0.1 Thermodynamics

0.1.1 Thermodynamic potentials

The energy $E(S, V, N)$ is an extensive function of its three extensive arguments. This entails the relation

$$E = TS - pV + \mu N \quad .$$

Since

$$dE = T\,dS - p\,dV + \mu\,dN \quad ,$$

we obtain the Gibbs-Duhem relation (GDR)

$$S\,dT - V\,dp + N\,d\mu = 0 \quad .$$

Thus, any one of the three intensive quantities (T, p, μ) may be written as a function of the other two. Dividing the GDR by N, for example, we obtain

$$d\mu = -s\,dT + v\,dp \quad ,$$

where $s = S/N$ and $v = V/N$ are the entropy and volume per particle. This says $\mu = \mu(T, p)$ with

$$s = -\left(\frac{\partial \mu}{\partial T}\right)_p \quad , \qquad v = \left(\frac{\partial \mu}{\partial p}\right)_T \quad .$$

The Helmholtz free energy $F = E - TS$, Gibbs free energy $E - TS + pV$, enthalpy $H = E + pV$, and grand potential $\Omega = E - TS - \mu N$ are Legendre transforms of the energy function. We also have $G = \mu N$ and $\Omega = -pV$. The various dependencies are given by

$$E = E(S, V, N) \quad , \quad F = F(T, V, N) \quad , \quad G = G(T, p, N) \quad , \quad H = H(S, p, N) \quad , \quad \Omega = \Omega(T, V, \mu) \quad ,$$

Their respective differentials are

$$dE = T\,dS - p\,dV + \mu\,dN$$
$$dF = -S\,dT - p\,dV + \mu\,dN$$
$$dG = -S\,dT + V\,dp + \mu\,dN$$
$$dH = T\,dS + V\,dp + \mu\,dN$$
$$d\Omega = -S\,dT - p\,dV - N\,d\mu \quad .$$

0.2 Statistical Ensembles

0.2.1 Classical distributions

Let $\varrho(\varphi)$ be a normalized distribution on phase space. Then

$$\langle f(\varphi) \rangle = \mathsf{Tr}\left[\varrho(\varphi)\,f(\varphi)\right] = \int d\mu\,\varrho(\varphi)\,f(\varphi) \quad ,$$

where $d\mu = W(\varphi) \prod_i d\varphi_i$ is the phase space measure. For a Hamiltonian system of N identical indistinguishable point particles in d space dimensions, we have

$$d\mu = \frac{1}{N!} \prod_{i=1}^{N} \frac{d^d p_i \, d^d q_i}{(2\pi\hbar)^d} \quad .$$

The $\frac{1}{N!}$ prefactor accounts for indistinguishability. Normalization means $\mathsf{Tr} \, \varrho = 1$.

0.2.2 Microcanonical ensemble (μCE)

The microcanonical distribution is given by

$$\varrho_E(\varphi) = \frac{\delta(E - \hat{H}(\varphi))}{D(E)} \quad ,$$

where $D(E) = \mathsf{Tr} \, \delta(E - \hat{H}(\varphi))$ is the density of states and $\hat{H}(\varphi) = \hat{H}(\boldsymbol{q}, \boldsymbol{p})$ is the Hamiltonian. The energy E, volume V, and particle number N are held fixed. Thus, the density of states $D(E, V, N)$ is a function of all three variables. The statistical entropy is $S(E, V, N) = k_{\mathrm{B}} \ln D(E, V, N)$, where k_{B} is Boltzmann's constant. Since D has dimensions of E^{-1}, an arbitrary energy scale is necessary to convert D to a dimensionless quantity before taking the log. In the thermodynamic limit, one has

$$S(E, V, N) = N k_{\mathrm{B}} \, \phi\left(\frac{E}{N}, \frac{V}{N}\right) \quad .$$

The differential of E is defined to be $dE = T \, dS - p \, dV + \mu \, dN$, thus $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$ is the temperature, $p = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$ is the pressure, and $\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$ is the chemical potential. Note that E, S, V, and N are all extensive quantities, *i.e.* they are halved when the system itself is halved.

0.2.3 Ordinary canonical ensemble (OCE)

In the OCE, energy fluctuates, while V, N, and the temperature T are fixed. The distribution is $\varrho = Z^{-1} e^{-\beta\hat{H}}$, where $\beta = 1/k_{\mathrm{B}}T$ and $Z = \mathsf{Tr} \, e^{-\beta\hat{H}}$ is the partition function. Note that Z is the Laplace transform of the density of states: $Z = \int dE \, D(E) \, e^{-\beta E}$. The Boltzmann entropy is $S = -k_{\mathrm{B}} \, \mathsf{Tr}(\varrho \ln \varrho)$. This entails $F = E - TS$, where $F = -k_{\mathrm{B}}T \ln Z$ is the Helmholtz free energy, a Legendre transform of the energy E. From this we derive $dF = -S \, dT - p \, dV + \mu \, dN$.

0.2.4 Grand canonical ensemble (GCE)

In the GCE, both E and N fluctuate, while T, V, and chemical potential μ remain fixed. The distribution function is then $\varrho = \Xi^{-1} e^{-\beta(\hat{H} - \mu\hat{N})}$, where

$$\Xi(T, V, \mu) = \mathsf{Tr} \, e^{-\beta(\hat{H} - \mu\hat{N})} = \sum_{N=0}^{\infty} e^{\beta\mu N} \, Z_N(T, V, N) = e^{-\beta\Omega(T,V,\mu)}$$

is the grand partition function and $\Omega = -k_{\mathrm{B}}T \ln \Xi$ is the grand potential. Assuming $[\hat{H}, \hat{N}] = 0$, we can label states $|n\rangle$ by both energy and particle number. Then $P_n = \Xi^{-1} e^{-\beta(E_n - \mu N_n)}$. We also have $\Omega = E - TS - \mu N$, hence $d\Omega = -S\,dT - p\,dV - N\,d\mu$. The quantity $z = e^{\beta\mu}$ is known as the *fugacity*.

0.2.5 Statistical thermodynamics

From $E = \mathsf{Tr}\,(\varrho\,\hat{H})$, we have $dE = \mathsf{Tr}\,(\hat{H}\,d\varrho) + \mathsf{Tr}\,(\varrho\,d\hat{H}) = đQ - đW$, where $đQ = T\,dS$ and

$$đW = -\mathsf{Tr}\,(\varrho\,d\hat{H}) = -\sum_n P_n \sum_i \frac{\partial E_n}{\partial X_i}\,dX_i = \sum_i F_i\,dX_i \quad ,$$

with $P_n = Z^{-1}e^{-E_n/k_{\mathrm{B}}T}$. Here $F_i = -\langle\frac{\partial \hat{H}}{\partial X_i}\rangle = sum_n P_n \frac{\partial E_n}{\partial X_i}$ is the generalized force conjugate to the generalized displacement X_i.

0.2.6 Thermal contact

In equilibrium, two systems which can exchange energy satisfy $T_1 = T_2$. Two systems which can exchange volume satisfy $p_1/T_1 = p_2/T_2$. Two systems which can exchange particle number satisfy $\mu_1/T_1 = \mu_2/T_2$.

0.2.7 Generalized susceptibilities

Within the OCE, let $\hat{H}(\boldsymbol{\lambda}) = \hat{H}_0 - \sum_i \lambda_i\,\hat{Q}_i$, where $\hat{Q}_i$ are observables with $[\hat{Q}_i, \hat{Q}_j] = 0$. Then

$$Q_k(T, V, N; \boldsymbol{\lambda}) = \langle\hat{Q}_k\rangle = -\frac{\partial F}{\partial \lambda_k} \quad , \qquad \chi_{kl}(T, V, N; \boldsymbol{\lambda}) = \frac{1}{V}\frac{\partial Q_k}{\partial \lambda_l} = -\frac{1}{V}\frac{\partial^2 F}{\partial \lambda_k\,\partial \lambda_l} \quad .$$

The quantities χ_{kl} are the generalized susceptibilities.

0.2.8 Ideal gases

For $\hat{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m}$, one finds $Z(T, V, N) = \frac{1}{N!}\left(\frac{V}{\lambda_T^d}\right)^N$, where $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_{\mathrm{B}}T}}$ is the thermal wavelength. Thus $F(T, V, N) = Nk_{\mathrm{B}}T \ln(N/V) - \frac{1}{2}dNk_{\mathrm{B}}T \ln T + Na$, where a is a constant. From this one finds $p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = nk_{\mathrm{B}}T$, which is the ideal gas law, with $n = \frac{N}{V}$ the number density. The distribution of velocities in $d = 3$ dimensions is given by

$$f(\boldsymbol{v}) = \left\langle\frac{1}{N}\sum_{i=1}^{N}\delta(\boldsymbol{v} - \boldsymbol{v}_i)\right\rangle = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} e^{-m v^2/2k_{\mathrm{B}}T} \quad ,$$

and this leads to a speed distribution $\bar{f}(v) = 4\pi v^2 f(v)$. In the GCE, we have $\Omega(T, V, \mu) = -Vk_{\mathrm{B}}T\lambda_T^{-3}\,e^{\mu/k_{\mathrm{B}}T}$.

0.2.9   Examples

Noninteracting Ising spins

For N noninteracting spins in an external magnetic field H, the Hamiltonian is $\hat{H} = -\mu_0 H \sum_{i=1}^{N} \sigma_i$, where $\sigma_i = \pm 1$. The spins, if on a lattice, are regarded as distinguishable. Then $Z = \zeta^N$, where $\zeta = \sum_{\sigma=\pm 1} e^{\beta \mu_0 H \sigma} = 2 \cosh(\beta \mu_0 H)$. The magnetization and magnetic susceptibility are then

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,N} = N\mu_0 \tanh\left(\frac{\mu_0 H}{k_{\mathrm{B}} T}\right) \quad , \quad \chi = \frac{\partial M}{\partial H} = \frac{N\mu_0^2}{k_{\mathrm{B}} T} \operatorname{sech}^2\left(\frac{\mu_0 H}{k_{\mathrm{B}} T}\right) \quad .$$

Ballistic particles with internal degrees of freedom

For noninteracting particles with kinetic energy $\frac{p^2}{2m}$ and internal degrees of freedom, $Z_N = \frac{1}{N!}\left(\frac{V}{\lambda_T^d}\right)^N \xi^N(T)$, where $\xi(T) = \mathsf{Tr}\, e^{-\beta \hat{h}_{\mathrm{int}}}$ is the partition function for the internal degrees of freedom, which include rotational, vibrational, and electronic excitations. One still has $pV = Nk_{\mathrm{B}}T$, but the heat capacities at constant V and p are

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \tfrac{1}{2}dNk_{\mathrm{B}} - NT\varphi''(T) \quad , \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = C_V + Nk_{\mathrm{B}} \quad ,$$

where $\varphi(T) = -k_{\mathrm{B}}T\ln\xi(T)$. Suppose that the internal degree of freedom for each particle is an angle $\phi \in [0, 2\pi)$, and that $\hat{h}_{\mathrm{int}} = -B\mu_0\cos\phi$. Then

$$\xi(T) = \int\limits_0^{2\pi} \frac{d\phi}{2\pi}\, e^{\mu_0 B \cos\phi / k_{\mathrm{B}} T} = I_0\left(\frac{\mu_0 B}{k_{\mathrm{B}} T}\right) \quad ,$$

where $I_0(z)$ is a modified Bessel function. If the internal degree of freedom is a three-dimensional unit vector $\hat{\boldsymbol{n}}$ and $\hat{h}_{\mathrm{int}} = -\mu_0\, \boldsymbol{B} \cdot \hat{\boldsymbol{n}}$, then the normalized trace over the internal degree of freedom is given by $\mathsf{Tr}\, e^{-\beta \hat{h}_{\mathrm{int}}} = \int \frac{d\hat{\boldsymbol{n}}}{4\pi}\, e^{-\beta \hat{h}_{\mathrm{int}}}$.

0.3   Quantum Statistics

0.3.1   Second-quantized Hamiltonian

A noninteracting quantum system is described by a Hamiltonian $\hat{H} = \sum_\alpha \varepsilon_\alpha\, \hat{n}_\alpha$, where ε_α is the energy eigenvalue for the single particle state ψ_α (possibly degenerate), and $\hat{n}_\alpha$ is the number operator. Many-body eigenstates $|\vec{n}\rangle$ are labeled by the set of occupancies $\vec{n} = \{n_\alpha\}$, with $\hat{n}_\alpha |\vec{n}\rangle = n_\alpha |\vec{n}\rangle$. Thus, $\hat{H}\,|\vec{n}\rangle = E_{\vec{n}}\,|\vec{n}\rangle$, where $E_{\vec{n}} = \sum_\alpha n_\alpha\, \varepsilon_\alpha$. The allowed values for n_α are $n_\alpha \in \{0, 1, 2, \ldots, \infty\}$ for bosons and $n_\alpha \in \{0, 1\}$ for fermions.

0.3.2 Grand canonical ensemble

Because of the constraint $\sum_\alpha n_\alpha = N$, the ordinary canonical ensemble is inconvenient. Rather, we use the grand canonical ensemble, in which case

$$\Omega(T, V, \mu) = \pm k_{\mathrm{B}} T \sum_\alpha \ln\left(1 \mp e^{-(\varepsilon_\alpha - \mu)/k_{\mathrm{B}}T}\right) \quad,$$

where the upper sign corresponds to bosons and the lower sign to fermions. The average number of particles occupying the single particle state ψ_α is then

$$\langle \hat{n}_\alpha \rangle = \frac{\partial\Omega}{\partial\varepsilon_\alpha} = \frac{1}{e^{(\varepsilon_\alpha - \mu)/k_{\mathrm{B}}T} \mp 1} \quad.$$

In the Maxwell-Boltzmann limit, $\mu \ll -k_{\mathrm{B}}T$ and $\langle n_\alpha \rangle = z\,e^{-\varepsilon_\alpha/k_{\mathrm{B}}T}$, where $z = e^{\mu/k_{\mathrm{B}}T}$ is the fugacity. Note that this low-density limit is common to both bosons and fermions.

0.3.3 Single particle density of states

The single particle density of states per unit volume is defined to be

$$g(\varepsilon) = \frac{1}{V}\,\mathsf{Tr}\ \delta(\varepsilon - \hat{h}) = \frac{1}{V}\sum_\alpha \delta(\varepsilon - \varepsilon_\alpha) \quad,$$

where $\hat{h}$ is the one-body Hamiltonian. If $\hat{h}$ is isotropic, then $\varepsilon = \varepsilon(k)$, where $k = |\boldsymbol{k}|$ is the magnitude of the wavevector, and

$$g(\varepsilon) = \frac{\mathsf{g}\,\Omega_d}{(2\pi)^d}\,\frac{k^{d-1}}{d\varepsilon/dk} \quad,$$

where g is the degeneracy of each single particle energy state. Recall $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$. Thus, we may write

$$\Omega(T, V, \mu) = \pm k_{\mathrm{B}} T \int\limits_{-\infty}^{\infty} d\varepsilon\ g(\varepsilon) \ln\left(1 \mp e^{(\mu - \varepsilon)/k_{\mathrm{B}}T}\right) \quad,$$

0.3.4 Quantum virial expansion

From $\Omega = -pV$, we have

$$n(T, z) = \int\limits_{-\infty}^{\infty} d\varepsilon\ \frac{g(\varepsilon)}{z^{-1}\,e^{\varepsilon/k_{\mathrm{B}}T} \mp 1} = \sum_{j=1}^{\infty} z^j\, C_j(T)$$

$$p(T, z) = \mp k_{\mathrm{B}} T \int\limits_{-\infty}^{\infty} d\varepsilon\ g(\varepsilon)\ \ln\left(1 \mp z\,e^{-\varepsilon/k_{\mathrm{B}}T}\right) = k_{\mathrm{B}} T \sum_{j=1}^{\infty} j^{-1}\, C_j(T)\, z^j \quad,$$

where

$$C_j(T) = (\pm 1)^{j-1} \int\limits_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, e^{-j\varepsilon/k_{\mathrm{B}}T} \quad .$$

One now inverts $n = n(T, z)$ to obtain $z = z(T, n)$, then substitutes this into $p = p(T, z)$ to obtain a series expansion for the equation of state,

$$p(T, n) = nk_{\mathrm{B}}T \Big(1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots \Big) \quad .$$

The coefficients $B_j(T)$ are the *virial coefficients*. One finds

$$B_2 = \mp \frac{C_2}{2C_1^2} \quad , \qquad B_3 = \frac{C_2^2}{C_1^4} - \frac{2\,C_3}{3\,C_1^3} \quad .$$

0.3.5 Photon statistics

Photons are bosonic excitations whose number is not conserved, hence $\mu = 0$. The number distribution for photon statistics is then $n(\varepsilon) = 1/(e^{\beta\varepsilon} - 1)$. Examples of particles obeying photon statistics include phonons (lattice vibrations), magnons (spin waves), and of course photons themselves, for which $\varepsilon(k) = \hbar c k$ with $\mathsf{g} = 2$. The pressure and number density for the photon gas obey $p(T) = A_d\, T^{d+1}$ and $n(T) = B_d\, T^d$, where d is the dimension of space and A_d and B_d are constants.

0.3.6 Blackbody radiation

The energy density per unit frequency of a three-dimensional blackbody is given by

$$\rho_\varepsilon(\nu, T) = \frac{8\pi h}{c^3} \cdot \frac{\nu^3}{e^{h\nu/k_{\mathrm{B}}T} - 1} \quad .$$

The total power emitted per unit area of a blackbody is $\frac{dP}{dA} = \sigma T^4$, where $\sigma = \pi^2 k_{\mathrm{B}}^4/60\hbar^3 c^2 = 5.67 \times 10^{-8}\ \mathrm{W/m^2\,K^4}$ is Stefan's constant.

Example: The total power radiated by the sun is $P_\odot = \sigma T_\odot^4 \times 4\pi R_\odot^2$ and the fraction incident upon the earth is $\pi R_{\mathrm{e}}^2/4\pi a_{\mathrm{e}}^2$, where $a_{\mathrm{e}} = 1\ \mathrm{AU}$. Assuming the earth is a perfect blackbody, the surface temperature of the earth T_{e} should satisfy

$$P_\odot = \sigma T_\odot^4 \times 4\pi R_\odot^2 \times \frac{R_{\mathrm{e}}^2}{4a_{\mathrm{e}}^2} = \sigma T_{\mathrm{e}}^4 \times 4\pi R_{\mathrm{e}}^2 \qquad \Rightarrow \qquad T_{\mathrm{e}} = \left(\frac{R_\odot}{2a_{\mathrm{e}}}\right)^{1/2} T_\odot \quad .$$

0.3.7 Ideal Bose gas

For Bose systems, we must have $\varepsilon_\alpha > \mu$ for all single particle states. The number density is

$$n(T, \mu) = \int\limits_{-\infty}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1} \quad .$$

This is an increasing function of μ and an increasing function of T. For fixed T, the largest value $n(T,\mu)$ can attain is $n_{\rm c}(T) \equiv n(T,\varepsilon_0)$, where ε_0 is the lowest possible single particle energy; $g(\varepsilon) = 0$ for $\varepsilon < \varepsilon_0$. If $n_{\rm c}(T) < \infty$, this establishes a *critical density* above which there is *Bose condensation* into the energy ε_0 state. Conversely, for a given density n there is a *critical temperature* $T_{\rm c}(n)$ such that n_0 is finite for $T < T_{\rm c}$. For $T < T_{\rm c}$, $n = n_0 + n_{\rm c}(T)$, with $\mu = \varepsilon_0$. For $T > T_{\rm c}$, $n(T,\mu)$ is given by the integral formula above, with $n_0 = 0$. For a ballistic dispersion $\varepsilon(\boldsymbol{k}) = \hbar^2 \boldsymbol{k}^2/2m$, one finds $n\lambda_{T_{\rm c}}^d = {\rm g}\,\zeta(d/2)$, where g is the internal degeneragy of each state. Thus $k_{\rm B}T_{\rm c} = \frac{2\pi\hbar^2}{m}\left(n/{\rm g}\,\zeta(d/2)\right)^{2/d}$. For $T < T_{\rm c}(n)$, one has $n_0 = n - {\rm g}\,\zeta(\tfrac{1}{2}d)\,\lambda_T^{-d} = n\left(1 - (T/T_{\rm c})^{d/2}\right)$ and $p = {\rm g}\,\zeta(1 + \tfrac{1}{2}d)\,k_{\rm B}T\,\lambda_T^{-d}$. For $T > T_{\rm c}(n)$, one has $n = {\rm g}\,{\rm Li}_{\frac{d}{2}}(z)\,\lambda_T^{-d}$ and $p = {\rm g}\,{\rm Li}_{\frac{d}{2}+1}(z)\,k_{\rm B}T\,\lambda_T^{-d}$, where

$$\mathrm{Li}_q(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^q}.$$

The implicit equation for $T_{\rm c}(n)$ is

$$n = \int_{-\infty}^{\infty} d\varepsilon \, \frac{g(\varepsilon)}{e^{\varepsilon/k_{\rm B}T_{\rm c}} - 1} \quad,$$

For a power law density of states $g(\varepsilon) = C\,\varepsilon^{r-1}$, we have $\varepsilon_0 = 0$ and

$$n = \int_0^{\infty} d\varepsilon \, \frac{C\,\varepsilon^{r-1}}{e^{\varepsilon/k_{\rm B}T_{\rm c}} - 1} \qquad \Rightarrow \qquad k_{\rm B}T_{\rm c}(n) = \left(\frac{n}{C\,\Gamma(r)\,\zeta(r)}\right)^{1/r} \quad.$$

0.3.8 Ideal Fermi gas

The Fermi distribution is $n(\varepsilon) = f(\varepsilon - \mu) = 1/\left(e^{(\varepsilon-\mu)/k_{\rm B}T} + 1\right)$. At $T = 0$, this is a step function: $n(\varepsilon) = \Theta(\mu - \varepsilon)$, and $n = \int_{-\infty}^{\mu} d\varepsilon\, g(\varepsilon)$. The chemical potential at $T = 0$ is called the *Fermi energy*; thus $\mu(T = 0, n) = \varepsilon_{\rm F}(n)$. If the dispersion is $\varepsilon(\boldsymbol{k})$, the locus of $\boldsymbol{k}$ values satisfying $\varepsilon(\boldsymbol{k}) = \varepsilon_{\rm F}$ is called the *Fermi surface*. For an isotropic and monotonic dispersion $\varepsilon(k)$, the Fermi surface is a sphere of radius $k_{\rm F}$, the *Fermi wavevector*. For isotropic three-dimensional systems, $k_{\rm F} = (6\pi^2 n/{\rm g})^{1/3}$.

0.3.9 Sommerfeld expansion

Let $\phi(\varepsilon) = \frac{d\Phi}{d\varepsilon}$. Then

$$\int_{-\infty}^{\infty} d\varepsilon \, f(\varepsilon - \mu)\,\phi(\varepsilon) = \pi D \csc(\pi D)\,\Phi(\mu)$$

$$= \left\{1 + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\,\frac{d^2}{d\mu^2} + \frac{7\pi^4}{360}\,(k_{\rm B}T)^4\,\frac{d^4}{d\mu^4} + \dots\right\}\Phi(\mu) \quad,$$

where $D = k_{\mathrm{B}}T\frac{d}{d\mu}$. One then finds, for example, $C_V = \gamma VT$ with $\gamma = \frac{1}{3}\pi^2 k_{\mathrm{B}}^2\, g(\varepsilon_{\mathrm{F}})$. Note that nonanalytic terms proportional to $\exp(-\mu/k_{\mathrm{B}}T)$ are invisible in the Sommerfeld expansion.