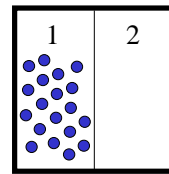


Statistical Thermo. and TD Properties

- 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

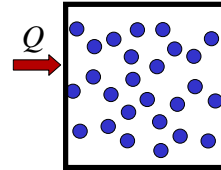


$$dS = \frac{1}{T} d\mathcal{U} + \frac{p}{T} dV = \frac{1}{T} dE + Nk \frac{dV}{V} \quad \begin{array}{l} \text{entropy increased with more} \\ \text{possible locations of finding} \\ \text{particles} \rightarrow \text{increased disorder} \end{array}$$

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

Entropy and Energy Change

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



- Gibbs for process $\rightarrow 0$

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

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

entropy increased with more possible (available) energy levels \rightarrow increased disorder

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

$c_v = \text{const.}$

Entropy and Microstates

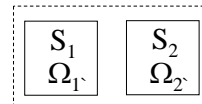
- Examples show there is relation between entropy and number of “places” particles can be
 - i.e., between S and Ω , or $S = \Phi(\Omega)$
- What should function Φ look like?
 - look at how systems combine

- Entropy is extensive

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

- Number of microstates are multiplicative

$$\Omega_{1+2} = \Omega_1 \times \Omega_2$$



- General form required

see V&K p. 114

Boltzmann's const.

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

absolute const. \rightarrow constant for given system

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

\uparrow

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 – 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
- 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)

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

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

Thermodynamic Relations

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

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

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

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

Thermodynamic Relations

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

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

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

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

$$\text{TD variables} \quad = \sum_i g_i e^{-\varepsilon_i/kT}$$

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

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

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

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

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

Is $Q=Q(V)$?

Yes!!

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

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.

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

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

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

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

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

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

Statistical Thermodynamic Relations-10

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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

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

$$E = -\frac{N}{Q} \frac{\partial Q}{\partial T} \frac{\partial T}{\partial \beta}$$

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

$$E = NkT^2 \frac{\partial \ln Q}{\partial T}$$

way to find E if N, Q, T known

– also $c_v = ?$

$$c_v = \frac{de}{dT}$$

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

$$R = k/m_{part}; m = Nm_{part}$$

$$e = RT^2 \frac{\partial \ln Q}{\partial T}$$

Summary

- Derived TD properties using

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

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

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

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

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

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

Partition Function Boltzmann Distribution

For given

- substance (g_i, ϵ_i)
- state (e.g., E, N, V)

we can find all

TD props.,

- including c_v

BE-FD Results

- If we remove Boltzmann limit assumption
 - but retain weakly interacting molec.

$$\ln W_{[BE, FD]} = \sum_i \left(N_i \ln \frac{g_i \pm N_i}{N_i} \pm g_i \ln \frac{g_i \pm N_i}{g_i} \right) \quad N_{i [BE, FD]}^* = g_i \frac{e^{-\alpha - \beta \epsilon_i}}{1 \mp e^{-\alpha - \beta \epsilon_i}}$$

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

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

- to get α, β compare to TD S expression

$$\left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{1}{T} = k\beta \Rightarrow \beta = 1/kT \quad \text{Same as what we found in Boltzmann limit!!}$$

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

$$N_{i [BE, FD]}^* = \frac{g_i}{e^{(\epsilon_i - \tilde{\mu})/kT} \mp 1} \quad \text{but modified energy pop. distribution}$$

BE-FD Results

- Plug back into S expression

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

- Pressure

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

- 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 ?

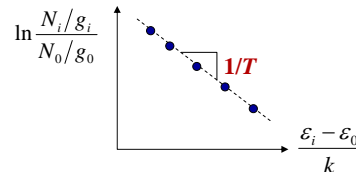
Stat. Thermo. Interpretation of T

- 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 gas (g_j, ε_i) in equilibrium, T is the ONLY thing needed to determine the energy population distribution