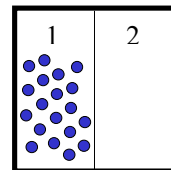


Statistical Thermo. and TD Properties

- Still need to find β and way to connect Statistical Mechanics to Thermodynamics
 - e.g., $Q, N_i/N \rightarrow p, T, S$, etc.
- Following Boltzmann... will look for analogy between *entropy* and *randomness* (disorder)
- Approach
 - examine some closed systems
 - motivate Boltzmann's relation

Entropy and Volume Change

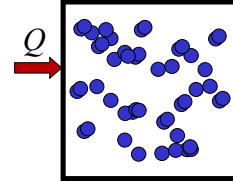
- Perfect gas in insulated rigid box divided into two equal cells by removable partition
 - start with all gas in cell #1
 - remove partition, end with gas in both cells
- Gibbs for process



$$\begin{aligned}
 dS &= \frac{1}{T} d\cancel{U} + \frac{p}{T} dV = \frac{1}{T} d\cancel{E} + Nk \frac{dV}{V} \quad \begin{array}{l} \text{entropy increased with more} \\ \text{possible locations of finding} \\ \text{particles} \rightarrow \text{increased disorder} \end{array} \\
 &= Nk \frac{dV}{V} \longrightarrow \Delta S = Nk \ln \frac{V_2}{V_1} = Nk \ln 2 = k \ln 2^N
 \end{aligned}$$

Entropy and Energy Change

- Now fix volume
 - and double energy (and temperature) through heat transfer



- Gibbs for process $dV = 0$

$$dS = \frac{1}{T} dE + Nk \frac{dV}{V}$$

$$= C_v \frac{dT}{T} = Nk \frac{c_v}{R} \frac{dE}{E}$$

entropy increased with more possible (accessible) energy levels
→ increased disorder

$$\Delta S = Nk \frac{c_v}{R} \ln \frac{E_2}{E_1} = Nk \frac{c_v}{R} \ln 2 = k \ln 2^{\frac{c_v}{R} N}$$

$c_v = \text{const.}$

Statistical Thermodynamic: Reactions-3

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Entropy and Microstates

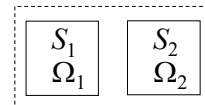
- Examples show there is relation between entropy and number of “places” particles can be
 - i.e., between S and Ω , or $S = \Phi(\Omega)$
- What should function Φ look like?
 - look at how systems combine

- Entropy is extensive

$$S_{1+2} = S_1 + S_2$$

- Number of microstates are multiplicative

$$\Omega_{1+2} = \Omega_1 \times \Omega_2 \quad \text{absolute const.}$$



- General form required

see V&K p. 114

Boltzmann's const.

$$S = a \ln \Omega + bN$$

$$S = k \ln \Omega + S_o$$

constant for given system

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Boltzmann's Relation

$$S = k \ln \Omega + S_0$$

- Analogous to 3rd Law, let $S=0$ for perfectly ordered system ($\Omega=1$)
 - $S_0=0$
- So $S = k \ln \Omega$ **Boltzmann's Relation**
 - our approach was not rigorous derivation
 - we used perfect gas to motivate – but true in general
 - also, based on postulate: **equal a priori probability**

Thermodynamic Relations

- For large N , we know we can get Ω from most probable macrostate $\ln \Omega \cong \ln W_{\max}$
- Using Boltzmann limit $\ln W_{\max} = N \left(1 + \ln \frac{Q}{N} \right) + \beta E$

$$Q \equiv \sum_i g_i e^{-\beta \epsilon_i}$$

$$S = k \left[N \left(1 + \ln \frac{Q}{N} \right) + \beta E \right]$$

$$S = kN \ln \frac{Q}{N} + kN + k\beta E$$
- Can now get β by comparing to TD state relation (Gibb's)

$$dS = \frac{\partial S}{\partial E} \bigg|_{V,N} dE + \frac{\partial S}{\partial V} \bigg|_{E,N} dV + \frac{\partial S}{\partial N} \bigg|_{E,V} dN$$

$$\frac{1}{T} \quad p/T \quad -\mu/T$$

Thermodynamic Relations

- So look at partial derivatives of Statistical Mechanics eqn. $S = kN \ln \frac{Q}{N} + kN + k\beta E$

- ∂E

$$\frac{\partial S}{\partial E} \bigg|_{V,N} = kN \left[\frac{\partial \ln Q}{\partial E} \bigg|_{V,N} - \frac{\partial \ln N}{\partial E} \bigg|_{V,N} \right] + k \left[\frac{\partial \beta}{\partial E} \bigg|_{V,N} E + \beta \right]$$

$$\frac{1}{T} = kN \frac{1}{Q} \frac{\partial Q}{\partial E} \bigg|_{V,N} + k \left[\frac{\partial \beta}{\partial E} \bigg|_{V,N} E + \beta \right]$$

$$\frac{\partial Q}{\partial \beta} \frac{\partial \beta}{\partial E} \bigg|_{V,N}$$

$$\frac{\partial Q}{\partial \beta} = - \sum \varepsilon_i g_i e^{-\beta \varepsilon_i} = - \sum \varepsilon_i \frac{Q N_i}{N} = - \frac{Q}{N} \sum \varepsilon_i N_i = - \frac{QE}{N}$$

Statistical Thermodynamic Relations-7

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Thermodynamic Relations

- ∂E (con't)

$$\frac{1}{T} = kN \frac{1}{Q} \frac{\partial Q}{\partial E} \bigg|_{V,N} + k \left[E \frac{\partial \beta}{\partial E} \bigg|_{V,N} + \beta \right]$$

$$= -kE \frac{\partial \beta}{\partial E} \bigg|_{V,N} + k \left[E \frac{\partial \beta}{\partial E} \bigg|_{V,N} + \beta \right]$$

$$\boxed{\beta = 1/kT} \rightarrow S = kN \ln \frac{Q}{N} + kN + \frac{E}{T}$$

$$\therefore S = S(N, E, T, Q) \quad \text{Partition Function}$$

TD variables

$$= \sum_i g_i e^{-\varepsilon_i/kT}$$

Statistical Thermodynamic Relations-8

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Pressure and Partition Function

Alternative to Helmholtz
Free Energy derivation
in V&K, p. 118

- Examine $\left. \frac{\partial S}{\partial V} \right|_{E,N} = \frac{p}{T}$
 - since $S=S(E,V,N,\beta)$ $S = kN \ln \frac{Q}{N} + kN + k\beta E$

$$\left. \frac{\partial S}{\partial V} \right|_{E,N} = \left. \frac{\partial S}{\partial V} \right|_{E,N,\beta=1/kT} + \left. \frac{\partial S}{\partial \beta} \right|_{E,V,N} \left. \frac{\partial \beta}{\partial V} \right|_{E,N}$$

$$\frac{p}{T} = \left. \frac{\partial}{\partial V} \left(kN \ln \frac{Q}{N} + kN + k\beta E \right) \right|_{E,N,\beta}$$

$$\frac{p}{T} = \left. \frac{\partial}{\partial V} \left(kN \ln \frac{Q}{N} \right) \right|_{E,N,\beta} = \left. \frac{\partial (kN \ln Q)}{\partial V} \right|_{E,N,\beta} - \left. \frac{\partial (kN \ln N)}{\partial V} \right|_{E,N,\beta}$$

$\frac{p}{T} = kN \left. \frac{\partial \ln Q}{\partial V} \right|_{E,N(T)}$

Is $Q=Q(V)$? Yes!!

$Q \equiv \sum_i g_i e^{-\beta \epsilon_i}$ $\epsilon_{i,tr} = f(L_x, L_y, L_z)$

Statistical Thermodynamic Relations-9

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Chemical Potential and Q

- Examine $\left. \frac{\partial S}{\partial N} \right|_{E,V} = \frac{-\tilde{\mu}}{T}$ per molec.
 - $S = kN \ln \frac{Q}{N} + kN + k\beta E$

$$\left. \frac{\partial S}{\partial N} \right|_{E,V} = \left. \frac{\partial S}{\partial N} \right|_{E,V,\beta} + \left. \frac{\partial S}{\partial \beta} \right|_{E,V,N} \left. \frac{\partial \beta}{\partial N} \right|_{E,V}$$

$$\frac{-\tilde{\mu}}{T} = \left. \frac{\partial}{\partial N} \left(kN \ln \frac{Q}{N} + kN + k\beta E \right) \right|_{E,V,\beta}$$

$$\frac{-\tilde{\mu}}{T} = \left. \frac{\partial}{\partial N} \left(kN \ln \frac{Q}{N} + kN \right) \right|_{E,V} = \left[kN \left(\left. \frac{\partial \ln Q}{\partial N} \right|_{E,V} - \frac{1}{N} \right) + k \ln \frac{Q}{N} \right] + k$$

$\frac{\tilde{\mu}}{T} = -k \ln \frac{Q}{N}$

– recall $e^{-\alpha} = \frac{N}{\sum_i g_i e^{-\beta \epsilon_i}} = \frac{N}{Q} \Rightarrow \alpha = \ln \frac{Q}{N} \Rightarrow \alpha = -\tilde{\mu}/kT$

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Energy and Partition Function

- Let's examine relationship between Q and other TD variables
- Recall in finding β , we saw $\frac{\partial Q}{\partial \beta} = -\frac{QE}{N} \Rightarrow E = -\frac{N}{Q} \frac{\partial Q}{\partial \beta}$
– so to find E

$$\beta = 1/kT \Rightarrow \frac{d\beta}{dT} = -\frac{1}{kT^2}$$

$$E = -\frac{N}{Q} \frac{\partial Q}{\partial T} \frac{\partial T}{\partial \beta} = -\frac{N}{Q} (-kT^2) \frac{\partial Q}{\partial T} = NkT^2 \frac{1}{Q} \frac{\partial Q}{\partial T}$$

$$E = NkT^2 \frac{\partial \ln Q}{\partial T} \quad \text{way to find } E \text{ if } N, Q, T \text{ known}$$

– also $c_v = ?$

$$c_v = \frac{de}{dT} \quad R = k/m_{part}; m = Nm_{part}$$

$$c_v = R \left[2T \frac{\partial \ln Q}{\partial T} + T^2 \frac{\partial^2 \ln Q}{\partial T^2} \right] \quad e = RT^2 \frac{\partial \ln Q}{\partial T}$$

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Summary

- Derived TD properties using
- **Boltzmann's relation** $S = k \ln \Omega$ *generally true (a priori prob.)*

$$\text{– Boltzmann (dilute) limit for weakly interacting molec.} \quad \ln W_{\max} = N \left(1 + \ln \frac{Q}{N} \right) + \frac{E}{kT}$$

$$\text{– examples} \quad Q \equiv \sum_i g_i e^{-\epsilon_i/kT} \quad \frac{N_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{Q}$$

$$S = kN \left(1 + \ln \frac{Q}{N} \right) + \frac{E}{T} \quad E = kNT^2 \frac{\partial \ln Q}{\partial T} \Big|_v$$

Partition Function *Boltzmann Distribution*

$$\frac{p}{T} = kN \frac{\partial \ln Q}{\partial V} \Big|_{E,N} \quad \frac{\tilde{\mu}}{T} = -k \ln \frac{Q}{N}$$

$$c_v = RT \left[\frac{2 \partial \ln Q}{\partial T} \Big|_v + T \frac{\partial^2 \ln Q}{\partial T^2} \Big|_v \right] \quad \boxed{+ \text{OTHERS}}$$

For given
– substance (g_i, ϵ_i)
– state (e.g., E, N, V)
we can find all
TD props.,
– including c_v

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BE-FD Results

- If we remove Boltzmann limit assumption
 - but retain **independent (weakly interacting) particles**

$$\ln W_{[BE, FD]} = \sum_i \left(N_i \ln \frac{g_i \pm N_i}{N_i} \pm g_i \ln \frac{g_i \pm N_i}{g_i} \right)$$

- For most probable macrostate $N_i^* = g_i \frac{e^{-\alpha - \beta \epsilon_i}}{1 \mp e^{-\alpha - \beta \epsilon_i}}$

$$\frac{g_i}{N_i^*} \pm 1 = \frac{1 \mp e^{-\alpha - \beta \epsilon_i} \pm e^{-\alpha - \beta \epsilon_i}}{e^{-\alpha - \beta \epsilon_i}} = e^{\alpha + \beta \epsilon_i}$$

$$\frac{1 \pm N_i^*}{g_i} = 1 \pm \frac{e^{-\alpha - \beta \epsilon_i}}{1 \mp e^{-\alpha - \beta \epsilon_i}} = \frac{1 \mp e^{-\alpha - \beta \epsilon_i} \pm e^{-\alpha - \beta \epsilon_i}}{1 \mp e^{-\alpha - \beta \epsilon_i}} = (1 \mp e^{-\alpha - \beta \epsilon_i})^{-1}$$

$$\Rightarrow \ln W_{\max [BE, FD]} = \sum_i \left\{ N_i^* (\alpha + \beta \epsilon_i) \mp g_i \ln (1 \mp e^{-\alpha - \beta \epsilon_i}) \right\}$$

$$S = k \ln W_{\max} \quad \therefore S = k(\alpha N + \beta E) \mp k \sum_i \left\{ g_i \ln (1 \mp e^{-\alpha - \beta \epsilon_i}) \right\}$$

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BE-FD Results

$$S = k(\alpha N + \beta E) \mp k \sum_i \left\{ g_i \ln (1 \mp e^{-\alpha - \beta \epsilon_i}) \right\}$$

- To get α, β for BE and FD statistics, compare to TD S expression

$$\left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{1}{T} = k\beta \Rightarrow \beta = 1/kT$$

Same results we found in Boltzmann limit!!

$$\left. \frac{\partial S}{\partial N} \right|_{E, V} = \frac{-\tilde{\mu}}{T} = k\alpha \Rightarrow \alpha = -\tilde{\mu}/kT$$

but we do have a modified population distribution over energy levels

$$N_i^* = \frac{g_i}{e^{(\epsilon_i - \tilde{\mu})/kT} \mp 1}$$

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BE-FD Results

- Plug back into S expression

$$S = \frac{E - \tilde{\mu}N}{T} + k \sum_i g_i \ln \left(1 + e^{-\frac{\varepsilon_i - \tilde{\mu}}{kT}} \right)$$

- Pressure

$$\left. \frac{\partial S}{\partial V} \right|_{E,N} = \frac{p}{T} \Rightarrow p = - \sum_i N_i \left. \frac{\partial \varepsilon_i}{\partial V} \right|_{E,N} \quad \text{In Boltzmann limit} \quad p = NkT \left. \frac{\partial \ln Q}{\partial V} \right|_{E,N}$$

- So properties still only function of g_i , ε_i ,
but now we no can longer employ the simpler partition
function expressions
- For most general case (interacting particles), need to
employ Gibbs method (canonical ensembles, see texts by
Denbigh or McQuarrie or Laurendeau)

Interpretation of Properties

- Originally, our examination of the “state” of a substance
(group of particles) depended only on the particles’
microscopic properties (ε_i , g_i) and the system’s extensive
properties (E , V , N)
- When we defined the Lagrange multipliers for the most
probably macrostate and related them to entropy, we then
found “definitions” for T , μ , p , etc.
 - thus properties like temperature and pressure can only be
defined for groups of particles
 - they are essentially statistical quantities, defined based on
averaging over groups of particles
- For example, what is the statistical thermodynamic
interpretation of T ?

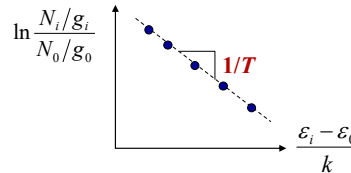
Stat. Thermo. Interpretation of T

- Consider Boltzmann (limit) population distribution

$$\frac{N_i}{N} = \frac{g_i e^{-\varepsilon_i/kT}}{Q} \Rightarrow \frac{N_i}{N_j} = \frac{g_i e^{-\varepsilon_i/kT}}{g_j e^{-\varepsilon_j/kT}} = \frac{g_i}{g_j} e^{-(\varepsilon_i - \varepsilon_j)/kT}$$

$$\ln \frac{N_i/g_i}{N_j/g_j} = -(\varepsilon_i - \varepsilon_j)/kT$$

$$T = \frac{\varepsilon_i - \varepsilon_j}{k} \left(\ln \frac{N_j/g_j}{N_i/g_i} \right)^{-1}$$



- So **temperature is the measure of how the particles are distributed amount the energy levels**
 - for a given tpg gas (g_i , ε_i) in *equilibrium*, T is the **ONLY** thing needed to determine the energy population distribution

Interpretation of Q

- Let's look at what the partition function (Q) represents
- Recall $Q = \sum g_i e^{-\varepsilon_i/kT} = g_0 + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + g_3 e^{-\varepsilon_3/kT} + \dots$
 - arbitrarily chose the lowest energy level to have $\varepsilon = 0$
- What happens as we raise the temperature to each term?
 - each term increases until $T \gg \varepsilon_i$
 - approaches $g_i \times 1 = g_i$
- Recall g_i is number of quantum states in energy level i
 - so Q is summing up all the quantum states, weighted by how **accessible** they are
molecules more likely to be found in energy levels that are more accessible and have more states
 - if $T \ll \varepsilon_i$, quantum states in energy level i aren't contributing much to the sum; their energy is too high at that T , and aren't very **accessible**
- Also note - for energy levels with $T \gg \varepsilon_i$, $N_i/N_j \cong g_i/g_j$

