Stat Mech Reference Sheet (only covers ch. 1-8 of Kittel and Kroemer)

Fundamentals

$g :=$ multiplicity function
$\sigma = \log(g)$
$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_{N,V}$
$S = k_B\sigma$; $\tau = k_B T$; $k_B = 1.381 \cdot 10^{-23}\frac{J}{K}$

Microcanonical Ensemble

Fixed U,V,N
$\mathcal{P}(n) = \frac{1}{g}$
$g_{tot} = \sum_{U_1} g_1(U_1)g_2(U-U_1) \approx g_{max}$

Canonical Ensemble

Fixed τ, V, N
for observable O, $\langle O\rangle = \sum_n \mathcal{P}(n)O(n)$

$$Z = \sum_n e^{-\varepsilon_n/\tau}$$

$\mathcal{P}(n) = \frac{1}{Z}e^{-\varepsilon/\tau}$

$$U = \langle \varepsilon\rangle = \frac{1}{Z}\sum_n \varepsilon_n e^{-\varepsilon_n/\tau} = \tau^2\frac{\partial}{\partial\tau}\log(Z)$$

$$Z_N = (Z_1)^N \text{ or } \frac{(Z_1)^N}{N!}; \langle\varepsilon\rangle_N = N\langle\varepsilon\rangle_1$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_\sigma = \tau\left(\frac{\partial \sigma}{\partial V}\right)_U$$

Laws of Thermodynamics

0th Law: Thermal Equilibrium is transitive. (A + B and A + C in equilibrium implies B + C are in equilibrium)
1st Law: $\Delta U = Q + W$; $dU = dQ + dW = \tau d\sigma - PdV$
2nd Law: Total entropy never decreases under some process. Heat spontaneously flows from high to low temperatures.
3rd Law: $\lim_{T\to 0} S = 0$

Free Energy

Helmholtz Free energy F is minimized at equilibrium.

$$F = U - \tau\sigma = -\tau\log(Z)$$

$$dF = dU - d\tau\sigma - \tau d\sigma = -\sigma d\tau - PdV$$

General Stat Mech Workflow

1. Compute Z
2. get F
3. $P = -\frac{\partial F}{\partial V}$; $\sigma = -\frac{\partial F}{\partial \tau}$ etc.

Or analogous methods (Ω) when working in grand canonical ensemble

Useful Math Tools

Stirling Approximation (usually use only first 2 terms):

$$\log(N!) \approx N\log(N) - N + \frac{1}{2}\log(N) + \frac{1}{2}\log(2\pi) + \frac{1}{2N}$$

$$N! \approx \sqrt{2\pi N}N^N e^{-N}$$

Taylor Series Expansions:

$$f(x+\delta x) \approx f(x) + \frac{\partial f}{\partial x}\delta x$$

Paramagnet

$g(N,S) = \frac{N!}{(\frac{N}{2}+S)!(\frac{N}{2}-S)!}$, $S = \frac{1}{2}(N_\uparrow - N_\downarrow)$
$g(N,S) \approx g(N,0)e^{-2s^2/N}, g(N,0) = \left(\frac{2}{\pi N}\right)^{1/2}2^N$
$(N >> 1$ and $\frac{S}{N} << 1)$
$U = -2smB$

Ideal Gas

$$PV = N\tau$$

$$Z_1 = n_Q V = \frac{n_Q}{n}$$

$$U = \frac{3}{2}N\tau$$

$$\sigma = N\left[\log\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right]$$

$$\mu = \tau\log\left(\frac{n}{n_Q}\right)$$

$n_Q = \left(\frac{M\tau}{2\pi\hbar}\right)^{\frac{3}{2}}$

$$C_V = k_B\left(\frac{\partial U}{\partial\tau}\right)_V = \tau\left(\frac{\partial\sigma}{\partial T}\right)_V = \frac{3}{2}Nk_B$$

$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \tau\left(\frac{\partial\sigma}{\partial T}\right)_P = \frac{5}{2}Nk_B$

Thermal Radiation

Photon Gas (Stefan-Boltzmann Law): $\frac{U}{V} = \frac{\pi^2}{15(\hbar c)^3}\tau^4$
$P = \frac{1}{3}\frac{U}{V} = \frac{\pi^2}{45(\hbar c)^3}\tau^4$
$\sigma = \frac{4\pi^2}{45(\hbar c)^3}V\tau^3$
$J_U = \frac{cU}{4V} = \frac{\pi^2}{60\hbar^3c^2}\tau^4 = \sigma_B T^4; \sigma_B = \frac{\pi^2 k_B^4}{60\hbar^3c^2}$
$J_{real} = aJ_U$ $a :=$ adsorptivity. $a = e :=$ emissivity
Phonons:
Einstein Model: $U = \frac{3N\hbar\omega}{e^{\hbar\omega/\tau}-1}$
Debye Model: $U = \frac{3}{2}\frac{V\tau^4}{\pi^2(\hbar c_S)^3}\int_0^{x_D}dx\frac{x^3}{e^x-1}; x_D = \frac{\hbar\omega_D}{\tau}$
If $\tau << \hbar\omega$: $U \approx \frac{3\pi^4 N\tau^4}{5(k_B\theta)^3}; \theta = \frac{\hbar c_S}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$

Chemical Potential

$$\mu := \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V} = -\tau\left(\frac{\partial\sigma}{\partial N}\right)_{U,V}$$

Conditions for Equilibrium

conserved thing	eq. condition	flow of thing
Energy	$\tau_1 = \tau_2$	$1 \to 2$ if $\tau_1 > \tau_2$
Volume	$P_1 = P_2$	$2 \to 1$ if $P_1 > P_2$
Particles	$\mu_1 = \mu_2$	$1 \to 2$ if $\mu_1 > \mu_2$

Grand Canonical Ensemble

Fixed τ, V, μ

$$\mathfrak{z} = \sum_N\sum_s e^{-(\varepsilon-\mu N)/\tau} = \sum_N \lambda^N\sum_s e^{-\varepsilon/\tau} = \sum_N\lambda^N Z_N$$

$\lambda = e^{\mu/\tau}$

$$\mathcal{P}(\varepsilon) = \frac{e^{-(\varepsilon-\mu N)/\tau}}{\mathfrak{z}}$$

$$N = \frac{1}{\mathfrak{z}}\sum_N\sum_s Ne^{-(\varepsilon-\mu N)/\tau} = \tau\frac{\partial}{\partial\mu}\log\mathfrak{z} = \lambda\frac{\partial}{\partial\lambda}\log\mathfrak{z}$$

$$U = \frac{1}{\mathfrak{z}}\sum_N\sum_s \varepsilon e^{-(\varepsilon-\mu N)/\tau} = \tau^2\left(\frac{\partial}{\partial\tau}\log\mathfrak{z}\right)_\lambda$$

Grand Potential

$$\Omega = U - \sigma\tau - \mu N = -\tau \log(\mathfrak{z})$$

$$d\Omega = -\sigma d\tau - PdV - Nd\mu$$

$$\sigma = -\left(\frac{\partial\Omega}{\partial\tau}\right)_{V,\mu}; P = -\left(\frac{\partial\Omega}{\partial V}\right)_{\tau,\mu}; N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{\tau,V}$$

Internal Degrees of Freedom

$$Z_{int} = \sum_\alpha e^{-\varepsilon_\alpha^{int}/\tau}$$

$\mu = \mu_{trans} - \tau \log Z_{int}$
$F = F_{trans} - N\tau \log Z_{int}$
$\sigma = \sigma_{trans} - \frac{\partial F}{\partial \tau}$

Fermions and Bosons

$$\mathfrak{z}_\alpha = \begin{cases} 1 + e^{-\left(\frac{\varepsilon_\alpha - \mu}{\tau}\right)} & \text{fermions} \\ \frac{1}{1-e^{-\left(\frac{\varepsilon_\alpha - \mu}{\tau}\right)}} & \text{bosons} \end{cases}$$

$$\langle n_\alpha \rangle = f(\varepsilon_\alpha) = \begin{cases} \frac{1}{e^{(\varepsilon_\alpha - \mu)/\tau}+1} & \text{fermions} \\ \frac{1}{e^{(\varepsilon_\alpha - \mu)/\tau}-1} & \text{bosons} \end{cases}$$

Fermi Gas

$$\varepsilon_F = \mu(\tau = 0); U_0 = U(\tau = 0)$$

Ideal Fermi Gas:
Ground state energy: $\frac{3}{5}N\varepsilon_F$
Degeneracy Pressure: $P = \frac{\partial U_0}{\partial V} = \frac{2}{3}\frac{U_0}{V}$

Classical Limit

Condition for classical limit:

$$\frac{\varepsilon_\alpha - \mu}{\tau} >> 1 \text{ or } \frac{n}{n_Q} << 1$$

$$\langle n_\alpha \rangle = f(\epsilon_\alpha) = e^{-\frac{\epsilon_\alpha - \mu}{\tau}}$$

Density of States

$\mathcal{D}(\epsilon)d\varepsilon =$ Number of orbitals of energy between ε and $\varepsilon + d\varepsilon$.

$$\mathcal{D}(\varepsilon) = \frac{dN}{d\varepsilon}$$

$$\sum_{\mathbf{n}}(\ldots) \to \int d\varepsilon \mathcal{D}(\varepsilon)(\ldots)$$

Integrals with no angular dependence

$$\sum_{n_x,n_y}(\ldots) \to \frac{1}{2^2}\int d^2n(\ldots) \to \frac{2\pi}{2^2}\int ndn(\ldots)$$

$$\sum_{n_x,n_y,n_z}(\ldots) \to \frac{1}{2^3}\int d^3n(\ldots) \to \frac{4\pi}{2^3}\int n^2dn(\ldots)$$

"Diagnosing" Bose-Einstein Condensation

1. Find $\mathcal{D}(\varepsilon)$
2. Compute $(N_e)_{\max} = \int_0^\infty d\varepsilon \frac{\mathcal{D}(\varepsilon)}{e^{\varepsilon/\tau}=1}$
   - If $(N_e)_{\max}$ diverges, then BEC is not possible
   - If $(N_e)_{\max}$ is finite then BEC is possible

If BEC is possible, you can solve for τ_c by setting $(N_e)_{\max} = N$ and solving for τ_c.

1st Law Revisited

$$dU = \text{đ}q + \text{đ}W$$

$\text{đ}Q = td\sigma$ and $\text{đ}W = -Pdv$ is true only for reversible processes.

$$W_{\text{by gas}} = \int PdV; W_{\text{on gas}} = -\int PdV$$

$$\Delta U = Q - W_{\text{by gas}}$$

Heat Engines

Heat engines use a cyclic process to convert heat into work.

$$Q_H = W + Q_\ell$$

Efficiency:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_\ell}{Q_H}$$

Carnot Limit (reversible process):

$$\eta_c = 1 - \frac{\tau_c}{\tau_h}$$

Also for reversible process:

$$\frac{Q_\ell}{Q_H} = \frac{\tau_\ell}{\tau_H}$$

Refrigerators

Refrigerators use a cyclic process to convert work into a movement of Heat.
Efficiency (aka coefficient of performance):

$$\gamma = \frac{Q_\ell}{W} = \frac{Q_\ell}{\frac{Q_H}{Q_\ell} - 1}$$

Carnot Limit:

$$\gamma_c = \frac{1}{\frac{\tau_H}{\tau_\ell} - 1}$$

Carnot Cycle

1. Isothermal expansion (τ fixed)
2. Isentropic expansion (σ fixed)
3. Isothermal compression (τ fixed)
4. Isentropic compression (σ fixed)