PHYS 4200
Summary of second half of course

Thermodynamics

Heat, work, entropy: $dQ = dE + dW \quad dW = pdV \quad dS = \dfrac{dQ}{T}$

Fundamental thermodynamic relation: $dE = TdS - pdV$

Enthalpy is energy change, including p-V work: $H = E + pV$

Helmholtz free energy is minimized at constant volume and temperature: $F = E - TS$

Gibbs free energy is minimized at constant pressure and temperature: $G = H - TS$

Table of "energies" and Maxwell relations:

$$dE = TdS - pdV \qquad dH = TdS + Vdp$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_p$$

$$dF = -SdT - pdV \qquad dG = -SdT + Vdp$$

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Connections between entropy and temperature: $\beta = \dfrac{\partial \ln \Omega}{\partial E}$ and $\dfrac{1}{T} = \left(\dfrac{\partial S}{\partial E}\right)_V$

Connections between pressure and volume: $p = \dfrac{1}{\beta}\dfrac{\partial \ln \Omega}{\partial V}$ and $p = T\left(\dfrac{\partial S}{\partial V}\right)_E$

Ideal gases

Equation of state: $pV = NkT = \nu RT$

Free expansion (expansion without work) does not change energy or temperature.

Density of states: $\Omega = BV^N E^{3N/2}$

Partition function: $Z = \dfrac{1}{N!}\zeta^N = \dfrac{1}{N!}\left(\dfrac{V}{\lambda^3}\right)^N$

Thermal de Broglie wavelength: $\lambda = \dfrac{h}{\sqrt{2\pi mkT}}$

Energy (from $\partial\Omega/\partial E$, or equipartition, or $\partial Z/\partial\beta$): $E = \dfrac{3}{2}NkT$

Molar heat capacity (from $\partial E/\partial T$): $c_V = \dfrac{3}{2}R \quad c_p = c_V + R = \dfrac{5}{2}R \quad \gamma \equiv \dfrac{c_p}{c_V} = 1 + \dfrac{R}{c_V} = \dfrac{5}{3}$

Isothermal expansion (from eq. of state): $pV = constant$

Adiabatic expansion: $pV^\gamma = constant$

Probability of momentum **p** or velocity **v**: $P(\mathbf{p}) \sim e^{-\beta\frac{\mathbf{p}^2}{2m}} \qquad P(\mathbf{v}) \sim e^{-\beta\frac{m\mathbf{v}^2}{2}}$

Entropy (from Z): $S = Nk\left[\ln\frac{V}{N} + \frac{3}{2}\ln T + \frac{3}{2}\ln\frac{2\pi mk}{h^2} + \frac{5}{2}\right]$

In classical limit if $\bar{R} >> \lambda$ where R is separation between particles and λ is thermal de Broglie wavelength. This is from Heisenberg uncertainty relation, $\Delta q \Delta p > \hbar$.

Maxwell velocity distributions: $f(\mathbf{v}) = n\sqrt{\frac{m}{2\pi kT}}e^{-\beta\frac{m\mathbf{v}^2}{2}}$ $\quad F(v) = 4\pi v^2 n\sqrt{\frac{m}{2\pi kT}}e^{-\beta\frac{mv^2}{2}}$

Average speeds: $v_{rms} = \sqrt{\frac{3kT}{m}}$ $\quad \tilde{v} = \sqrt{\frac{2kT}{m}}$ $\quad \bar{v} = \sqrt{\frac{8kT}{\pi m}}$ $\quad v_{sound} = \sqrt{\frac{\gamma kT}{m}}$

Flux of molecules striking a surface (or effusion): $\Phi_0 = \frac{n\bar{v}}{4} = \frac{\bar{p}}{\sqrt{2\pi mkT}}$

Quantum states of particle in a box: $\varepsilon = \frac{\hbar^2}{2m}\left(\kappa_x^2 + \kappa_y^2 + \kappa_z^2\right) = \frac{2\pi^2\hbar^2}{m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$

Density of states of κ and over ε: $\rho_\kappa = \frac{V}{(2\pi)^3}$ $\quad \rho_\varepsilon = \frac{V(2m)^{3/2}}{4\pi^2\hbar^3}\sqrt{\varepsilon}$

Non-ideal gases

van der Waals equation of state: $p = \frac{RT}{v-b} - \frac{a}{v^2}$

v is volume per mole, a is attraction coefficient, and b is repulsion from volume exclusion.

virial equation of state: $p = kT\left[n + B_2(T)n^2 + B_3(T)n^3 + \cdots\right]$, $n = N/V$.

Heat engines and refrigerators

Heat engines obey conservation of energy (e.g. $q_1 = w+q_2$, for q_1 as heat flow from hot reservoir, w as work done, and q_2 as heat flow into cold reservoir) and entropy of entire system must increase over time (e.g. $\Delta S \geq 0$ for $\Delta S = -q_1/T_1 + q_2/T_2$).

Efficiency is η (e.g. $\eta = w/q_1 \leq 1-T_2/T_1 < 1$); if engine is quasi-static, $\eta = 1$.

A Carnot engine performs a cycle on a p-V graph: adiabatic compression, isothermal expansion, adiabatic expansion, and isothermal compression.

Refrigerators are identical, but arrow directions are reversed.

Heat pumps are similar as well.

Ensembles

Microcanonical ensemble uses $\Omega(E)$; particularly useful for system with fixed energy.

Probability of being in state r is: $P(r) = \left\{\begin{array}{cc} 1/\Omega(E) & E \leq E_r \leq E + \delta E \\ 0 & E_r \text{ not in range} \end{array}\right\}$.

Canonical ensemble uses $Z(T)$; particularly useful for system with fixed temperature.

Probability of being in state r is: $P(r) = \frac{e^{-\beta E_r}}{Z(T)}$

$Z(T)$ is the partition function, $Z(T) = \sum_r e^{-\beta E_r}$.

Classical version: $Z = \frac{1}{h^N} \int\int \cdots \int e^{-\beta E(q_1, q_2, \cdots, p_N)} \, dq_1 \, dq_2 \cdots dp_N$

Divide this by N! for indistinguishable particles (recall Gibbs's paradox).

Probability of having energy E, given temperature T, is $P(E) = \frac{\Omega(E)}{Z(T)} e^{-\beta E}$

Mean energy and variance: $E = \frac{1}{Z(T)} \sum_r E_r e^{-\beta E_r} = -\frac{\partial \ln Z(T)}{\partial \beta}$, $\langle \Delta E^2 \rangle = -\frac{\partial E}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}$

Generalized forces: $\bar{X} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x}$

Entropy: $S = k\left(\ln Z + \beta \bar{E}\right)$

Helmholtz free energy: $F = -kT \ln Z$

Combining ensembles: $\Omega^{(0)} = \Omega_1 \Omega_2 \quad Z^{(0)} = Z_1 Z_2$

Grand canonical ensemble: $P(r) = \frac{1}{\cancel{Z}(T, N)} e^{-\beta E_r - \alpha N_r} \qquad \cancel{Z} = \sum_r e^{-\beta E_r - \alpha N_r}$

Chemical potential is μ: $\mu = -kT\alpha$, or $\alpha = -\beta\mu$.

Magnetization (and other two-level systems)

Atoms have magnetic moment μ, field is H, energies are $\varepsilon = \pm\mu H$.

Using canonical ensemble: $\bar{\mu} = P_+ \mu + P_-(-\mu) = \mu \frac{e^{\beta\mu H} - e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}} = \mu \tanh \beta\mu H$

Magnetization is $\bar{M} = N\bar{\mu}$. It is $N\mu$ for low temperature, 0 for infinite temperature, and χH for high temperature where $\chi = N\beta\mu^2$, which is magnetic susceptibility. (Note that $\tanh(x) \sim x$ for $x << 1$).

Equipartition theorem

Each x^2 term in the Hamiltonian adds thermal energy of $kT/2$ to each particle, if kT is much larger than the mode's quantum energy levels.

Examples: ideal gas ($E = 3NkT/2$), harmonic oscillator ($E = kT$), Brownian particle, atoms in a crystal, etc.

Quantum statistics

Bosons: photons, He atoms, Cooper pairs, neutral atoms with even number of neutrons. Wavefunction is symmetric upon particle exchange. Indistinguishable, multiple particles may occupy the same state.

Bose-Einstein distribution, for mean bosons per state: $\bar{n}_r = \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1}$

Bose-Einstein partition function: $\ln Z = -\beta\mu N - \sum_r \ln\left(1 - e^{-\beta(\varepsilon_s - \mu)}\right)$

Photons are bosons, but number of particles is not conserved and $\mu = 0$.

Planck distribution, for mean photons per state: $\bar{n}_r = \frac{1}{e^{\beta\varepsilon_r} - 1}$

Fermions: electrons, protons, neutrons, quarks, neutral atoms with odd number of neutrons. Wavefunction is antisymmetric upon particle exchange. Indistinguishable, only 1 particle per state (Pauli exclusion principle).

Fermi-Dirac distribution, for mean fermions per state: $\bar{n}_r = \dfrac{1}{e^{\beta(\varepsilon_r-\mu)}+1}$

Fermi-Dirac partition function: $\ln Z = -\beta\mu N + \sum_r \ln\left(1+e^{-\beta(\varepsilon_s-\mu)}\right)$

Maxwell-Boltzmann statistics: the classical case, ignoring indistinguishability. Particles are distinguishable and multiple particles may occupy the same state. Bose-Einstein and Fermi-Dirac approach MB in the high temperature and low density limits (however, their partition functions approach $1/N!$ times the MB partition function due to indistinguishability).

Maxwell-Boltzmann distribution, for mean particles per state: $\bar{n}_r = N\dfrac{e^{-\beta\varepsilon_r}}{\sum_s e^{-\beta\varepsilon_s}}$

Blackbody radiation

Derived from Planck distribution and density of states for particle in a box.

Energy density in a cavity (Planck's law): $\bar{u}(\omega) = \dfrac{\hbar\omega^3}{\pi^2 c^2}\dfrac{1}{e^{\beta\hbar\omega}-1}$.

Wein's displacement law: $\omega \approx \dfrac{3kT}{\hbar}$, $\tilde{\lambda} = \dfrac{b}{T}$, $b = 2.898\times10^{-3}$ m K.

Total energy density in cavity: $\bar{u}_0(T) = \dfrac{\pi^2 k^4}{15(\hbar c)^3}T^4$

Radiation pressure on cavity walls: $p = \dfrac{\bar{u}_0}{3}$

For radiation emitted by a body at temperature T, good absorbers are good emitters (Kirchoff's law) and radiation emission is ~ $\cos(\theta)$ where θ is the angle away from the normal (Lambert's law).

Stefan-Boltzmann law is emitted power: $P = \sigma T^4$ $\sigma = \dfrac{\pi^2 k^4}{60c^2\hbar^3} \approx 5.670\cdot10^{-8}\ \mathrm{Wm^{-2}K^{-4}}$

Electrons in metals

Fermi energy at $T = 0$: $\mu_0 = \dfrac{\hbar^2}{2m}\left(3\pi^2\dfrac{N}{V}\right)^{\frac{2}{3}}$

Usually, $\mu >> kT$, so $\mu = \mu_0$.

At Fermi level: $T_F = \dfrac{\mu_0}{k} \approx 80{,}000\mathrm{K}$ $\quad \mu_0 = \dfrac{p_F^2}{2m} = \dfrac{mv_F^2}{2} = \dfrac{\hbar^2\kappa_F^2}{2m}$

de Broglie wavelength: $\lambda_F = \dfrac{\hbar}{p_F} = \dfrac{2\pi}{\kappa_F} = \dfrac{2\pi}{(3\pi^2)^{1/3}}\left(\dfrac{V}{N}\right)^{1/3} \approx \left(\dfrac{V}{N}\right)^{1/3}$

Heat capacity from electrons: $C_V \approx \dfrac{3}{2}Nk\left(\dfrac{T}{T_F}\right)$