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

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

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

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

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

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

Gaussian integrals: $\int_{-\infty}^{\infty} e^{-x^2}\,dx = \sqrt{\pi}$ $\qquad \int_{-\infty}^{\infty} x^2 e^{-x^2}\,dx = \frac{\sqrt{\pi}}{2}$

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

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

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

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

Alternative formulation with independent variables σ, V, N

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

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

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

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: $Z_N = \frac{(Z_1)^N}{N!}$

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

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

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

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

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 by the system.

Physics 410 -- Useful Formulas #2

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

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

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

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

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

VI. Quantum distribution functions for systems of weakly-interacting particles:

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

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

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

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

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

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

Allowed wavevectors k (with periodic boundary conditions):

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

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

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 $\sigma_B = \dfrac{\pi^2 k_B^4}{60\hbar^3 c^3} = 5.67 \times 10^{-8}\, W m^{-2} K^{-4}$

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

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

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

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