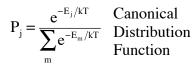
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5.62 Lecture #3: Canonical Partition Function: Replace {P_i} by Q



Denominator of canonical distribution function has a special name ...

$$Q(N,V,T) = \sum_{j} e^{-E_{j}/kT}$$

CANONICAL PARTITION FUNCTION

Sum of "Boltzmann factor", $e^{-Ej/kT}$, over states of the assembly

originally called "zustandsumme" $\equiv Z \equiv$ sum over states

Q is a <u>very very</u> important quantity.

We will use Q to calculate macroscopic properties from microscopic properties

Rewrite Canonical Distribution Function in terms of Q ...

$$P_{j} = \frac{e^{-E_{j}/kT}}{\sum_{m} e^{-E_{m}/kT}} = \frac{e^{-E_{j}kT}}{Q}$$

 $\underline{\text{FEEL THE POWER OF}}\,P_{j}-$ can now calculate macroscopic properties from ensemble average

... but more convenient to use Q.

<u>REPLACING</u> P₁ IN ENSEMBLE AVERAGE BY Q

example: $\overline{E} = \sum_{i}$

 $\overline{E} = \sum_{j} P_{j} E_{j} = f(Q)$

Define $\beta \equiv 1/kT$

$$Q(N, V, T) = \sum_{j} e^{-E_{j}/kT} = \sum_{j} e^{-\beta E_{j}}$$
$$\frac{\partial Q}{\partial \beta} = -\sum_{j} E_{j} e^{-\beta E_{j}}$$
$$P_{j} = \frac{e^{-\beta E_{j}}}{Q} \text{ so } e^{-\beta E_{j}} = QP_{j}$$
$$Therefore$$
$$\frac{\partial Q}{\partial \beta} = -\sum_{j} P_{j} E_{j} Q = -Q\sum_{j} P_{j} E_{j}$$
$$But$$
$$\overline{E} = \sum_{j} P_{j} E_{j}$$

So

$$\frac{\partial Q}{\partial \beta} = -\overline{E}Q$$
 or $\overline{E} = -\frac{1}{Q}\frac{\partial Q}{\partial \beta}$

$$\overline{E} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial (1/kT)} = -\frac{\partial \ln Q}{\partial T} \frac{\partial T}{\partial (1/kT)}$$

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

This is the ensemble average for E written in terms of Q instead of $P_{\rm j}$ Writing S in terms of Q instead of $P_{\rm j}$

$$S = -k\sum_{j} P_{j} \ln P_{j} = -k\sum_{j} P_{j} \ln \left(\frac{e^{-E_{j}/kT}}{Q}\right)$$
$$S = -k\sum_{j} P_{j} \left[\frac{-E_{j}}{kT} - \ln Q\right] = \frac{\sum_{j} P_{j}E_{j}}{T} + k \ln Q$$
$$S = k \ln Q + \frac{\overline{E}}{T} = k \ln Q + k \left(\frac{\partial \ln Q}{\partial \ln T}\right)_{N,V}$$

WRITING ALL THERMODYNAMIC FUNCTIONS OR MACROSCOPIC

PROPERTIES IN TERMS OF Q

From thermo ...

$$A = \overline{E} - TS = \overline{E} - T(k \ln Q + \overline{E} / T) = \overline{E} - kT \ln Q - T\frac{\overline{E}}{T}$$

$$A = -kT \ln Q$$
Helmholtz free energy

Note that both A and Q have natural variables N, V, T.

From thermo ...

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} \qquad \text{pressure}$$
$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

from thermo ...

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$
 chemical potential (For μ , always natural
variables held constant.)
$$\mu = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$$

 $H \equiv \overline{E} + pV$ $G \equiv A + pV$ write in terms of Q in homework

Now we have a rudimentary structure or framework for relating the microscopic properties as given by Q, the sum over states of assemblies present in the canonical ensemble, to macroscopic or thermodynamic properties. Note that Q (or P_j) tells us the distribution of assembly states present in the ensemble. We see that it is the energy of the state of the assembly that determines its probability of being in the ensemble. So now we need to know what are the energies of the assemblies, E_j, so that Q for <u>specific systems</u> may be calculated. Once Q is known, we can calculate all macroscopic thermodynamic properties from the above expressions!!

A LOOSE END: DEGENERACY - BACK TO Pi

Sometimes a more useful form of P_i is P(E).

GOAL: Derive P(E)

 $P(E) \equiv$ probability of finding an assembly state with energy E.

Each j in Q stands for a distinguishable state of the assembly.

$$Q = ... + e^{-E_{\alpha}/kT} + e^{-E_{\beta}/kT} + e^{-E_{\gamma}/kT} + ... = \sum_{j} e^{-E_{j}/kT}$$

But many distinguishable assembly states are <u>degenerate</u> (i.e. have the same energy)

$$E_{\alpha} = E_{\beta} = E_{\gamma} = E$$

$$Q = \dots + 3e^{-E/kT} + \dots = \sum_{E} \Omega(N, V, E) e^{-E/kT}$$

$$\uparrow$$

$$\Omega(N, V, E) \equiv \text{degeneracy} = \text{no. of distinguishable}$$

assembly states with energy E.

So

$$Q(N, V, T) = \sum_{j} e^{-E_{j}/kT} = \sum_{E} \Omega(N, V, E) e^{-E/kT}$$
sum over states of assemblies
sum over energy levels present in ensemble

$$P(E) = \sum_{j \ge E_j = E} P_j = \sum_{j \ge E_j = E} e^{-E_j/kT} / Q(N, V, T)$$

Sum over those assembly states that belong to the set of assembly states whose $E_i = E$

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

probability of finding an assembly state with energy E in ensemble