Thermodynamics and Statistical Mechanics

1 General Definitions and Equations

- First Law of Thermodynamics: *Heat Q is a form of energy, and energy is conserved.*
  - $dU = dQ - dW$
- Second Law of Thermodynamics: *The entropy S of a system must increase.*
  - $\Delta S \geq 0$
- Third Law of Thermodynamics: *For a system with a nondegenerate ground state $S \to 0$ as $T \to 0$.*
  - $\lim_{T\to 0} S = k_B \ln \Omega_0$, where Ω_0 is the degeneracy of the ground state
- A system is equally likely to be in any of the quantum states accessible to it.
- Equipartition theorem: each "degree of freedom" of a particle contributes $\frac{1}{2}k_BT$ to its thermal average energy
  - Any quadratic term in the energy counts as a "degree of freedom"
  - E.g. monoatomic: 3 translational, 0 rotational, 0 vibrational $\to \langle E\rangle = \frac{3}{2}kT$
  - E.g. diatomic: 3 translational, 2 rotational, 0 vibrational (2 at high T) $\to \langle E\rangle = \frac{5}{2}kT \left(\frac{7}{2}kT \text{ at high T}\right)$
- Binomial Distribution: $P\left(n, N-n\right) = \binom{N}{n} p^n (1-p)^{N-n}$
  - $\binom{N}{n} = \frac{N!}{n!(N-n)!}$
  - Normalization: $\sum_{n=0}^{N} P\left(n, N-n\right) = 1$
  - Mean: $\langle n\rangle = \sum_{n=0}^{N} nP\left(n, N-n\right) = Np$
  - Variance: $\left\langle n^2\right\rangle - \langle n\rangle^2 = \sum_{n=0}^{N} n^2 P\left(n, N-n\right) - (Np)^2 = Np(1-p)$

- Gaussian Distribution: $P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$
  - Normalization: $\int_{-\infty}^{\infty} P(x)\, dx = 1$
  - Mean: $\langle x \rangle = \int_{-\infty}^{\infty} xP(x)\, dx = \mu$
  - Variance $\left\langle (x-\mu)^2 \right\rangle = \int_{-\infty}^{\infty} (x-\mu)^2 P(x)\, dx = \sigma^2$
  - $P(a < x < b) = \int_a^b P(x)\, dx$
- Heat capacity, c: $Q = C\Delta T$, $C = mc$, where c is the specific heat capacity
- Molar heat capacity, C: $Q = nC\Delta T$, where n is the number of moles
- Latent heat of fusion (Q to make melt): $Q = mL_f$
- Latent heat of vaporization (Q to vaporize): $Q = mL_v$
- Ideal Gas Law: $PV = nRT = Nk_BT$
- For an ideal gas, $C_p = C_V + R, \quad$ where $C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial Q}{\partial T}\right)_P$
- Adiomatic index: $\gamma = \frac{C_P}{C_V}$
  - $\gamma = \frac{5}{3}$ for monoatomic gases, $\gamma = \frac{7}{5}$ for diatomic gases
- Stirling's Approximation: $\ln(n!) \approx n\ln(n) - n$, for $n >> 1$

2 Energy equations

- Thermodynamic Identity: $dE = TdS - PdV + \mu dN$
- Helmholtz Free Energy: $A = E - TS \Rightarrow dA = -PdV - SdT + \mu dN$
- Enthalpy: $H = E + PV \rightarrow dH = TdS + \mu dN + VdP$
- Gibbs free energy: $G = A + PV = E + PV - TS \rightarrow dG = VdP - SdT + \mu dN$
- Maxwell relations: $\frac{\partial}{\partial x_j}\left(\frac{\partial \Phi}{\partial x_i}\right) = \frac{\partial}{\partial x_i}\left(\frac{\partial \Phi}{\partial x_j}\right)$

3 Thermodynamic Processes

- Reversible process: happens very slowly, $\Delta S = \int \frac{dQ}{T}$
- Irreversible process: happens very suddenly
- Work: $W = \int PdV$
- Isothermal: T held constant
  - $dU = 0 \rightarrow dQ = dW$
- Isochoric: V held constant
  - $W = 0 \rightarrow dU = dQ$
- Isobaric: P held constant
  - $W = P\Delta V$
- Isoentropic: S held constant
- Adiabatic: $dQ = 0$
  - $dU = -dW$
  - Also isoentropic if reversible
  - $PV^\gamma = constant$
- Heat engine thermal efficiency: $e = 1 + \frac{Q_C}{Q_H}$
- Refridgerator coefficient of performance: $k = \frac{|Q_C|}{|Q_H| - |Q_C|}$
- Carnot cycle thermal efficiency (ideal): $e = 1 - \frac{T_C}{T_H}$
- Carnor refridgerator coefficient of performance: $k = \frac{T_C}{T_H - T_C}$

4 Microcanonical Ensemble

- $S = k_B \ln \Omega$, Ω is number of microstates accessible

5 Canonical Ensemble

- Partition function: $Z = \sum_s e^{-\beta\varepsilon_s}$, where $\beta = \frac{1}{k_B T}$
- With degeneracies: $Z = \sum_s g_s e^{-\beta\varepsilon_s}$, where g_s is the degeneracy of the s state
- $P(\varepsilon_s) = \frac{e^{-\varepsilon_s/k_B T}}{Z}$
- $\langle\varepsilon\rangle = \frac{1}{Z}\sum_s \varepsilon_s e^{-\beta\varepsilon_s} = -\frac{d\ln Z}{d\beta}$
- $A = -k_B T \ln Z$
- $S = \frac{\partial}{\partial T}(k_B T \ln Z) = -\frac{\partial A}{\partial T}$
- For N indistinguishable particles, $Z_N = \frac{Z^N}{N!}$

6 Grand Canonical Ensemble

- Chemical potential $\mu = -T\frac{\partial S}{\partial N}\Big|_E$
- Grand partition fucntion: $\mathcal{Z} = \sum_{N=0}^{\infty}\sum_{s(N)} \exp\left(-\frac{\varepsilon_s(n) - \mu N}{k_B T}\right)$
- $P(N, \varepsilon) = \frac{1}{\mathcal{Z}}\exp\left(-\frac{\varepsilon_s(n) - \mu N}{k_B T}\right)$
- $\langle N\rangle = k_B T\frac{\partial \ln \mathcal{Z}}{\partial \mu}$

7 Blackbody Radiation

- Stephan Boltzmann Law: $\Phi = \sigma T^4$
  - Φ is energy flux of star
  - T is the temperature of the star
  - $\sigma = 5.67 \times 10^{-8} JK^{-4}m^{-2}s^{-1}$ is Stephan-Boltzmann constant

- Planck radiation Law: $u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{-\beta\hbar\omega} - 1}$
  - u_ω is spectral density, energy per unit volume per unit frequency
- Wein's Law
  - $\lambda_{peak} = \frac{2.9 \times 10^{-3} mK}{T}$

8 Particle Distributions

- Maxwell-Boltzmann (for classical, distinguishable particles): $n(\varepsilon) = e^{-\beta(\varepsilon - \mu)}$
- Fermi-Dirac (for identical fermions): $n(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$
  - As $T \to 0$, $n(\varepsilon) \to \begin{cases} 1 & \text{if } \varepsilon < \mu(0) \\ 0 & \text{if } \varepsilon > \mu(0) \end{cases}$
  - Fermi energy $E_F = \mu(0)$, all states filled below E_F no states filled above E_F
- Bose-Einstein (for identical bosons): $n(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}$