Statistical Mechanics/Thermal Physics

General Statistical Formulas

$W_N(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$ $\quad W(n) = \frac{\bar{n}^n e^{-\bar{n}}}{n!}$

$W(n) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(n-\bar{n})^2/2\sigma^2}$ $\quad \bar{n} = Np$ $\quad \bar{s} = \int_{-\infty}^{\infty} sw(s)ds$

$\sigma^2 = Npq$ $\quad \sigma^2 = \overline{(\Delta s)^2} = \overline{(s-\bar{s})^2} = \overline{s^2} - \bar{s}^2$ $\quad ln n! = n \ln n - n$

Velocity and Speed Distributions

$h(v_i) = \sqrt{\frac{m}{2\pi kT}} e^{-mv_i^2/2kT}$ $\quad R(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-mv^2/2kT}$

$\hat{f}(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mv^2/2kT}$ $\quad \overline{v_i} = 0$ $\quad \overline{v_i^2} = \frac{kT}{m}$ $\quad \bar{v} = \sqrt{\frac{8kT}{\pi m}}$

$\overline{v^2} = \frac{3kT}{m}$ $\quad \tilde{v} = \sqrt{\frac{2kT}{m}}$ $\quad erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$

Flux and Effusion

$\bar{p} = nkT$ $\quad \bar{p}V = NkT$ $\quad \Phi(\vec{v})d\vec{v} = nv_z h(v_x)h(v_y)h(v_z)dv_x dv_y dv_z = nv_z \hat{f}(\vec{v})d\vec{v}$ $\quad \Phi_0 = \frac{1}{4}n\bar{v}$

Transport Processes

$P(t) = e^{-wt}$ $\quad w = n\sigma\bar{v}$ $\quad \tau = \frac{1}{w}$ $\quad \mathcal{P}(t)dt = e^{-t/\tau}\frac{dt}{\tau}$ $\quad t = \frac{L^2}{6D}$

$t = \frac{R^2}{6D}$ $\quad \eta = \frac{1}{3}n\bar{v}ml$ $\quad \kappa = \frac{1}{3}n\bar{v}lc$ $\quad D = \frac{1}{3}\bar{v}l$ $\quad l = \frac{1}{\sqrt{2}n\sigma_0}$

$\sigma_0 \sim T^{-0.2}$ $\quad Q_r = -\kappa\frac{\partial T}{\partial r}$

Random Walk

$\vec{R}_N = \sum_{n=1}^N \vec{r}_n$ $\quad \langle\vec{R}_N\rangle = \sum_{n=1}^N \langle\vec{r}_n\rangle$

$\langle\vec{r}_n\rangle = \sum_i P_i\vec{r}_i$ $\quad P$ = probabilty for each type of step i

$\langle\vec{R}_N^2\rangle = \langle\sum_{i=1}^N \vec{r}_i \cdot \sum_{j=1}^N \vec{r}_j\rangle = \sum_{ij}\langle\vec{r}_i \cdot \vec{r}_j\rangle = \sum_{i=j}\langle\vec{r}_i^2\rangle + 2\sum_{i<j}\langle\vec{r}_i \cdot \vec{r}_j\rangle$

Thermodynamics

$\Delta U = Q - W$ $\quad dW = \bar{p}dV$ $\quad S = kln\Omega(E)$ $\quad \beta = \frac{\partial ln\Omega}{\partial E} = \frac{1}{kT}$

$dS = \frac{dQ}{T}$ $\quad (dQ)_v = C_v dT$ $\quad (dQ)_p = C_p dT$ $\quad \Delta S = \frac{L}{T}$ $\quad pV = \nu RT$

$c_v + R = c_p$ $\quad C_v + \nu R = C_p$ $\quad \gamma = \frac{C_p}{C_v}$ $\quad \Omega \propto \frac{V^N}{N!}$

Maxwell Relations

	E	$dE = TdS - pdV$
enthalpy	$H = E + pV$	$dH = TdS + Vdp$
Helmholtz	$A = E - TS$	$dA = -SdT - pdV$
Gibbs	$G = E - TS + pV$	$dG = -SdT + Vdp$

ex. $E = E(S,V) \rightarrow dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$

identify $T = \left(\frac{\partial E}{\partial S}\right)_V$ and $P = -\left(\frac{\partial E}{\partial V}\right)_S$

now $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_S$

Thermodynamic Relations

$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$ $\quad \left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{P}{T}$ $\quad \left(\frac{\partial S}{\partial N}\right)_{V,E} = -\frac{\mu}{T}$

$P = \left(\frac{\partial S}{\partial V}\right)_{N,E} / \left(\frac{\partial S}{\partial E}\right)_{N,V} = -\left(\frac{\partial E}{\partial V}\right)_{N,S}$

$\mu = -\left(\frac{\partial S}{\partial N}\right)_{V,E} / \left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial E}{\partial N}\right)_{V,S}$

$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$ $\quad C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \left(\frac{\partial E}{\partial T}\right)_{N,V}$

$C_P = T\left(\frac{\partial S}{\partial T}\right)_{N,P} = \left(\frac{\partial(E+PV)}{\partial T}\right)_{N,P} = \left(\frac{\partial H}{\partial T}\right)_{N,P}$

Heat Capacity

heat capacity	C	$Q = C\Delta T$
specific heat capacity	c'	$Q = mc'\Delta T$
molar heat capacity	c	$Q = \nu c\Delta T$

m = mass $\quad \nu$ = number of moles

C: value for each system $\quad$ c,c': value for each substance

R: for number of moles $\quad$ k: for number of particles

Ideal Gases

$\Delta U = Q - W$ $\quad W = \int pdV$

Q=heat added to system $\quad$ W=work done on surroundings

$pV = \nu RT$ $\quad \Delta U = \nu c_v\Delta T$ $\quad \gamma = c_p/c_v$ $\quad c_p = c_v + R$

monatomic gas: $c_v = \frac{3}{2}R$ or $c_v = \frac{3}{2}k$ $\quad c_p = \frac{5}{2}R$ or $c_p = \frac{5}{2}k$

$\gamma = 5/3$ $\quad \bar{E} = \frac{3}{2}\nu RT = \frac{3}{2}NkT$

diatomic gas: $c_v = \frac{5}{2}R$ or $c_v = \frac{5}{2}k$ $\quad c_p = \frac{7}{2}R$ or $c_p = \frac{7}{2}k$

$\gamma = 7/5$

polyatomic gas: $\gamma = 4/3$

in general: $E = f\left(N\frac{1}{2}kT\right)$ $\quad C_v = \frac{f}{2}Nk$ $\quad f$ =degrees of freedom

isotherm	$dT = 0$	$W = \int \frac{nRT}{V}dV$	$Q = W$
isobar	$dp = 0$	$W = p\Delta V$	$Q = C_p\Delta T$
isochor	$dV = 0$	$W = 0$	$Q = C_v\Delta T$
adiabat		$W = -\Delta U$	$Q = 0$

adiabat: PV^γ =const, S =const

$dS = \frac{dQ}{T}$ $\quad (dQ)_v = C_v dT$ $\quad (dQ)_p = C_p dT$

Critical Points

$P = \frac{RT}{v-b} - \frac{a}{v^2}$ $\quad$ critical point: $\left(\frac{\partial P}{\partial v}\right)_T = 0$ $\quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$

usually taking derivatives of P or free energy A

Statistical Basis of Thermodynamics

$TdS = dE + PdV - \mu dN \Rightarrow S = S(N,V,E)$ $\quad \Omega = \Omega(N,V,E)$

$\beta = \left(\frac{\partial \ln\Omega}{\partial E}\right)_{N,V,E=\bar{E}} = \frac{1}{kT}$

Canonical Ensemble

$Q_N = \sum_i g_i e^{-\beta E_i}$ $\quad Q_N = \frac{1}{N!}[Q_1]^N$ if independent

g_i=multiplicity of i^{th} state $\quad \frac{1}{N!}$ if indistinguishable

ensemble average: $\langle C\rangle = \frac{\sum_i Cg_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$

$A = -kT\ln Q_N$ $\quad U = -\frac{\partial}{\partial\beta}\ln Q_N = A + TS = -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V}$ $\quad S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$ $\quad \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$

$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$ $\quad C = \left(\frac{\partial U}{\partial T}\right)$

Going to the Continuim Limit

$\sum_i \rightarrow \int \frac{d^d x d^d p}{(2\pi\hbar)^d} \rightarrow \int \frac{d^d x d^d k}{(2\pi)^d}$ $\quad d^3p = 4\pi p^2 dp$

$\sum_i e^{-\beta E_i} \Rightarrow \frac{1}{N!}\frac{1}{h^{3N}}\int d^3q_1 \ldots \int d^3q_N \int d^3p_1 \ldots \int d^3p_N e^{-\beta H(q_1,\ldots,q_N,p_1,\ldots,p_N)}$

$\sum_i \rightarrow \int dEg(E)$

Density of States

$\sum_i \rightarrow \int g(\epsilon)d\epsilon$

for a gas with $\epsilon \propto p^s$, confined to a space of n dimensions

$g(\epsilon)d\epsilon \sim p^{n-1}dp \sim \epsilon^{(n/s)-1}d\epsilon$

Magnetic Systems

$\bar{M} = \frac{1}{\beta Q_N} \frac{\partial}{\partial H} Q_N$ where H is the magnetic field

$\bar{M^2} = \frac{1}{\beta^2 Q_N} \frac{\partial^2}{\partial H^2} Q_N$ $\chi = \frac{\partial \bar{M}}{\partial H}$

Solid-Vapor Equilibrium

μ and T same for two phases: $z_{solid} = z_{gas}$

Clausius Clapeyron: $\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L_{12}}{T\Delta V}$

Grand Canonical Ensemble

$\mathcal{Z}(z, V, T) = \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V, T)$

$q = \ln \mathcal{Z}$ $\mu = kT \ln z$

$P = \frac{kT}{V} q$ $N = z \left. \frac{\partial q}{\partial z} \right|_{V,T}$ $U = - \left. \frac{\partial q}{\partial \beta} \right|_{z,V}$

Quantum Statistics

$$\mathcal{Z}(z, V, T) = \begin{cases} \prod_\epsilon \frac{1}{1 - ze^{-\beta\epsilon}} & Bose - Einstein \\ \prod_\epsilon \left(1 + ze^{-\beta\epsilon}\right) & Fermi - Dirac \end{cases}$$

fugacity: $z = e^{\mu/kT}$

BE: $a = -1$, FD: $a = 1$, MB: $a \to 0$

$q = \ln \mathcal{Z} = \frac{PV}{kT} = \frac{1}{a} \sum_\epsilon \ln \left(1 + aze^{-\beta\epsilon}\right)$

$\bar{N} = z \left(\frac{\partial q}{\partial z}\right)_{V,T} = \sum_\epsilon \frac{1}{z^{-1} e^{\beta\epsilon} + a}$

$U = \bar{E} = \sum_\epsilon \frac{\epsilon}{z^{-1} e^{\beta\epsilon} + a} = - \left(\frac{\partial q}{\partial \beta}\right)_{z,V} = kT^2 \left(\frac{\partial}{\partial T} \left(\frac{PV}{kT}\right)\right)_{z,V}$

$\langle n_\epsilon \rangle = \frac{1}{\mathcal{Z}} \left[-\frac{1}{\beta} \left(\frac{\partial \mathcal{Z}}{\partial \epsilon}\right)_{z,T,other\ \epsilon} \right] = -\frac{1}{\beta} \left(\frac{\partial q}{\partial \epsilon}\right) = \frac{1}{z^{-1} e^{\beta\epsilon} + a}$

Ideal Bose Gas

$\frac{PV}{kT} = \ln \mathcal{Z} = - \sum_\epsilon \ln \left(1 - ze^{-\beta\epsilon}\right)$

$\bar{N} = \sum_\epsilon \langle n_\epsilon \rangle = \sum_\epsilon \frac{1}{z^{-1} e^{\beta\epsilon} - 1} \to \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty \frac{p^2 dp}{z^{-1} e^{\beta\epsilon} - 1} + N_0$

$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1} dx}{z^{-1} e^x - 1} = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \ldots$

$z \frac{\partial}{\partial z} g_\nu(z) = g_{\nu-1}(z)$ at $T = T_c$, $z \to 1$ so $g_\nu(z) \to \xi(\nu)$

$\lambda = \frac{h}{\sqrt{2\pi mkT}}$

Ideal Fermi Gas

$\frac{PV}{kT} = \ln \mathcal{Z} = \sum_\epsilon \ln \left(1 + ze^{-\beta\epsilon}\right)$

$\bar{N} = \sum_\epsilon \langle n_\epsilon \rangle = \sum_\epsilon \frac{1}{z^{-1} e^{\beta\epsilon} + 1} \to \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty \frac{p^2 dp}{z^{-1} e^{\beta\epsilon} + 1}$

$f_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1} dx}{z^{-1} e^x + 1} = z - \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} - \ldots$

$z \frac{\partial}{\partial z} f_\nu(z) = f_{\nu-1}(z)$ at $T \to 0$, $\mu_0 \to \epsilon_f$

as $T \to 0$ $\langle n_\epsilon \rangle = \frac{1}{e^{(\epsilon - \mu)/kT} + 1} = \begin{cases} 1 & for\ \epsilon < \mu_0 = \epsilon_f \\ 0 & for\ \epsilon > \mu_0 = \epsilon_f \end{cases}$

$\int_0^{\epsilon_F} g(\epsilon) d\epsilon = N$ $p_f = \left(\frac{3N}{4\pi gV}\right)^{1/3} h$

Critical Exponents

	VDW	$CriticalExponent$	$Relation$
$orderparameter$	$\Delta V = V_g - V_l$	$\beta = 1/2$	$\Delta V \sim \lvert T_c - T \rvert^\beta$
$conjugatequantity$	P	$\delta = 3$	$\Delta V^\delta = P$
$responsefunction$	κ_T	$\gamma = 1$	$\kappa_T = -\frac{1}{V}\left(\frac{\partial P}{\partial V}\right)_T \sim \lvert t \rvert^{-\gamma}$
$heatcapacity$	C	$\alpha = 0$	$C \sim \lvert t \rvert^\alpha$
$correlationlength$	ξ	$\nu = 1/2$	$\xi \sim \lvert t \rvert^{-\nu}$

$t = \frac{T - T_c}{T_c}$

MFT predicts the same critical exponents for any system

Ising Model/Mean Field Theory

consider the following Hamiltonian:

$H = -J \sum_{i<j} s_i s_j - \mu \sum_i s_i^2$

MFT says turn the interaction term sum to one over nearest neighbors:

$H = -J \sum_{<ij>} s_i s_j - \mu \sum_i s_i^2 \to H = \sum_i s_i \left[-J \sum_{j,nn} s_j - \mu s_i\right]$

Now replace s_j with the spatial average $\bar{s}$ and make $\sum_{j,nn} \to c$ where c is the coordination number or number of neighbors (c=2 for 1D lattice, c=4 for 2D cubic lattice, etc) so the new MFT Hamiltonian is:

$H = -\sum_i s_i \left(cJ\bar{s} - \mu s_i\right)$

Say that the spatial average $\bar{s}$ equals the canonical ensemble average $\langle s \rangle$. Now an ensemble average of s can be taken to find a transcendental equation for $\langle s \rangle$. Expand to get critical exponents.