Equilibrium Distribution Functions. II: Canonical Distribution

Setup and Derivation

• Goal: Describe a system in thermal equilibrium with a much larger heat bath or reservoir with which it can exchange energy in the form of heat, but not other forms of work or matter. The total system is isolated.

• Distribution function, simplified derivation: If the system S consists of two uncoupled subsystems A and B, both in thermal equilibrium with the reservoir, and with microstates labeled by variables a and b, we can treat the subsystems as statistically independent and the distribution function for S is a product

$$\rho_S(s) = \rho_A(a) \rho_B(b)$$
, or $\ln \rho_S(s) = \ln \rho_A(a) + \ln \rho_B(b)$

In equilibrium, each ρ is time-independent and can only be a function of the corresponding microstates through constants of the motion, in practice the energy H, and the relation above says that $\ln \rho$ is additive,

$$\ln \rho(s) = \alpha - \beta H(s)$$
, or $\rho(s) = \frac{1}{Z} e^{-\beta H(s)}$,

where $Z = e^{-\alpha}$. The quantity $e^{-\beta H}$ is the *Boltzmann factor*. The values of α , β and the *partition function* Z depend on the thermodynamic variables of the system (e.g., T, V, N); α or Z are fixed by normalizing ρ , and β is related to the temperature. [Many texts denote the partition function by Q rather than Z.]

• Somewhat more detailed derivation: We can view the reservoir R and the system S of interest, which together form a total system T, as not having a significant interaction and being statistically independent, so that $H_T(r,s) = H_R(r) + H_S(s)$ and $\rho_T(r,s) = \rho_R(r) \rho_S(s)$. The total system T is isolated and we use a microcanonical state of fixed energy U to describe it, so by the principle of equal a priori probabilities each of its microstates is equally probable. Then the probability that the system S is in a microstate s of energy H(s) is proportional to the number of states of energy U - H(s) the reservoir can be in,

$$\rho_S(s) \propto \Omega_R(U - H(s)),$$

where $H(s) \ll U$ and the proportionality factor will be fixed later by normalizing $\rho_S(s)$ as a probability distribution. Taking the log and expanding the expression on the right-hand side in powers of H(s),

$$k_{\rm B} \ln \rho_S(s) = C + k_{\rm B} \ln \Omega_R(U - H(s)) = C + S_R(U - H(s)) = C + S_R(U) - \frac{\partial S_R}{\partial U}H(s) + \dots$$

 $(\ln \Omega_R \text{ varies more slowly with its argument, and a truncated power series gives a better approximation).$ Keeping only the two leading terms, and recalling that for a system in a microcanonical state $\partial S/\partial U = T^{-1}$,

$$\rho(s) = \mathcal{N} e^{-H(s)/k_{\rm B}T} = \frac{1}{Z} e^{-\beta H(s)}, \quad \text{with} \quad Z := \sum_{s} e^{-\beta H(s)}.$$

Here, the normalization factor is $\mathcal{N} := \exp\{[C + S_R(U)]/k_{\rm B}\}, \beta := 1/k_{\rm B}T$, and it is understood that when s is labeled by continuous variables the sum in the partition function is to be calculated as $Z = \int_{\Gamma} \mathrm{d}\Omega \,\mathrm{e}^{-\beta H(q,p)}$.

Properties and Remarks

• Degenerate energies and density of states: If we call as before $g(E_i)$ the number of states with the same energy in the discrete spectrum case, or g(E) the density of states in the continuous spectrum case (which may be calculated in general as $g(E) = d\Omega(E)/dE$), then the canonical partition function can also be written in the form (similar to a Laplace transform of g(E))

$$Z = \sum_{i} g(E_i) e^{-\beta E_i} , \quad \text{or} \quad Z = \int_{\Gamma} d\Omega e^{-\beta H(q,p)} = \int_{-\infty}^{+\infty} dE g(E) e^{-\beta E}$$

Thus, the probability distribution for the energy is $P(E_i) = g(E_i) e^{-\beta E_i}$, resp. $P(E) dE = g(E) e^{-\beta E} dE$.

• Change in Hamiltonian: If a constant C (or an extensive function $C(\vec{X})$ of the system parameters) is added to the Hamiltonian for a system, $H(s) \mapsto H(s) + C$, the canonical distribution is unchanged. (Z gets multiplied by $e^{-\beta C}$, but remains equivalent to the original one.)

• Uncoupled systems: If two subsystems A and B of the system are uncoupled, in the sense that the Hamiltonian $H(s) = H_A(a) + H_B(b)$ does not contain an interaction term, then $Z = Z_A Z_B$.

Thermodynamics: Potentials and First-Order Quantities

• Energy: The thermodynamical energy is identified with the mean energy in the canonical ensemble,

$$\bar{E} = \frac{1}{Z} \sum_{s} \left(H(s) e^{-\beta H(s)} \right) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z$$

• Entropy: We cannot use the Boltzmann entropy $S_{\rm B} = k_{\rm B} \ln \Omega$ because the states s are not all equally probable—and their number Ω is in general infinite. We can however use the more general Gibbs entropy $S_{\rm G} = -k_{\rm B} \sum_{s} \rho(s) \ln \rho(s)$. Substituting for $\rho(s)$ its expression in the canonical ensemble, we get

$$S := -kB\sum_{s} \frac{e^{-\beta H(s)}}{Z} \ln \frac{e^{-\beta H(s)}}{Z} = -k_{\rm B}\sum_{s} \frac{e^{-\beta H(s)}}{Z} \left(-\beta H(s) - \ln Z\right) = k_{\rm B}\beta \,\bar{E} + k_{\rm B} \ln Z \,.$$

• Temperature: This result for S is consistent with the interpretation of β from the second derivation of $\rho(s)$ above. If the relationship between \overline{E} , S and T is the usual one, we must have

$$T^{-1} = \frac{\partial S}{\partial \bar{E}} \Big|_{V,N} = \frac{\partial}{\partial \bar{E}} (k_{\rm\scriptscriptstyle B} \beta \, \bar{E} + k_{\rm\scriptscriptstyle B} \ln Z) = k_{\rm\scriptscriptstyle B} \beta \;, \quad {\rm or} \quad \beta = 1/k_{\rm\scriptscriptstyle B} T \;.$$

• Helmholtz free energy: Substituting the above S in the definition, $F := \overline{E} - TS$, we get

$$F = \bar{E} - T \left(\bar{E}/T + k_{\rm\scriptscriptstyle B} \ln Z \right) = -k_{\rm\scriptscriptstyle B} T \ln Z \;, \qquad {\rm so} \qquad Z = {\rm e}^{-\beta F} \;. \label{eq:F}$$

Notice that in terms of F we can also express $\overline{E} = \partial(\beta F)/\partial\beta$.

• First-order quantities: From expressions for Z and $F = -\beta^{-1} \ln Z$, we can define as usual

$$S = -\frac{\partial F}{\partial T}\Big|_{\vec{X}} = \frac{1}{k_{\rm B}T^2} \left. \frac{\partial F}{\partial \beta} \right|_{\vec{X}}, \qquad \text{and for a fluid} \qquad p = -\frac{\partial F}{\partial V}\Big|_{T,N}, \quad \mu = \frac{\partial F}{\partial N}\Big|_{T,V}$$

Additional Comments, Heat Capacity and Energy Fluctuations

• Use of the partition function: For many purposes, in particular to derive expressions for thermodynamic quantities for a system, the partition function is all we need. It may be interpreted as something like the 'effective number of states' available to the system. To obtain more detailed results on the system (for example the speed distribution for particles in a gas) we will need the full distribution function, but second-order thermodynamic quantities can still be obtained from the partition function.

• Heat capacity: There is a simple expression for any system in a canonical state. Using $(\partial/\partial\beta)Z = -Z\bar{E}$,

$$C_{\vec{X}} = \frac{\partial \bar{E}}{\partial T}\Big|_{\vec{X}} = \frac{\mathrm{d}\beta}{\mathrm{d}T} \frac{\partial}{\partial\beta} \Big(\frac{1}{Z} \sum_{s} H(s) \,\mathrm{e}^{-\beta H(s)}\Big) = -\frac{1}{k_{\mathrm{B}}T^2} \left[\frac{1}{Z^2} (Z \,\bar{E})^2 - \frac{1}{Z} \sum_{s} H^2(s) \,\mathrm{e}^{-\beta H(s)}\right] = \frac{(\Delta E)^2}{k_{\mathrm{B}}T^2} \,,$$

a special case of a more general fluctuation-dissipation theorem. Two important consequences are that

$$(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2} \ln Z$$
 or $\Delta E = \sqrt{k_{\rm\scriptscriptstyle B} T^2 C_{\vec{X}}} \propto \sqrt{N}$,

so that $\Delta E/\bar{E} \propto 1/\sqrt{N}$ and energy fluctuations become negligible for large N, and that $C_{\vec{X}} > 0$ always. Reading

• Our textbook: Kennett, Chapter 4. Other books: Halley, part of Ch 1; Mattis & Swendsen, §§ 4.1–4.4; Pathria & Beale, Ch 3; Plischke & Bergersen, §§ 2.1–2.3; Reif, Ch 3; Schwabl, Ch 2.