lead to

$$S = \frac{\bar{E}}{T} - \frac{\bar{N}\mu}{T} + \kappa \log \Xi \qquad GCE$$

Integrating: $dE = Tds - pdv + \mu dN$ single component.

$E = TS - pV + \mu N$ and, solving for S

$S = \dfrac{E}{T} - \dfrac{\mu N}{T} + \dfrac{pV}{T}$ allows the identification that

$$\boxed{PV = \kappa T \log \Xi(\mu,V,T)}$$ which is equivalent to

$A = -\kappa T \log Q(N,V,T)$ for the canonical ensemble

Characteristic Equation

From $E = TS - pV + \mu N$ above, we have

$dE = Tds + sdT - pdv - vdp + \mu dn + nd\mu = \emptyset$ and from

the first law

$dE = Tds - Pdv + \mu dn$

Comparison Then gives:

$$S\,dT - V\,dp + n\,d\mu = 0 \quad \text{Gibbs Duhem}$$

multiply through by (-1) & add $P\,dv$ to both sides giving

$$\boxed{d(PV) = P\,dv + S\,dT + N\,d\mu}$$

which is the characteristic eq'n for the GCE & is equivalent to

$$dA = -S\,dT - P\,dv + \mu\,dN$$

for the CE,

Now using $PV = k \log \Xi (\mu, V, T)$, we have

$$S = \left[\frac{\partial (PV)}{\partial T}\right]_{\mu,V} = kT\left(\frac{\partial \log \Xi}{\partial T}\right)_{V,\mu} + k\log \Xi$$

$$\bar{N} \equiv N = kT\left(\frac{\partial \log \Xi}{\partial \mu}\right)_{V,T}$$

$$PV = kT \log \Xi$$

$$A = \bar{N}\mu - kT\log \Xi \quad \text{after int. WRT N of } dA = -S\,dT - P\,dv + \mu\,dN$$

$$G = \mu\bar{N} \quad \text{single component} \quad \text{as } G = A + PV$$

$$E = \bar{N}\mu + kT^2\left(\frac{\partial \log \Xi}{\partial T}\right)_{V,\mu} \quad \text{from } A = E - TS$$

The GPF is often easier to use for certain applications as it is more mathematically tractable. For example, when dealing $\underline{w}$ N body problems, like an imperfect gas, we can reduce the problem to a 1 or 2 body system. Eg, $\Xi(T, V, \mu) = \sum_N Q(N, V, T) e^{N\mu/kT} = Q(0, V, T) + Q(1, V, T)\lambda + Q(2, V, T)\lambda^2 + \cdots$ where $\lambda = e^{\mu/kT}$ = absolute activity.

Other Ensembles

Starting $\underline{w}$ the M.C. ensemble written in terms of $\underline{energy\ levels}$ $\underline{w}$ $\beta = \frac{1}{kT}$ we have ($-\Omega = $ m.c. deg).

1) m.c.
$$\log \Omega(N,V,E) = \frac{S}{k}$$

Sum over one variable:

2) $Q = \sum_{E} \Omega(N,V,E) e^{-\beta E}$ Canonical

3) $\sum_{N} \Omega(N,V,E) e^{\beta \mu N}$ No Name

4) $\sum_{V} \Omega(N,V,E) e^{-\beta PV}$ " "

Sum on 2 Variable:

5) $\Xi = \sum_{E,N} \underbrace{\Omega(N,V,E) e^{-\beta E}}_{\text{Note: } Q(N,V,E)} e^{\beta \mu N}$ Grand Canonical

6) $\Delta = \sum_{E,V} \Omega(N,V,E) e^{-\beta E} e^{-\beta PV}$ Isothermal-Isobaric

7) ?? $\sum_{N,V} \Omega(N,V,E) e^{\beta \mu N} e^{-\beta PV}$ No Name

Sum on all Variables

8) $\Psi = \sum_{E,V,N} \Omega(N,V,E) e^{-\beta E} e^{\beta \mu N} e^{-\beta PV}$ Generalized.

Characteristic Eq'n

In each of these equations one can derive the characteristic equation by the rule:

Replace the Ω by βTS & then add the rest of the exponents. For example:

#2 Canonical

$$\beta TS - \beta E = -\beta A \quad \text{or, dropping the } \beta$$

$$A = E - TS \quad \text{and} \quad dA = -Tds - pdv + \mu dN$$

#6 Isothermal Isobaric

$$\beta TS - \beta E - \beta PV = -\beta G \quad \text{ie}$$

$$G = E - TS + PV \equiv A + PV; \quad dG = -SdT + Vdp + \sum \mu_i dm_i$$

and $G = -kT \log \Delta$ is thermal/isobaric P.f.

$*$
$$S = k \log \Omega \quad \text{so} \quad \frac{S}{k} = \log \Omega = \beta TS \quad \text{as} \quad \beta TS = \frac{S}{k}$$

Fluctuations

The systems in the canonical ensemble all have the same fixed N, V, T and energy state spectrum. It has been assumed that, even though the systems are in thermal equilib., the interaction is sufficiently weak as to not perturb the energy state spectrum although the systems will be continuously changing their actual average energies, pressures etc. The question is how much do these average non-fixed variables change.

a) Microcanonical Ensemble N, V, E fixed.
   No fluctuations as each system is isolated.

b) Canonical Ensemble; N, V, T fixed. E, P are variable.

   Measure of dispersion:
   We use the RMS deviation, $\sigma_E = \sqrt{\overline{\sigma_E^2}}$

   $$\overline{\sigma_E^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2 \quad \text{variance}$$

   and we treat E as a continuous variable.

   From

   $$\bar{E} = \frac{1}{Q} \sum_i E_i e^{-E_i(N,V)/kT}$$

Differentiating wrt T gives:

$$\left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V} Q + \frac{\bar{E}}{kT^2}\sum_{k}' E_k e^{-E_k/kT} = \frac{1}{kT^2}\sum_{k}' E_k^2 e^{-E_i/kT}$$

or

$$\overline{E^2} - (\bar{E})^2 = kT^2\left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V} = kT^2 C_V$$

OR

$$\frac{\overline{E^2} - (\bar{E})^2}{(\bar{E})^2} = \frac{kT^2 C_V}{\bar{E}^2}$$

So

$$\frac{\sigma_{\bar{E}}}{\bar{E}} = \left[\frac{\overline{E^2} - (\bar{E})^2}{(\bar{E})^2}\right]^{1/2} = \frac{T\sqrt{V k C_V}}{\bar{E}}$$
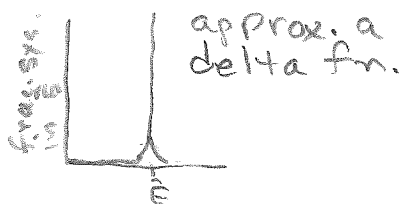
Since

$$C_V \sim O(Nk)$$

$$\bar{E} \sim O(NkT)$$

Then

$$\frac{\sigma_{\bar{E}}}{\bar{E}} = \text{relative stn. deviation} \sim \frac{1}{\sqrt{N}}$$

So if $N \simeq 10^{20}$ fluctuations in $E_{system} \sim 10^{-10}$ which is pretty negligible. Even for $N = 10^{10}$ (10^{-13} of a mole) fluctuation are still small ie, $O(10^{-3}\%)$.

approx. a delta fn.

3) Grand Canonical Ensemble

Here μ, V, T fixed; N, E can vary

Starting w

$$\bar{N} = \frac{1}{\Xi} \sum_{N} N Q(N, V, T) e^{-N\mu/kT}$$

and diff. WRT μ we can show that

$$\bar{N} = \left(\frac{V}{kT\bar{K}}\right)^{1/2} \sigma_N \quad \& \quad \bar{K} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T}$$

So again,

$$\sigma_N \simeq 10^{-10} \bar{N}$$

and we conclude that deviations from $\bar{N}$ are negigible. The exception is in the region of the critical point where $\bar{K} \to \infty$

Equivalence of Ensembles

Since deviations from the mean for non-fixed properties are usually negligible we can conclude that, for all practical purposes, that all systems in a canonical ensemble are in the same energy LEVEL $E_j = \bar{\bar{E}}$ and likewise for the Grand Canonical ensemble, $E_j = \bar{\bar{E}}$ & $N_j = \bar{N}$ where $\bar{N}$ is the average number of particles in every system. Thus if every system is in the same energy level with the same $\bar{\bar{E}}, \bar{N}$, etc., we have only one degeneracy to deal w namely $\Omega(\bar{N}, \bar{E}, V)$ so we can write:

$$P_j = \frac{1}{\Omega(\bar{N}, V, \bar{E})}$$

in which case

$$S = k \log \Omega(\bar{N}, V, \bar{E})$$

where $\Omega(\bar{N}, V, \bar{E})$ is the deg. of the energy level $\bar{E}(\bar{N}, V)$.

ie, for all practical purposes, all ensembles are microcanonical even though the canonical & grand canonical are not isolated. Thus all ensembles are functionally equivalent and the choice of which one to use is dictated by mathematicle convenience.

An alternative method of view this is to start w the canonical ensemble

$$Q(N,V,T) = \sum_i e^{-E_i/kT}$$
states

$$= \sum_i \underbrace{\Omega(N,V,E)}_{\text{degeneracy}} e^{-E_i/kT}$$
levels

and now replace the sum by its largest term so

$$Q(N,V,T) \simeq \Omega(N,V,\bar{E}) e^{-\bar{E}/kT} \quad \circledast$$

Now compute $\bar{E}$ which is the value of E which maximizes Ω to get $\Omega(N,V,\bar{E})$ ie, calc,

$$\left(\frac{\partial \Omega e^{-E/kT}}{\partial E} \right)_{N,V,T} = 0$$

$\otimes$ $\bar{E}$ is the aug. energy of a system when the ensemble is in its most probable state at equilibrium.
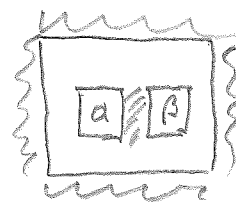
which gives

$$\left(\frac{\partial \log \Omega}{\partial E} \right)_{N,V} = \frac{1}{kT}$$

which is identical to the expression for the microcanonical ensemble. The same holds for the grand canonical ensemble where we write:

$$\Xi(\mu,V,T) = \sum_N e^{N\mu/kT} Q(N,V,T) = e^{N^*\mu/kT} Q(N_i^*,V,T)$$

and from which we can derive all the m.c. expressions.

Second Law

isothermal & isobaric throughout

Statement of the Second Law:

If a process occurs in an isolated composite system then the entropy,

$$dS_{TOTAL} \geq 0 \quad \text{where} \quad \begin{cases} = & \text{reversible process} \\ > & \text{irrev. process} \end{cases}$$

Here $dS_{TOTAL} = dS^{\alpha} + dS^{\beta}$ ie dS refers to the system + surroundings. Hence $dS > 0$ implies nothing about the relative sign of dS^{α} & dS^{β}, only that their sum is positive and greater than 0.

DIGRESSION

Use of $\Delta G_{T,P}$ as a criterion for spontaniety

While $\Delta S \geq 0$ is the basic criterion for whether or not a process can occur (not <u>will</u> occur!) it is not very useful since ΔS^{β} is difficult or impossible to compute. Consider the Gibbs energy ΔG. For an isolated composite

$$dS^{\beta} = \frac{dQ^{\beta}(rev)}{T^{\beta}} = -\frac{dQ^{\alpha}(actual)}{T^{\beta}} = -\frac{dQ^{\alpha}(actual)}{T^{\alpha}}$$

since the surroundings are assumed to be isothermal & isobaric at all times.

Furthermore

$$dH^{\alpha} = dQ^{\alpha} + V^{\alpha}dp^{\alpha} + dW' + (P^{\alpha} - p^{\beta})dV = dQ^{\alpha} \text{ at const } P,$$
and W',

$$\text{so } dS^{\beta} = -\frac{dQ^{\alpha}}{T^{\alpha}} = -\frac{dH^{\alpha}}{T^{\alpha}}$$

In which case

$$dS_{TOTAL} = dS^\alpha + dS^\beta = dS^\alpha - \frac{dH^\alpha}{T^\alpha} = -\frac{1}{T^\alpha}\left[dH^\alpha - T^\alpha dS^\alpha\right]$$

But $dG_{T,P} = dH - TdS$ so

$$dS_{TOTAL} = -dG_{T,P} \text{ from which we conclude that}$$

$$dS_{TOTAL} \geqslant \phi \implies dG_{T,P,W'} \leq \phi$$

$$dS_{TOTAL} \geqslant \phi \implies dA_{T,V,W'} \leq \phi$$

The criteria for spontaneous irrev. change can be any one of the three statements,

$$\Delta S_{TOTAL} \geqslant 0 \quad \text{always}$$

$$\Delta G_{T,P,W'} \leq \phi \quad \text{const } T, P, W'$$

$$\Delta A_{T,V,W'} \leq \phi \quad \text{''} \quad T, V, W'$$

End Digression

Statistical Mechanics and the Second Law

Since all ensembles are basically microcanonical we have

$$P_j = \frac{1}{\Omega(\bar{N}, V, \bar{E})} \qquad \text{where } \Omega \text{ is the degeneracy of the most probable energy level}$$

and from

$$S = -k\sum P_j \log P_j = -k \, \Omega \cdot \frac{1}{\Omega} \log \frac{1}{\Omega} \quad \text{or}$$

$$S = k \log \Omega(\bar{N}, V, \bar{E})$$

Then, for a spontaneous process between I & F we have

$$\Delta S = S_F - S_I = k \log \Omega_F - k \log \Omega_I = k \log \frac{\Omega_F}{\Omega_I} > 0$$

OR, for a spontaneous process, $\Omega_F > \Omega_I$.

Example:

Say we expand an ideal gas so that $V_F = 2V_I$.

Assuming the process is isothermal, we have:

$$dS = \frac{C_v dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV \quad OR$$

$$\Delta S = \int \left(\frac{\partial P}{\partial T}\right)_V dV = k \log \frac{\Omega_F}{\Omega_I} \quad SO$$

$$\begin{cases} du = Tds - Pdv \\ ds = \frac{du}{T} - \frac{P}{T} dv \\ = \frac{C_v dT}{T} + \frac{1}{T}\left(\frac{\partial u}{\partial v}\right)_T dv - \frac{P}{T} dv \\ = \frac{C_v dT}{T} + \frac{1}{T}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] - \frac{P}{T} dv \end{cases}$$

$$\frac{\Omega_F}{\Omega_I} = \exp\left(\frac{\Delta S}{k}\right) = \exp\left[\frac{1}{k}\int_V^{2V}\left(\frac{\partial P}{\partial T}\right)_V dV\right] = 2^N$$

OR

$$\Omega_F \sim 10^{10^{23}} \Omega_I \quad \text{if } N \sim 6\times10^{23}$$

Which is a perfectly general result that is ensemble independent.

Third Law

The 3rd Law states that for any isothermal isobaric process involving only pure phases, then

$$\text{Limit } \Delta S_{Reaction} \to \emptyset \quad \text{Nernst}$$
$$T \to \emptyset$$

This says nothing about the values of S_I & S_F only that they are equal at 0K.

The Planck statement went a step further and said

$$S_F = S_I = \emptyset \text{ at } T \to \emptyset$$

which is largely a convention and is certainly not true for the nuclear states, for example.

However, since we are interested only in $\Delta S = S_F - S_I$ where $\Delta S = k \log \frac{\Omega_f}{\Omega_I}$ then it only matters that $\Omega_I = \Omega_f$ at $T \to 0$ which is the case for the nuclear states. For all other degrees of freedom, like, translation, vibration, rotation & electronic, we assume $\Omega_F = \Omega_I = 1$ at $T = 0K$. In these cases, since $\Omega = 1$ then $\Delta S = 0$ at $T = 0°K$ and we have agreement w the 3rd Law.