Equilibrium Distribution Functions. III: Grand Canonical Distribution

Setup and Derivation

• *Idea:* A distribution function describing a system in equilibrium with a heat bath with which it exchanges both energy and particles. It can be used classically in situations where chemical reactions, phase transitions, osmosis or other processes change the number of particles, and in quantum field theory where particles are created and annihilated. It is also useful as a tool to derive results for fixed-particle-number situations.

• *Distribution function:* For fixed total values of N_t and E_t, the probability that the system has $N_s \ll N_t$ particles in a microstate s of energy $H(s) = E_s \ll E_t$ is $\rho(N, s) \propto \Omega_R(N_t - N, E_t - E)$. To leading order,

$$k_{\text{B}} \ln \rho(N, s) = C + k_{\text{B}} \ln \Omega_R(N_t, E_t) - \frac{\partial S}{\partial N}\bigg|_E N_s - \frac{\partial S}{\partial E}\bigg|_N E_s + ... = C' - \frac{H(s)}{T} + \frac{\mu N}{T} + ... \,,$$

$$\text{so} \quad \rho(N, s) = \frac{1}{Z_{\text{g}}} \, \mathrm{e}^{-\beta H(s) + \beta \mu N} \,, \quad Z_{\text{g}} := \sum_{\text{states}} \mathrm{e}^{-\beta H(s) + \beta \mu N} = \sum_{N=0}^{\infty} \mathrm{e}^{\beta \mu N} \int_{\Gamma_{(N)}} \mathrm{d}\Omega_{(N)} \, \mathrm{e}^{-\beta H(q,p)} \,,$$

where $\beta = 1/k_{\text{B}}T$ as before, and we have used the fact that from the thermodynamic identity $\partial S/\partial E|_N = T^{-1}$ and $\partial S/\partial N|_E = -\mu T^{-1}$. We can also define the *fugacity* $z := \mathrm{e}^{\beta \mu}$, and write

$$Z_{\text{g}} = \sum_{N=0}^{\infty} z^N Z_{(N)} \,.$$

Obtaining Thermodynamics from the Grand Canonical Distribution

• *Mean particle number:* Taking a derivative of Z_{g} with respect to μ we find that

$$\bar{N} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{\text{g}} = z \frac{\partial}{\partial z} \ln Z_{\text{g}} \,.$$

• *Mean energy:* If we take a derivative of Z_{g} with respect to β, as we did in the case of a canonical ensemble to get $\bar{E}$, in this case we obtain

$$-\frac{\partial}{\partial \beta} \ln Z_{\text{g}} = \bar{E} - \mu \bar{N} \,, \qquad \text{so} \qquad \bar{E} = -\frac{\partial}{\partial \beta} \ln Z_{\text{g}} + \mu \bar{N} \,.$$

• *Entropy:* Substituting in the Gibbs entropy $S_{\text{G}} = -k_{\text{B}} \sum_{N,s} \rho(N,s) \ln \rho(N,s)$ the $\rho(N,s)$ above, we get

$$S = -k_{\text{B}} \sum_{N,s} \frac{\mathrm{e}^{-\beta H + \beta \mu N}}{Z_{\text{g}}} \ln \frac{\mathrm{e}^{-\beta H + \beta \mu N}}{Z_{\text{g}}} = -k_{\text{B}} \sum_{N,s} \frac{\mathrm{e}^{-\beta H + \beta \mu N}}{Z_{\text{g}}}(-\beta E + \beta \mu N - \ln Z_{\text{g}}) = \frac{\bar{E}}{T} - \frac{\mu \bar{N}}{T} + k_{\text{B}} \ln Z_{\text{g}} \,.$$

• *Grand potential:* From the definition, $\Omega := \bar{E} - TS - \mu \bar{N}$, and again substituting for S,

$$\Omega = \bar{E} - T(\bar{E}/T + \mu \bar{N}/T + k_{\text{B}} \ln Z_{\text{g}}) - \mu \bar{N} = -k_{\text{B}} T \ln Z_{\text{g}} \,.$$

Notice that we can write the mean particle number in terms of the grand potential, as $\bar{N} = -\partial \Omega / \partial \mu|_{\beta,V}$.

• *Pressure equation of state:* The grand potential version of the fundamental thermodynamic identity,

$$\mathrm{d}\Omega = -S \, \mathrm{d}T - p \, \mathrm{d}V - N \, \mathrm{d}\mu \,,$$

can be derived similarly to how we derived those in terms of F and other potentials. Using this, we find

$$p = -\frac{\partial \Omega}{\partial V}\bigg|_{T,\mu} \,.$$

• *Particle-number fluctuations:* Taking a further μ derivative of $\ln Z_{\text{g}}$, we see that

$$\frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \ln Z_{\text{g}}\bigg|_{\beta,V} = \overline{N^2} - \bar{N}^2 \equiv (\Delta N)^2 \equiv \sigma_N^2 \,, \quad \text{or} \quad \sigma_N^2 = k_{\text{B}} T \frac{\partial \bar{N}}{\partial \mu}\bigg|_{T,V} \,,$$

whose dependence on $\bar{N}$ as $\bar{N} \to \infty$ is best expressed as a relative fluctuation

$$\frac{\sigma_N}{\bar{N}} = \frac{1}{\bar{N}} \sqrt{k_{\text{B}} T \frac{\partial \bar{N}}{\partial \mu}} \propto \frac{1}{\sqrt{\bar{N}}} \,.$$

This shows that in this limit particle-number fluctuations become negligible and predictions based on Z_{g} coincide with those based on Z_{c} (for specific systems we can also calculate explicitly the coefficient of $\bar{N}^{-1/2}$).

Example: Non-Interacting Particles

• *Grand partition function:* Here Z_{g} is a sum over all states, each of which is a specification of a number N of particles and N one-particle states $s = \{s_1, ..., s_N\}$, with $H_N(s) = \sum_{i=1}^{N} H_1(s_i)$,

$$Z_{\mathrm{g}} = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} \sum_{s\in\Gamma_{(N)}} \mathrm{e}^{-\beta H_N(s)} = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} Z_N = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} \frac{Z_1^N}{N!} = \exp\left\{\mathrm{e}^{\beta\mu} Z_1\right\},$$

where we have used the definition of the N-particle canonical partition function Z_N, its expression in terms of Z_1 when the particles are non-interacting, and in the last step the power-series expansion of an exponential.

• *Ideal gas:* In this case $Z_1 = (V/\lambda^3)\, Z_{\mathrm{int}}$, with Z_{int} an internal partition function, so the grand potential is

$$\Omega(T, V, \mu) = -k_{\mathrm{B}}T \ln Z_{\mathrm{g}} = -k_{\mathrm{B}}T\, \mathrm{e}^{\beta\mu} Z_1 = -\frac{\mathrm{e}^{\beta\mu} V}{\beta\,\lambda^3} Z_{\mathrm{int}},$$

where as usual $\lambda := h/\sqrt{2\pi m k_{\mathrm{B}} T}$. For the pressure and mean particle number we then get

$$p = -\left.\frac{\partial\Omega}{\partial V}\right|_{\beta,\mu} = \frac{\partial}{\partial V}\frac{\mathrm{e}^{\beta\mu} V}{\beta\,\lambda^3} Z_{\mathrm{int}} = \frac{\mathrm{e}^{\beta\mu}}{\beta\,\lambda^3} Z_{\mathrm{int}}, \qquad \bar{N} = -\left.\frac{\partial\Omega}{\partial\mu}\right|_{\beta,V} = \frac{\partial}{\partial\mu}\frac{\mathrm{e}^{\beta\mu} V}{\beta\,\lambda^3} = \frac{\mathrm{e}^{\beta\mu} V}{\lambda^3} Z_{\mathrm{int}}.$$

From these we see by inspection that the usual ideal-gas equation of state holds, $pV = \bar{N} k_{\mathrm{B}} T$.

• *Mean energy and chemical potential:* For the mean energy we use the general result $\bar{E} = -\partial \ln Z_{\mathrm{g}}/\partial\beta + \mu\,\bar{N}$. The chemical potential μ in principle is a parameter like β (temperature) and V, but it is less easy to control and in practice we often use the grand canonical ensemble in situations in which what we know is the number of particles N, treating the relative fluctuations $\Delta N/\bar{N}$ as negligibly small. In those cases, we can identify the latter with $\bar{N}$ and find μ by inverting the expression for $\bar{N}(\mu)$ to find $\mu(N)$.

Fluctuation-Response Relation

• *Idea:* For any system in a grand canonical ensemble we can derive a relationship between the typical size of the particle-number fluctuations and the isotermal compressibility, analogously to the way we derived the relationship between the energy variance σ_E^2 and the heat capacity for a canonical ensemble.

• *Derivation:* We saw in the previous page that the particle-number fluctuation can be written as

$$(\Delta N)^2 \equiv \sigma_N^2 = k_{\mathrm{B}} T \left.\frac{\partial\bar{N}}{\partial\mu}\right|_{T,V}.$$

The right-hand side of this equation can be rewritten using mathematical identities for functions of several variables and thermodynamic identities such as $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$ (where we identify $\bar{N}$ with N),

$$\left.\frac{\partial N}{\partial\mu}\right|_{T,V} = \left.\frac{\partial N}{\partial V}\right|_{T,\mu}\left.\frac{\partial V}{\partial\mu}\right|_{T,N}, \quad \text{with} \quad \left.\frac{\partial\mu}{\partial V}\right|_{T,N} = -\left.\frac{\partial p}{\partial N}\right|_{T,V} \quad \text{(a Maxwell relation)},$$

$$\left.\frac{\partial p}{\partial N}\right|_{T,V} = -\left.\frac{\partial p}{\partial V}\right|_{T,N}\left.\frac{\partial V}{\partial N}\right|_{T,p}.$$

Combining these equations and using

$$\left.\frac{\partial N}{\partial V}\right|_{T,\mu} = \left.\frac{\partial N}{\partial V}\right|_{T,p} = \frac{N}{V},$$

where we have used the fact that $\mu = \mu(T, p)$, we finally get the fluctuation-response relation

$$\sigma_N^2 = -k_{\mathrm{B}} T \frac{N^2}{V^2}\left.\frac{\partial V}{\partial p}\right|_{T,N} = k_{\mathrm{B}} T \frac{N^2}{V} \kappa_T.$$

Reading

• *Main references:* Kennett, Ch 6; Pathria & Beale, Ch 4.
• *Partial treatments:* Halley (mentioned on page 33), Kardar (briefly treated in § 7.3, for bosons and fermions), Mattis & Swendsen (§ 4.4, very short), and Reif (briefly treated in § *6.9).
• *More extensive:* Plischke & Bergersen (§ 2.3), Reichl (§ 6.2, a good one), and Schwabl (§ 2.7).