The Canonical Distribution

• *Idea:* Describes a system in equilibrium with a heat bath, with which it exchanges energy but not matter.
• *Large-system approximation:* We only deal with very large systems with short-range interactions (with respect to the system size). Then, if we partition the system into two large parts 1 and 2, most of the variables in each part are statistically independent of those in the other part, and the distribution function must be a product $\rho(q,p) = \rho_1(q_1,p_1)\,\rho_2(q_2,p_2)$ of probability distributions for the statistically independent sets of variables (q_1,p_1) and (q_2,p_2).
• *Form of the distribution function:* Taking the log of both sides, $\ln\rho(q,p) = \ln\rho_1(q_1,p_1) + \ln\rho_2(q_2,p_2)$, which means that $\ln(p,q)$ must be a linear combination of additive constants of the motion. The only such constants of the motion are the generators of spacetime and internal symmetries [see ref below]. Restricting our attention to energy, we get

$$\ln\rho(q,p) = \alpha - \beta\,H(q,p)\;, \quad \text{for some constants } \alpha \text{ and } \beta\;.$$

The constant α is fixed by renormalization, so we get

$$\rho(q,p) = \frac{1}{Z_{\rm c}}\,{\rm e}^{-\beta\,H(q,p)}\;, \quad \text{with} \quad Z_{\rm c} := \int_\Gamma {\rm d}q\,{\rm d}p\,{\rm e}^{-\beta\,H(q,p)}\;.$$

• *Alternative derivation:* Considering the system as part of a large one in a microcanonical state, and calling the rest of the larger system a bath, $\rho(q_{\rm b},p_{\rm b},q_{\rm s},p_{\rm s}) = \text{constant} \times \delta(H_{\rm b}+H_{\rm s}-E)$ with $E_{\rm b} \gg E_{\rm s}$. If we define $\Omega(E)$ for a system to be the number of states of energy E accessible to the system, then

$$\rho(q_{\rm s},p_{\rm s}) = \int {\rm d}q_{\rm b}\,{\rm d}p_{\rm b}\,\rho(q_{\rm b},p_{\rm b},q_{\rm s},p_{\rm s}) = \text{const} \times \Omega_{\rm b}(E-H_{\rm s}(q_{\rm s},p_{\rm s})) = \frac{\Omega_{\rm b}(E-H_{\rm s}(q_{\rm s},p_{\rm s}))}{\int {\rm d}q_{\rm b}{\rm d}p_{\rm b}\,\Omega_{\rm b}(E-H_{\rm s}(q_{\rm s},p_{\rm s}))}\;,$$

where we have again used implicitly the principle of equal a priori probabilities. Now, since $E_{\rm s} \ll E$, we can think of $H_{\rm s}$ as a small perturbation in $\Omega_{\rm b}$. However, for most systems $\Omega_{\rm b}$ varies extremely rapidly with its argument, while its log is a function for which a truncated power series is likely to give a better approximation, so

$$\rho(q_{\rm s},p_{\rm s}) = \frac{\Omega_{\rm b}(E-H_{\rm s}(q_{\rm s},p_{\rm s}))/\Omega_{\rm b}(E)}{\int {\rm d}q_{\rm b}{\rm d}q_{\rm b}\,\Omega_{\rm b}(E-H_{\rm s}(q_{\rm s},p_{\rm s})/\Omega_{\rm b}(E)} = \mathcal{N}\,{\rm e}^{\ln[\Omega_{\rm b}(E-H_{\rm s}(q_{\rm s},p_{\rm s}))/\Omega_{\rm b}(E)]} = \frac{1}{Z}\,{\rm e}^{-\beta H(q_{\rm s},p_{\rm s})}\;,$$

where

$$\beta := \frac{\partial}{\partial E}\,\ln\frac{\Omega_{\rm b}(E-H_{\rm s}(q_{\rm s},p_{\rm s}))}{\Omega_{\rm b}(E)}\;,$$

or, if $S(E-H_{\rm s}) := k_{\rm B}\,\ln[\Omega_{\rm b}(E-H_{\rm s}(q_{\rm s},p_{\rm s}))/\Omega_{\rm b}(E)]$, then $\beta := (1/k_{\rm B})\,(\partial S(E+x)/\partial x)_{x=0}$.

The Grand Canonical Distribution

• *Idea:* Describes a system in equilibrium with a heat bath with which it exchanges both energy and particles.
• *Form of the distribution function:* From similar considerations to the ones that led to $Z_{\rm c}$,

$$\rho(q,p) = \frac{1}{Z_{\rm g}}\,{\rm e}^{-\beta H(q,p)+\beta\,\mu N}\;, \quad \text{with} \quad Z_{\rm g} := \int {\rm d}q\,{\rm d}p\,{\rm e}^{-\beta H(q,p)+\beta\,\mu N}\;,$$

where μ, the chemical potential, can be interpreted as the energy required to add a particle to the system when it is in the equilibrium state characterized by T, V and N (and other possible quantities if relevant).

Relevant Sections: Phys 731; Chandler; Halley, second half of Ch 1; Reif; Schwabl.