Physics 410 -- Useful Formulas #1

0. Physical Constants

$$N_A = 6.02 \times 10^{23} \, \text{mol}^{-1} \qquad k_B = 1.38 \times 10^{-23} \, \text{J/K} \qquad N_A k_B = 8.31 \, \text{J/(mol - K)}$$

$$\hbar = 1.055 \times 10^{-34} \, \text{J - s} \qquad e = 1.60 \times 10^{-19} \, \text{C} \qquad m_p = 1.67 \times 10^{-27} \, \text{kg}$$

Kittel and Kroemer notation: $\tau = k_B T$, $\sigma = S / k_B$

I. Probability and statistics, and other mathematical formulas:

mean value and variance: $\qquad \overline{X} \equiv \langle X \rangle = \sum_s X(s) P(s)$, $\langle (\Delta X)^2 \rangle = \langle X^2 \rangle - \langle X \rangle^2$

where P(s) is a normalized probability distribution: $\sum_s P(s) = 1$

binomial distribution: $\qquad (p+q)^N = \sum_{n=0}^{N} \dfrac{N!}{n!(N-n)!} p^n q^{N-n}$

geometric series: $\qquad \sum_{n=0}^{N} x^n = \dfrac{1 - x^{N+1}}{1 - x}$, $\qquad \sum_{n=0}^{\infty} x^n = \dfrac{1}{1-x}$, for $|x| < 1$

Stirling's approximation: $\qquad \ln(n!) \approx \frac{1}{2} \ln(2\pi) + (n + \frac{1}{2}) \ln(n) - n$

binomial multiplicity for large N: $\quad g(N, s) = \dfrac{N!}{(\frac{N}{2} + s)!(\frac{N}{2} - s)!} \approx \left(\dfrac{2}{\pi N}\right)^{1/2} 2^N e^{-2s^2 / N}$

Gaussian integrals: $\quad \displaystyle\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi} \qquad \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \dfrac{\sqrt{\pi}}{2}$

Normalized Gaussian probability distribution: $P(x) = \dfrac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x - \overline{x})^2}{2\sigma^2}}$

Taylor series: $\qquad f(x_0 + \Delta x) = f(x_0) + f'(x_0)\Delta x + \dfrac{f''(x_0)}{2!}(\Delta x)^2 + \ldots$

examples: $\qquad \ln(1 + x) = x - \dfrac{x^2}{2} + \dfrac{x^3}{3} - \ldots \qquad e^x = 1 + x + \dfrac{x^2}{2!} + \dfrac{x^3}{3!} + \ldots$

II. Microcanonical ensemble: independent variables U, V, N

multiplicity function: $g(U,V,N)$;   entropy: $\sigma(U,V,N) = \ln g(U,V,N)$

temperature: $\dfrac{1}{\tau} = \left(\dfrac{\partial \sigma}{\partial U}\right)_{V,N}$ pressure: $p = \tau \left(\dfrac{\partial \sigma}{\partial V}\right)_{U,N}$

Alternative formulation with independent variables σ, V, N

temperature: $\tau = \left(\dfrac{\partial U}{\partial \sigma}\right)_{V,N}$ pressure: $p = -\left(\dfrac{\partial U}{\partial V}\right)_{\sigma,N}$

III. Canonical ensemble: independent variables τ, V, N

Partition function: $Z = \sum e^{-\frac{\varepsilon_s}{\tau}}$, Canonical distribution function: $P_S = \dfrac{e^{-\frac{\varepsilon_s}{\tau}}}{Z}$

The numerator of P_s is called the "Boltzmann factor"

Partition function for a system of N identical subsystems or particles:

Distinguishable: $Z_N = (Z_1)^N$ indistinguishable, Classical limit: $Z_N = \dfrac{(Z_1)^N}{N!}$

Mean Energy: $U = \tau^2 \dfrac{\partial(\ln Z)}{\partial \tau} = -\dfrac{\partial(\ln Z)}{\partial \beta}$ where $\beta = \dfrac{1}{\tau}$

Helmholtz free energy: $F = U - \tau\sigma = -\tau \ln Z$

entropy: $\sigma = -\left(\dfrac{\partial F}{\partial \tau}\right)_{V,N}$ pressure: $p = -\left(\dfrac{\partial F}{\partial V}\right)_{\tau,N}$

chemical potential: $\mu = \left(\dfrac{\partial F}{\partial N}\right)_{\tau,V}$ heat capacity: $C_V = \left(\dfrac{\partial U}{\partial \tau}\right)_V = \tau\left(\dfrac{\partial \sigma}{\partial \tau}\right)_V$

IV. Thermodynamic Identity: $dU = \tau d\sigma - pdV + \mu dN = TdS - pdV + \mu dN$

For reversible processes: $dQ = \tau d\sigma$, $dW = pdV$, so $dU = dQ - dW$ for constant N

Compare 1st Law of Thermodynamics: $\Delta U = Q - W$, W is work done <u>by</u> the system.

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V. Grand canonical ensemble: independent variables τ, V, μ

Grand Partition function, also called the "Gibbs sum": $\mathscr{Z} = \sum\limits_{N=0}^{\infty} \sum\limits_{s(N)} e^{[(N\mu - \varepsilon_s)/\tau]}$,

Grand canonical distribution function: $P(N, \varepsilon) = \dfrac{e^{[(N\mu - \varepsilon)/\tau]}}{\mathscr{Z}}$

The numerator of $P(N, \varepsilon)$ is called the "Gibbs factor"

Mean number of particles: $\langle N \rangle = \lambda \dfrac{d(\ln \mathscr{Z})}{d\lambda}$, where $\lambda = e^{\mu/\tau}$ is the "absolute activity".

VI. Quantum distribution functions:

$f(\varepsilon) \equiv$ average number of particles per orbital with τ and μ specified.

Planck distribution: $\qquad\qquad f(\varepsilon) = \dfrac{1}{e^{\hbar\omega/\tau} - 1}$ $\qquad\qquad$ photon energy: $\varepsilon = \hbar\omega$

Fermi-Dirac distribution: $\qquad f(\varepsilon) = \dfrac{1}{e^{(\varepsilon - \mu)/\tau} + 1}$

Bose-Einstein distribution: $\qquad f(\varepsilon) = \dfrac{1}{e^{(\varepsilon - \mu)/\tau} - 1}$

Classical limit: $\qquad\qquad\qquad f(\varepsilon) = e^{(\mu - \varepsilon)/\tau}$ valid when $\varepsilon - \mu \gg \tau$, so $f(\varepsilon) \ll 1$

VII. Particles (or photons) in a box of volume V:

Allowed wavevectors k (with periodic boundary conditions):

$$k_x = \frac{2\pi n_x}{L_x}, \; k_y = \frac{2\pi n_y}{L_y}, \; k_z = \frac{2\pi n_z}{L_z}, \qquad n_x, n_y, n_z = 0, \pm 1, \pm 2, ...$$

Counting modes in k-space: $\sum\limits_{k} ... = 2 \dfrac{V}{(2\pi)^3} \int d^3 k$

where the 2 is the spin or polarization degeneracy (if any).

You should know how to generalize this procedure to 1 or 2 dimensions!

VIII. Blackbody radiation: $J_U = \sigma_B T^4$, where $\sigma_B = \dfrac{\pi^2 k_B^4}{60\hbar^3 c^3} = 5.67 \times 10^{-8}\, Wm^{-2} K^{-4}$

IX. Monatomic Ideal Gas of N particles with mass m, in a box of volume V:

energy of state with wavevector k: $\varepsilon_k = \dfrac{\hbar^2 k^2}{2m}$

Total number of particles is the sum over orbital occupancies:

$$\langle N \rangle = \sum_s f(\varepsilon_s) = e^{\mu/\tau} \sum_s e^{-\varepsilon_s/\tau} = e^{\mu/\tau} Z_1$$

Partition function for 1 particle: $Z_1 = V n_Q = V\left(\dfrac{m\tau}{2\pi\hbar^2}\right)^{3/2}$ (Know how to derive this!)

Combine previous two results: $\mu = \tau \cdot \ln\dfrac{n}{n_Q}$, where $n = \dfrac{N}{V}$ and we've set $N = \langle N \rangle$

Helmholtz free energy: $F(\tau, V, N) = \displaystyle\sum_{N'=1}^{N} \mu(\tau, V, N') = N\tau\left(\ln\dfrac{n}{n_Q} - 1\right)$

Using formulas from Section III on Formula Sheet #1, you can find:

$$U = \tfrac{3}{2} N\tau \qquad \sigma = N\left(\ln\dfrac{n_Q}{n} + \tfrac{5}{2}\right) \qquad\qquad pV = N\tau \qquad C_V = \tfrac{3}{2} N$$

General ideal gas relations (not just for monatomic gas): $C_p = C_V + N$, $\gamma \equiv \dfrac{C_p}{C_V}$

where $C_V = \tfrac{3}{2} N + C_{rotations} + C_{vibrations}$

Isentropic expansion: $\tau_1 V_1^{\gamma-1} = \tau_2 V_2^{\gamma-1}$, $\quad \dfrac{\tau_1^{\gamma/(\gamma-1)}}{p_1} = \dfrac{\tau_2^{\gamma/(\gamma-1)}}{p_2}$, $\quad p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$

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X. Fermi gas

Ground state (3D): $\varepsilon_F = \dfrac{\hbar^2 k_F^2}{2m} = \dfrac{\hbar^2}{2m}\left(\dfrac{3\pi^2 N}{V}\right)^{2/3}$ $\qquad U_0 = \tfrac{3}{5} N\varepsilon_F$

Density of orbitals in 3D: $D(\varepsilon) = \dfrac{V}{2\pi^2}\left(\dfrac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}$ $\qquad$ Know how to derive $D(\varepsilon)$ also in 1D and 2D.

In general: $N = \displaystyle\int_0^\infty d\varepsilon\, D(\varepsilon) f(\varepsilon,\tau,\mu)$ $\qquad U = \displaystyle\int_0^\infty d\varepsilon\, D(\varepsilon)\,\varepsilon\, f(\varepsilon,\tau,\mu)$

XI. Heat and Work:

Carnot efficiency: $\eta_c \equiv \left(\dfrac{W}{Q_h}\right)_{reversible} = \dfrac{\tau_h - \tau_l}{\tau_h}$ $\qquad$ Know how to derive this!

Carnot refrigerator performance: $\gamma_c \equiv \left(\dfrac{Q_l}{W}\right)_{reversible} = \dfrac{\tau_l}{\tau_h - \tau_l}$ $\qquad$ This too!

Carnot cycle: 2 isothermal steps + 2 isentropic steps. Understand how it works, and be able to calculate the heat absorbed and work done by the system in each step using the Thermodynamic relations in Section IV and the ideal gas relations in Section IX.

XII. Gibbs free energy, useful for a system in contact with thermal and pressure reservoirs.

$G = U - \tau\sigma + pV$, independent variables τ, p, N

$$\sigma = -\left(\frac{\partial G}{\partial \tau}\right)_{p,N} \qquad V = \left(\frac{\partial G}{\partial p}\right)_{\tau,N} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{\tau,p}$$

$G(\tau, p, N) = N\mu(\tau, p)$

XIII. Chemical reactions: $\sum_j v_j A_j = 0$ where A_j are the reactants and v_j are integers.

Condition for equilibrium for fixed τ and p: $dG = \sum_j \mu_j dN_j = 0 \implies \sum_j v_j \mu_j = 0$

Law of mass action (for ideal gases): $\prod_j n_j^{v_j} = K(\tau) = \prod_j n_{Qj}^{v_j} e^{-v_j F_j(\text{internal})}/\tau$

XIV. Phase transitions

Equilibrium between phases: $\mu_1(p,\tau) = \mu_2(p,\tau)$

Clausius-Clapeyron equation: $\dfrac{dp}{d\tau} = \dfrac{L}{\tau\,\Delta v}$

where L = latent heat/molecule and Δv = volume change/molecule.

If $\Delta v \approx v_g = \dfrac{\tau}{p}$, then $\dfrac{dp}{d\tau} = \dfrac{Lp}{\tau^2}$.