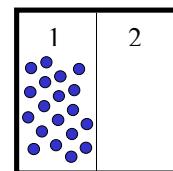


## Statistical Thermo. and TD Properties

- Still need to find  $\beta$  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



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

*entropy increased with more possible locations of finding particles → increased disorder*

$$= Nk \frac{dV}{V} \quad \longrightarrow \quad \Delta S = Nk \ln \frac{V_2}{V_1} = Nk \ln 2 = k \ln 2^N$$

## Entropy and Energy Change

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

- Gibbs for process

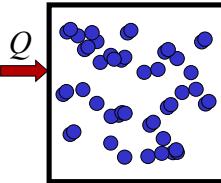
$$dS = \frac{1}{T} dE + Nk \frac{dV}{V} \xrightarrow{0}$$

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

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

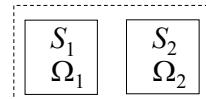
$$\Delta S = Nk \frac{c_v}{R} \ln \frac{E_2}{E_1} = Nk \frac{c_v}{R} \ln 2 = k \ln 2^{\frac{c_v}{R} N}$$

$c_v = \text{const.}$



## Entropy and Microstates

- Examples show there is relation between entropy and number of “places” particles can be
  - i.e., between  $S$  and  $\Omega$ , or  $S = \Phi(\Omega)$
- What should function  $\Phi$  look like?
  - look at how systems combine
- Entropy is extensive
  - $S_{1+2} = S_1 + S_2$
- Number of microstates are multiplicative
  - $\Omega_{1+2} = \Omega_1 \times \Omega_2$  absolute const. → constant for given system
- General form required
  - see V&K p. 114
  - $S = a \ln \Omega + bN$
  - $S = k \ln \Omega + S_o$
  - Boltzmann's const. ↑



## Boltzmann's Relation

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

- Analogous to 3<sup>rd</sup> 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  $\Omega$   $\ln \Omega \approx \ln W_{\max}$  from most probable macrostate
- Using Boltzmann limit  $\ln W_{\max} = N \left( 1 + \ln \frac{Q}{N} \right) + \beta E$ 

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

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

$$S = kN \ln \frac{Q}{N} + kN + k\beta E$$
- Can now get  $\beta$  by comparing to TD state relation (Gibb's)
 
$$dS = \frac{\partial S}{\partial E} \bigg|_{V,N} dE + \frac{\partial S}{\partial V} \bigg|_{E,N} dV + \frac{\partial S}{\partial N} \bigg|_{E,V} dN$$

$$1/T \quad p/T \quad -\mu/T$$

## Thermodynamic Relations

- So look at partial derivatives of Statistical Mechanics eqn

$$S = kN \ln \frac{Q}{N} + kN + k\beta E$$

- $\partial E$

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

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

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

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

## Thermodynamic Relations

- $\partial E$  (con't)

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

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

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

$$\therefore S = S \left( \underbrace{N, E, T, Q}_{TD \text{ variables}} \right) \quad \begin{array}{l} \text{Partition} \\ \text{Function} \end{array}$$

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

## Pressure and Partition Function

- Examine  $\frac{\partial S}{\partial V} \Big|_{E,N} = \frac{p}{T}$

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

– since  $S = S(E, V, N, \beta)$   $S = kN \ln \frac{Q}{N} + kN + k\beta E$

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

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

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

$$\boxed{\frac{p}{T} = kN \frac{\partial \ln Q}{\partial V} \Big|_{E,N,(T)}} \quad \text{Is } Q = Q(V)? \quad \text{Yes!!}$$

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

$$\varepsilon_{i,tr} = f(L_x, L_y, L_z)$$

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## Chemical Potential and $Q$

- Examine  $\frac{\partial S}{\partial N} \Big|_{E,V} = -\frac{\tilde{\mu}}{T} \leftarrow \text{per molec.}$

$$S = kN \ln \frac{Q}{N} + kN + k\beta E$$

$$\frac{\partial S}{\partial N} \Big|_{E,V} = \frac{\partial S}{\partial N} \Big|_{E,V,\beta} + \frac{\partial S}{\partial \beta} \Big|_{E,V,N} \frac{\partial \beta}{\partial N} \Big|_{E,V} \quad Q = \sum_i g_i e^{-\beta \varepsilon_i} = Q(T, V)$$

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

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

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

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

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## Energy and Partition Function

- Let's examine relationship between  $Q$  and other TD variables

- Recall in finding  $\beta$ , we saw  $\frac{\partial Q}{\partial \beta} = -\frac{QE}{N} \Rightarrow E = -\frac{N}{Q} \frac{\partial Q}{\partial \beta}$   
so to find  $E$

$$\begin{aligned} \beta = 1/kT \Rightarrow \frac{d\beta}{dT} &= -\frac{1}{kT^2} & E &= -\frac{N}{Q} \frac{\partial Q}{\partial T} \frac{\partial T}{\partial \beta} \\ & & &= -\frac{N}{Q} (-kT^2) \frac{\partial Q}{\partial T} = NkT^2 \frac{1}{Q} \frac{\partial Q}{\partial T} \\ \text{--- also } c_v &=? & E &= NkT^2 \frac{\partial \ln Q}{\partial T} \quad \text{way to find } E \text{ if } N, Q, T \text{ known} \\ c_v &= \frac{de}{dT} & c_v &= R \left[ 2T \frac{\partial \ln Q}{\partial T} + T^2 \frac{\partial^2 \ln Q}{\partial T^2} \right] \quad R = k/m_{part}; m = Nm_{part} \\ & & & e = RT^2 \frac{\partial \ln Q}{\partial T} \end{aligned}$$

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## Summary

- Derived TD properties using

– Boltzmann's relation  $S = k \ln \Omega$  generally true (a priori prob.)

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

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

$$S = kN \left( 1 + \ln \frac{Q}{N} \right) + \frac{E}{T} \quad E = kNT^2 \frac{\partial \ln Q}{\partial T} \Big|_v \quad \begin{array}{l} \text{Partition} \\ \text{Function} \end{array} \quad \begin{array}{l} \text{Boltzmann} \\ \text{Distribution} \end{array}$$

$$\frac{p}{T} = kN \frac{\partial \ln Q}{\partial V} \Big|_{E,N} \quad \frac{\tilde{\mu}}{T} = -k \ln \frac{Q}{N} \quad \text{For given} \\ \text{- substance } (g_i, \varepsilon_i) \\ \text{- state (e.g., } E, N, V \text{)}$$

$$c_v = RT \left[ \frac{2 \partial \ln Q}{\partial T} \Big|_v + T \frac{\partial^2 \ln Q}{\partial T^2} \Big|_v \right] \quad \boxed{+ OTHERS} \quad \text{we can find all} \\ \text{TD props.,} \\ \text{- including } c_v$$

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## BE-FD Results

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

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

- For most probable macrostate  $N_i^{*}_{[FD]} = g_i \frac{e^{-\alpha - \beta \varepsilon_i}}{1 \mp e^{-\alpha - \beta \varepsilon_i}}$

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

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

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

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

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## BE-FD Results

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

- To get  $\alpha, \beta$  for BE and FD statistics, compare to TD  $S$  expression

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

Same results we found in Boltzmann limit!!

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

but we do have a modified population distribution over energy levels

$$N_i^{*}_{[FD]} = \frac{g_i}{e^{(\varepsilon_i - \tilde{\mu})/kT} \mp 1}$$

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## BE-FD Results

- Plug back into  $S$  expression

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

- Pressure

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

$$p = NkT \left. \frac{\partial \ln Q}{\partial V} \right|_{E,N}$$

- So properties still only function of  $g_i$ ,  $\varepsilon_i$ , but now we no 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

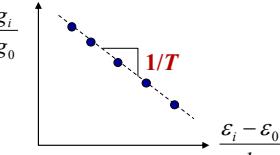
- Originally, our examination of the “state” of a substance (group of particles) depended only on the particles’ microscopic properties ( $\varepsilon_i$ ,  $g_i$ ) and the system’s extensive properties ( $E$ ,  $V$ ,  $N$ )
- When we defined the Lagrange multipliers for the most probable macrostate and related them to entropy, we then found “definitions” for  $T$ ,  $\mu$ ,  $p$ , 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

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

$$\ln \frac{N_i/g_i}{N_j/g_j} = -(\varepsilon_i - \varepsilon_j)/kT \quad \ln \frac{N_i/g_i}{N_0/g_0} = -(\varepsilon_i - \varepsilon_0)/kT$$

$$T = \frac{\varepsilon_i - \varepsilon_0}{k} \left( \ln \frac{N_j/g_j}{N_i/g_i} \right)^{-1}$$


- So temperature is the measure of how the particles are distributed among the energy levels
  - for a given tpg gas ( $g_i, \varepsilon_i$ ) 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  $T \gg \varepsilon_i$ ,  $N_i/N \approx g_i/g_j$

