5.62 Physical Chemistry II
Spring 2008

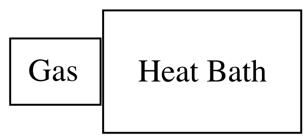
<u>5.62 Lecture #4</u>: Microcanonical Ensemble: Replace $\{P_i\}$ by Ω. Q vs. Ω.

To this point, we have worked with the CANONICAL ENSEMBLE:

$$P(E) = \frac{\Omega(N,V,E)e^{-E/kT}}{Q(N,V,T)}$$

- probability of finding an assembly state with energy E in the ensemble
- probability of finding the “gas” with energy E

A physical picture that describes the canonical framework is



- N is constant
- V is constant
- T is constant
- E fluctuates (HOW MUCH?)

The energy of the gas fluctuates (with time or for different states within the ensemble). Extra energy is withdrawn from the heat bath or is deposited in the heat bath so that the temperature of the gas remains constant.

A simpler ensemble that is also quite useful is the <u>microcanonical ensemble</u>

The <u>MICROCANONICAL ENSEMBLE</u> is a collection of assemblies in states in which N, V, and E are fixed.

Since all states of a microcanonical ensemble have same energy, $E_\alpha = E_\beta = E_\gamma = \ldots$ E, all assembly states are <u>degenerate</u>.

Ω(N,V,E) = degeneracy [e.g. particles in cube: (n_x,n_y,n_z) = (211), (121), (112)]

= number of *distinguishable* assembly states with N, V, and E fixed

= total number of assembly states in microcanonical ensemble.

A physical picture of microcanonical framework is

Gas

SYSTEM IS ISOLATED
- E is constant
- T fluctuates

Why have different ensembles?

- Some physical situations more closely correspond to one ensemble or another (there are more than these two).
- Some problems are easier to solve in the context of one ensemble or another
- Results for macroscopic properties are independent of which type of ensemble is used.

MICROCANONICAL ENSEMBLE: CALCULATION OF THERMODYNAMIC PROPERTIES (Macroscopic Observables from Microscopic Properties)

As in Lecture #2, we want the set of assembly state probabilities which maximizes entropy subject to the normalization constraint.

entropy: $$S = -k\sum_{j=1}^{\Omega} P_j \ln P_j$$

take differential to maximize (i.e. to find extremum)

$$0 = \delta S = -k\sum_{j=1}^{\Omega} \delta\left[P_j \ln P_j\right] = -k\sum_{j=1}^{\Omega}\left(\delta P_j \ln P_j + \frac{P_j \delta P_j}{P_j}\right)$$

$$= -k\sum_{j=1}^{\Omega} \delta P_j\left(\ln P_j + 1\right)$$

constraint:

$$\sum_{j=1}^{\Omega} P_j = 1 = \sum_{j=1}^{\Omega} (P_j + \delta P_j)$$

thus

$$\sum_{j=1}^{\Omega} \delta P_j = 0 \quad \text{or} \quad \delta P_1 = -\sum_{j=2}^{\Omega} \delta P_j.$$

Inserting this equation into the extremum condition for S,

$$0 = \delta S = -k\delta P_1 \left(\ln P_1 + 1\right) - k\sum_{j=2}^{\Omega} \delta P_j \left(\ln P_j + 1\right)$$

where we partitioned out the first term in the sum

introduce constraint on δP_1

$$\delta S = +k\sum_{j=2}^{\Omega} \delta P_j \left(\ln P_1 + 1\right) - k\sum_{j=2}^{\Omega} \delta P_j \left(\ln P_j + 1\right)$$

$$\delta S = -k\sum_{j=2}^{\Omega} \delta P_j \left(\ln P_j - \ln P_1\right) = 0$$

and since the δP_j are independent for all j = 2, 3, 4, … , Ω, the coefficient of each δP_j is zero:

$$\left.\begin{aligned} \ln P_j - \ln P_1 &= 0 \\ \ln P_j &= \ln P_1 \\ P_j &= P_1 \end{aligned}\right\} \qquad \text{for } j = 2, 3, 4, \ldots \Omega$$

That is, each distinguishable (same E) state is of equal probability in the micro-canonical ensemble

normalize: $$1 = \sum_{i=1}^{\Omega} P_j = \sum_{i=1}^{\Omega} P_1 = \Omega P_1 \text{ so } P_1 = \frac{1}{\Omega} = P_j$$

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

MICROCANONICAL DISTRIBUTION FUNCTION

Thus

$$S = -k\sum_{j=1}^{\Omega} P_j \ln P_j = -k\sum_{j=1}^{\Omega} \left(\frac{1}{\Omega}\right)\ln\left(\frac{1}{\Omega}\right)$$

$$= -k\underbrace{(\Omega)}_{\text{Ω terms in sum}}\left(\frac{1}{\Omega}\right)\ln\left(\frac{1}{\Omega}\right) = -k\ln\left(\frac{1}{\Omega}\right) = k\ln\Omega$$

$$\boxed{S(N,V,E) = k \ln \Omega(N,V,E)}$$ written on Boltzmann's tombstone

WRITING THERMODYNAMIC FUNCTIONS IN TERMS OF MICROCANONICAL FRAMEWORK

from thermodynamics:

$dU = TdS - pdV$ (the thermodynamic U is the same thing as the $\bar{E}$ used here)

since $dE = 0$ for (microcanonical) isolated

$$TdS = pdV \qquad \text{or} \qquad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

since $S = k \ln \Omega$

$$\boxed{p = kT\left(\frac{\partial \ln\Omega}{\partial V}\right)_{E,N}}$$ pressure

from thermo…

$$H = \bar{E} + pV = \bar{E} + kT\left(\frac{\partial \ln\Omega}{\partial V}\right)_{E,N} \quad V = \bar{E} + kT\left(\frac{\partial \ln\Omega}{\partial \ln V}\right)_{E,N}$$

$$\boxed{H = \bar{E} + kT\left(\frac{\partial \ln\Omega}{\partial \ln V}\right)_{E,N}}$$ enthalpy

from thermo… $A = \bar{E} - TS$

$$\boxed{A = \bar{E} - kT \ln \Omega}$$ Helmholtz free energy

from thermo… G = A + pV

$$\boxed{G = \bar{E} - kT\ln\Omega + kT\left(\frac{\partial \ln\Omega}{\partial \ln V}\right)_{E,N}} \text{ Gibbs free energy}$$

<u>Which ensemble</u>?

An obvious question that arises is which ensemble to use in solving a given problem.

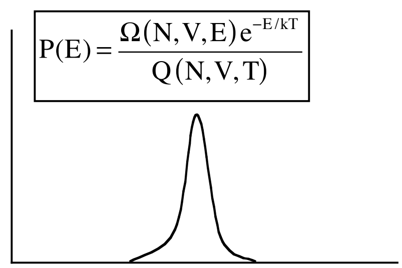
Frequently the conditions of the problem will dictate:

- interpreting an experiment carried out at constant N, V, T ⇔ canonical

- interpreting an experiment carried out in isolated system ⇔ microcanonical

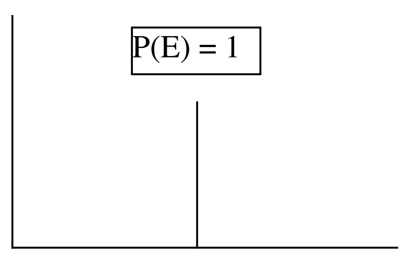
Other times, whichever ensemble is easiest to use turns out to be best, because in limit of large N, ensembles are quite similar. For example, compare energy distribution for canonical and microcanonical ensembles:

CANONICAL ENSEMBLE



The numerator is a product of increasing (Ω) and decreasing ($e^{-E/kT}$) functions of E.

MICROCANONICAL ENSEMBLE



On the surface, the functions look quite different, but let's compare their widths. Width of microcanonical distribution is zero.

For canonical $\Delta E_i = E_i - \bar{E} =$ deviation of i-th energy from average. One measure of width of distribution is

$$\sqrt{\overline{(\Delta E)^2}} = \text{ root mean square deviation}$$

$$\overline{(\Delta E)^2} = \sum_i P_i \left(E_i - \bar{E}\right)^2 = \sum_i P_i \left(E_i^2 - 2\bar{E}E_i + \bar{E}^2\right)$$

$$= \overline{(E)^2} - 2\bar{E}^2 + \bar{E}^2 = \overline{(E)^2} - \bar{E}^2 \qquad \text{average square deviation}$$

$$\sqrt{\overline{(\Delta E)^2}} = \sqrt{\overline{(E)^2} - (\bar{E})^2} \qquad \text{rms deviation}$$

It turns out that

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

as will be shown here

$$\boxed{P_i = e^{-\beta E_i}/Q}$$

$$\frac{\partial Q}{\partial \beta} = \frac{\partial \sum_i e^{-\beta E_i}}{\partial \beta} = \sum_i (-E_i) e^{-\beta E_i} = -\sum_i E_i P_i Q = -\bar{E} Q$$

and take $\frac{\partial}{\partial \beta}$ again, starting from the definition of Q,

$$\frac{\partial^2 Q}{\partial \beta^2} = \sum_i E_i^2 e^{-\beta E_i} = \sum_i E_i^2 P_i Q = \overline{E^2} Q$$

Therefore … $\overline{\Delta E^2} \equiv \overline{E^2} - \bar{E}^2 =$

$$\underbrace{\frac{1}{Q}\frac{\partial^2 Q}{\partial\beta^2}}_{\overline{E^2}}-(\bar{E})^2=\frac{1}{Q}\frac{\partial}{\partial\beta}\left(-\bar{E}Q\right)-(\bar{E})^2=-\frac{\partial\bar{E}}{\partial\beta}-\bar{E}\underbrace{\frac{1}{Q}\frac{\partial Q}{\partial\beta}}_{\bar{E}}-(\bar{E})^2$$

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

Now, to convert to $\dfrac{\partial}{\partial T}$

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

$$=-\left(\frac{\partial\beta}{\partial T}\right)^{-1}\left(\frac{\partial\bar{E}}{\partial T}\right)_{N,V}=-\left(\frac{\partial(1/kT)}{\partial T}\right)^{-1}\left(\frac{\partial\bar{E}}{\partial T}\right)_{N,V}$$

$$=\left(\frac{+1}{kT^2}\right)^{-1}\underbrace{\left(\frac{\partial\bar{E}}{\partial T}\right)_{N,V}}_{C_V}$$

$$\overline{\Delta E^2}=kT^2C_V$$

Relative (fractional) fluctuation about average energy in canonical ensemble

$$\frac{\sqrt{\overline{\Delta E^2}}}{\bar{E}}=\frac{\sqrt{kT^2C_V}}{\bar{E}}\propto\frac{N^{1/2}}{N}\propto\frac{1}{\sqrt{N}}$$

[Both C_V and $\bar{E}$ are extensive variables, which by the definition of extensive are proportional to N.]

$$\frac{\sqrt{\overline{\Delta E^2}}}{\bar{E}}\propto N^{-1/2}$$

For large $N \approx 10^{24}$

$10^{-12} \ll 1$

Conclusion: For large N (macroscopic systems), P(E) is *very narrow* in the canonical framework. For most purposes, it can be considered to be as narrow as that in microcanonical framework.

$$\frac{\sqrt{\overline{\Delta E^2}}}{\bar{E}} = \begin{cases} 0 \text{ microcanonical} \\ 10^{-12} \text{ canonical} \end{cases}$$

Thus, can use either ensemble.

SUMMARY

THERMODYNAMIC FUNCTION	CANONICAL	MICROCANONICAL
$\bar{E}$ OR T	$\bar{E}(N,V,T) = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$	$T = \left[k\left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V}\right]^{-1}$
S	$k \ln Q + \bar{E}/T$	$k \ln \Omega$
A	$-kT \ln Q$	$\bar{E} - kT \ln \Omega$
p	$kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$	$kT\left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E}$
H	$kT\left[\left(\frac{\partial \ln Q}{\partial \ln T}\right)_{N,V} + \left(\frac{\partial \ln Q}{\partial \ln V}\right)_{N,T}\right]$	$\bar{E} + kT(\partial \ln \Omega/\partial \ln V)_{N,E}$
G	$-kT\ln Q + kT\left(\frac{\partial \ln Q}{\partial \ln V}\right)_{N,T}$	$\bar{E} + kT(\partial \ln \Omega/\partial \ln V)_{N,E}$ $-kT \ln \Omega$
μ	$-kT(\partial \ln Q/\partial N)_{V,T}$	$-kT(\partial \ln \Omega/\partial N)_{E,V}$
Partition Functions	$Q(N,V,T) = \sum_j e^{-E_j/kT}$ $= \sum_E \Omega(E)e^{-E/kT}$	$\Omega(N,V,E) = \sum_j (1)$ sum over states with energy E

Derive $T = \left[k\left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V}\right]^{-1}$

$$Q = \sum_E \Omega e^{-E/kT}$$

find extremum in Q wrt E (i.e., find most probable E)

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

every term in sum (for each value of E) must be 0

$$\left(\frac{\partial\Omega}{\partial E}\right)_{N,V}=\frac{\Omega}{kT} \qquad \frac{1}{\Omega}\left(\frac{\partial\Omega}{\partial E}\right)_{N,V}=\frac{1}{kT} \qquad k\left(\frac{\partial\ln\Omega}{\partial E}\right)_{N,V}=\frac{1}{T}$$