Math

$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y \rightarrow \left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y$ [Maxwell Relations]

$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$ [Triple Product Rule]

$g = f - \sum I_j X_j$; $I_j = \frac{\partial f}{\partial X_j}$ [Legendre Transformations]

$f(\lambda x) = \lambda^n f(x) \rightarrow f(x) = \frac{1}{n}\sum \left(\frac{\partial f}{\partial x_i}\right) x_i$ [Euler's Theorem]

$(\delta^n f) = \frac{1}{n!}\left(\frac{\partial^n f}{\partial \vec{X}^n}\right)(\delta\vec{X})^n$

$< G >= \sum P_\nu G_\nu$ [Expected Value]

$$\begin{aligned} I_s &= \int_0^\infty f_{F.D.}(\epsilon) g(\epsilon)\mathrm{d}\epsilon \\ &= \int_0^\mu g(\epsilon)\mathrm{d}\epsilon + \sum a_{2i}(k_B T)^{2i}\mathrm{d}_\epsilon^{2i-1} g(\epsilon) \end{aligned}$$ [Sommerfeld]

$a_{2i} = 2(1 - 2^{1-2i})\zeta(2i)$

$\sum \exp(-\beta(\epsilon - \mu))^i = (1 - \exp[-\beta(\epsilon - \mu)])^{-1}$ [Sum $|x| < 1$]

$\zeta(s) = \sum s^{-i} = \frac{1}{\Gamma(s)}\int_0^\infty \frac{x^{s-1}}{e^x - 1}\mathrm{d}x$ [Riemann-Zeta Function]

$\Gamma(s) = \int_0^\infty x^{s-1}e^{-s}\mathrm{d}x$ [Gamma Function]

Laws of Thermodynamics

$\mathrm{d}E = \text{đ}Q + \text{đ}W$ [First Law]

$(\Delta S)_{adiabatic} \geq 0$ [Second Law]

Thermodynamic Variables

$\{T\,\mathrm{d}S, -p\,\mathrm{d}V, \mu\,\mathrm{d}N, f\,\mathrm{d}L, E\,\mathrm{d}q, M\,\mathrm{d}H, \gamma\,\mathrm{d}A\}$ [Conjugate Pairs]

$T \equiv \left(\frac{\partial E}{\partial S}\right)_{\vec{X}} \geq 0$ [Temperature]

$C_X \equiv T\left(\frac{\partial S}{\partial T}\right)_X$ [Heat Capacity]

$K_X \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{X,N}$ [Compressibility]

Thermodynamic Potentials

$E = T\,S - p\,V + \sum \mu_i\,N_i$ [Internal Energy]

$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum \mu_i\,\mathrm{d}N_i$

$0 = S\,\mathrm{d}T - V\,\mathrm{d}p + \Sigma_i N_i\,\mathrm{d}\mu_i$ [Gibbs-Duhem Equation]

$A = E - T\,S$ [Helmholtz Free Energy]

$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum \mu_i\,\mathrm{d}N_i$

$H = E + p\,V$ [Enthalpy]

$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \sum \mu_i\,\mathrm{d}N_i$

$G = E + p\,V - T\,S$ [Gibbs Free Energy]

$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum \mu_i\,\mathrm{d}N_i$

Ensembles

$$\begin{aligned} Q(N,V,T) &= \textstyle\sum_E \exp(S/k_B)\exp(-\beta E) = \exp(-\beta A) \\ \Xi(\mu,V,T) &= \textstyle\sum_N Q(N,V,T)\exp(\beta\mu N) = \exp(\beta pV) \\ \Delta(N,p,T) &= \textstyle\sum_V Q(N,V,T)\exp(-\beta pV) = \exp(-\beta G) \\ \phi(V,E,\beta\mu) &= \textstyle\sum_N \Omega(N,V,E)\exp(\beta\mu N) = \exp(\beta H) \\ \Psi(V,T,\mu_1,N_2) &= \textstyle\sum_{N_1} Q(N_1,N_2,T,V)\exp(\beta\mu_1 N_1) \\ &= \exp(\beta pV)\exp(-\beta\mu_2 N_2) \\ W(p,\gamma,T,N) &= \textstyle\sum_{V,A} Q(N,V,A,T)\exp(-\beta pV)\exp(\beta\gamma A) \\ &= \exp(-\beta G) \end{aligned}$$

Equilibriums

$(\delta E)_{S,\vec{X}} \geq 0$; $(\Delta E)_{S,\vec{X}} > 0$ [Equilibrium]

$(\delta^2 E)_{S,\vec{X}} \geq 0; 0 \leq \left(\frac{\partial I_i}{\partial X_i}\right)_{X_{i\neq j}}$ [Stability]

$0 \leq \delta E = \sum_{j\neq i}(I^{(j)} - I^{(i)})\delta X^{(j)}$ [Equality of Intensives]

Entropy

$\Omega = \frac{N!}{(N-m)!m!}$ [Number of Microstates]

$S = k_b \log(\Omega)$ [Entropy]

$S = -k_b \sum P_\nu \log(P_\nu)$ [Gibbs Entropy Formula]

$P_\nu = \frac{1}{\Omega}$

$P_\nu = Q^{-1}\exp[-\beta E_\nu]$

Phase Space

$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta s(T)}{\Delta v(t)}$ [Clausius-Clapeyron Equation]

$f = 2 + r - \nu$ [Gibbs Phase Rule]

$\frac{\partial p}{\partial V} = 0 = \frac{\partial^2 p}{\partial V^2}$ [Critical Point]

$I^{(1)} = I^{(2)}$ [Equality of Intensive Variables Across Transition]

$\delta\mu = 0$ & $\frac{\partial\mu}{\partial p} = v$ [Equal Area]

Ideal Gas

$Q = \frac{1}{N!}q^N$ [Partition Function]

$q_{mona} = q_{trans}q_{el}q_{nuc}$ [Single Monatomic Partition]

$q_{dia} = q_{mona}q_{rot}q_{vib}$ [Single Diatomic Partition]

$q_{trans} = \frac{V}{\Lambda^3}$; where $\Lambda = \sqrt{\frac{m}{2\pi\beta\hbar^2}}$ [Translational]

$q_{el} = \exp[-\beta\epsilon_0]\,(g_0 + \sum g_i \exp[-\beta(\epsilon_i - \epsilon_0)])$ [Electron]

(N.B. large spacing makes higher terms ignorable)

$q_{nuc} = (2S_{nuc} + 1)\exp[-\beta\epsilon_{0,nuc}]$ [Nucleus]

(N.B. $\epsilon_{0,nuc} = 0$ is a general good approximation)

$q_{rot} = \frac{T}{\Theta_{rot}}$; where $\Theta_{rot} = \frac{\hbar^2}{2Ik_B}$ [Rotational]

(N.B. Only when $\Theta_{rot} \ll T$ & $I = \mu r^2$)

$q_{vib} = [2\sinh(\beta\hbar\omega_{vib}/2)]^{-1}$ [Vibrational]

(N.B. If $\hbar\omega_{vib} \ll k_B T$ then equal to $(\beta\hbar\omega_{vib})^{-1}$)

Chemical Equilibrium

For $[\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D]$

$K_c(T) = \frac{\rho_C^{\nu_C}\rho_D^{\nu_D}}{\rho_A^{\nu_A}\rho_B^{\nu_B}} = \frac{(q_C/V)^{\nu_C}(q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A}(q_B/V)^{\nu_B}}$

$K_p(T) = \frac{p_C^{\nu_C}p_D^{\nu_D}}{p_A^{\nu_A}p_B^{\nu_B}} = (k_B T)^{\nu_C + \nu_D - \nu_A - \nu_B}K_c(T)$

Fermion/Boson Statistics

$f(\epsilon)_{F.D./B.E.} = [\exp(\beta(\epsilon - \mu)) \pm 1]^{-1}$ [Statistics]

$\Xi_{F.D./B.E.} = \Pi[1 \pm \exp(-\beta(\epsilon_i - \mu)]^{\pm 1}$ [Grand Canonical]

Density of State

$D(\epsilon) = \frac{g}{\gamma}S_{d-1}\left(\frac{2\pi L}{\hbar\alpha^{1/\gamma}}\right)^d \epsilon^{d/\gamma - 1}$ [d-space D.o.S. of $\epsilon = \alpha|p|^\gamma$]

$<E> = \int \epsilon D(\epsilon)f(\epsilon)\mathrm{d}\epsilon$ [Expected Energy]

$<N> = \int D(\epsilon)f(\epsilon)\mathrm{d}\epsilon$ [Expected Number]

Virial Expansion

$$\begin{aligned} Q &= \frac{1}{h^{3N}}\int\ldots\int \exp[-\beta H]\mathrm{d}\mathbf{p}_1\ldots\mathrm{d}\mathbf{p}_N\mathrm{d}\mathbf{r}_1\ldots\mathrm{d}\mathbf{r}_N \\ &= \frac{1}{\Lambda^{3N}N!}Z_N \end{aligned}$$ [Classical Partition Function]

$Z_N = \int\ldots\int \exp[-\beta U_N]\mathrm{d}\mathbf{r}_1\ldots\mathrm{d}\mathbf{r}_N$ [Configuration Function]

$\Xi = \sum \frac{Z_N}{N!}s^N$

$s = \exp[\beta\mu]/\Lambda^3$ [Activity]

$p = kT\sum b_i s^i$ [Activity Expansion]

$\beta p = \sum B_n(T)\rho^n$ [Virial Expansion]

$f_{ij} = \exp[-\beta u(r_{ij})] - 1$ [Meyer's f-function]

$b_2 = \frac{1}{2!V}(Z_2 - Z_1^2) = \frac{1}{2!V}\int \mathrm{d}\mathbf{r}_1\int \mathrm{d}\mathbf{r}_2 f_{12} = \frac{1}{2!V}[\cdot - \cdot]$

$$\begin{aligned} b_3 &= \frac{1}{3!V}(Z_3 - 3Z_2Z_1 + 2Z_1^3) \\ &= \frac{1}{3!V}\int \mathrm{d}\mathbf{r}_1\int \mathrm{d}\mathbf{r}_2\int \mathrm{d}\mathbf{r}_3[f_{12}f_{13}f_{23} + 3f_{12}f_{23}] \\ &= \frac{1}{3!V}(\triangle + 3\wedge) = \frac{1}{6V}\triangle - \frac{1}{2V^2}[\cdot - \cdot]^2\text{; since } \wedge = V^{-1}[\cdot - \cdot]^2 \end{aligned}$$

$B_n(T) = -\frac{(n-1)}{n!V}S'_n$; $S'_{1,2} = —$ $S'_{1,2,3} = \triangle$ $S'_{1,2,3,4} = 3\square + 6\boxslash + \boxtimes$ [Virial Coefficients]

$p = \frac{Nk_B T}{V} - \frac{1}{3V}\left\langle \sum_{i<j} r_{ij}\frac{\partial}{\partial r_{ij}}u(r_{ij})\right\rangle$ [Virial Pressure]

Reduced Distribution Functions

$\rho^{(n/N)} = \frac{N!}{(N-n)!}\int \mathrm{d}r^{N-n}\frac{\exp[-\beta U(r^N)]}{\int \mathrm{d}r^N \exp[-\beta U(r^N)]}$

$g(r) = \rho^{(2/N)}/\rho^2$ [Pair Correlation Function]

(N.B. For ideal gas $g(r) = (1 - N^{-1})$)

$$\begin{aligned} \left\langle \sum_{i<j} u(r_{ij})\right\rangle &= \frac{N(N-1)}{2}\frac{1}{Z_N}\int u(r_{12})\exp[-\beta U]\mathrm{d}\mathbf{r} \\ &= \frac{N}{2}\int \rho g(r)u(r)\mathrm{d}\mathbf{r} \end{aligned}$$

$<E> = \frac{3Nk_B T}{2} + \frac{N\rho}{2}\int g(r)u(r)\mathrm{d}\mathbf{r}$

$\left\langle \sum u^{(3)}(r_{ij}, r_{jk})\right\rangle = \frac{N\rho^2}{6}\int \mathrm{d}\mathbf{r}_{12}\int \mathrm{d}\mathbf{r}_{23}\,g^{(3)}u^{(3)}$

$\frac{\beta p}{\rho} = 1 - \frac{\beta\rho}{6}\int r\,g(r)\frac{\partial u(r)}{\partial r}\mathrm{d}\mathbf{r}$ [Virial Pressure]

Random Equations

$\left\langle \Gamma_i \frac{\partial H}{\partial \Gamma_j}\right\rangle = \delta_{ij}k_B T$ [Generalized Equipartition]

$<(\delta N)^2> = <N^2> - <N>^2 = \frac{\partial^2 \log \Xi}{\partial(\beta\mu)^2}$

Random Identities

$<E> = -\left(\frac{\partial \log(Q)}{\partial \beta}\right)_{N,V}$

$\left(\frac{\partial \beta A}{\partial \beta}\right)_{N,V} = E$

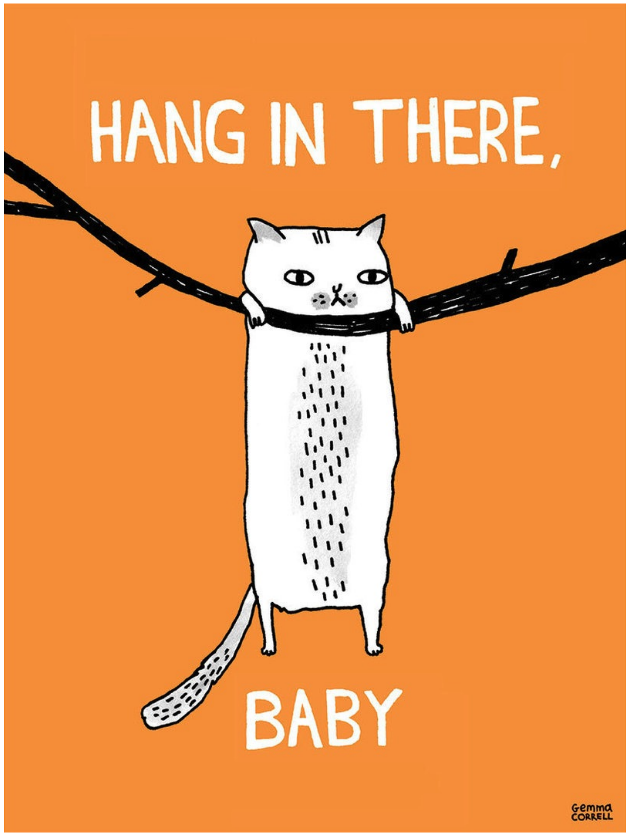
$<(\delta^2 E)> = k_B T^2 C_v$

$\left(\frac{\partial \log(Q)}{\partial V}\right)_{T,N} = -\left(\frac{\partial \beta A}{\partial V}\right)_{T,N} = \beta p$

$\left(\frac{\partial \log(Q)}{\partial(-\beta)}\right)_{V,N} = \left(\frac{\partial(-\beta A)}{\partial(-\beta)}\right)_{V,N} = < E >$

$\frac{\partial\mu}{\partial v} = v\frac{\partial p}{\partial v}$

$\beta = \left(\frac{\partial \log(\Omega)}{\partial E}\right)_{N,V}$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Hang in There, Baby!


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