CHAPTER 3

The statistical ensembles

We have seen that a thermodynamic system is specified by a thermodynamic potential, such as the entropy, the free energy, the enthalpy, etc... Then we have seen that the entropy can be defined from microscopic laws. It turns out that the free energy and the grand-canonical potentials are also given by the thermodynamic limit of suitable microscopic expressions. This has practical advantages, as it offers alternative paths to the computation of thermodynamic quantities, that can be much simpler.

We start by defining the quantities, then we state in Theorem I their important mathematical properties. We then comment about their relations with thermodynamics.

The three basic quantities are the microcanonical, canonical, and grandcanonical *partition functions*. All three involve microscopic variables. The **microcanonical partition function** $X(U, D, N)$ depends on energy and number of particles. The **canonical partition function** $Y(\beta, D, N)$ depends on the temperature and number of particles. Actually, it is convenient to use the *inverse temperature* β as the variable, instead of the temperature. The **grandcanonical partition function** $Z(\beta, D, \mu)$ depends on temperature and chemical potential. In a system of classical monoatomic particles, they are defined by

$$X(U, D, N) = \frac{1}{h^{dN} N!} \int_{\mathbb{R}^{dN}} \mathrm{d}p_1 \dots \mathrm{d}p_N \int_{D^N} \mathrm{d}q_1 \dots \mathrm{d}q_N \, \mathbb{1}_{[H(\{p_i, q_i\}) < U]}, \tag{3.1}$$

$$Y(\beta, D, N) = \beta \int_{-\infty}^{\infty} X(U, D, N) \, \mathrm{e}^{-\beta U} \, \mathrm{d}U, \tag{3.2}$$

$$Z(\beta, D, \mu) = \sum_{N \geqslant 0} Y(\beta, D, N) \, \mathrm{e}^{\beta \mu N}. \tag{3.3}$$

The corresponding thermodynamic potentials are the entropy $S = k_{\mathrm{B}} \log X$, the Helmholtz free energy $F = -\frac{1}{\beta} \log Y$, and the grand-canonical potential $G = \log Z$.

Let us mention two equivalent expressions for Y and Z. They follow from the definitions above, and constitute the usual starting point for computations.

$$Y(\beta, D, N) = \frac{1}{h^{dN} N!} \int_{\mathbb{R}^{dN}} \mathrm{d}p_1 \dots \mathrm{d}p_N \int_{D^N} \mathrm{d}q_1 \dots \mathrm{d}q_N \; \mathrm{e}^{-\beta H(\{p_i, q_i\})}, \tag{3.4}$$

$$Z(\beta, D, \mu) = \sum_{N \geqslant 0} \frac{1}{h^{dN} N!} \int_{\mathbb{R}^{dN}} \mathrm{d}p_1 \dots \mathrm{d}p_N \int_{D^N} \mathrm{d}q_1 \dots \mathrm{d}q_N \; \mathrm{e}^{-\beta [H(\{p_i, q_i\}) - \mu N]}. \tag{3.5}$$

These quantities are related with each other as follows.

THEOREM I. *Under the same hypothesis as in Theorem ??, the following thermodynamic limits exist:*

(a) *For any $\beta, n > 0$, and any $n_D \to n$,*

$$\lim_{D\nearrow\mathbb{R}^d} -\frac{1}{\beta|D|} \log Y(\beta, D, |D|n_D) = f(\beta, n),$$

where f is given by a Legendre transform of s, namely

$$f(\beta, n) = \inf_u \Big[u - \tfrac{1}{\beta}s(u, n)\Big].$$

(b) *For any $\beta > 0$ and any μ,*

$$\lim_{D\nearrow\mathbb{R}^d} \frac{1}{\beta|D|} \log Z(\beta, D, \mu) = p(\beta, \mu),$$

where the pressure p is given by a Legendre transform of f, namely

$$p(\beta, \mu) = \sup_{n>0} \Big[\mu n - f(\beta, n)\Big].$$

The limit over increasing domains is in the sense of Fisher, Definition ??. It is important to realize how closely it is related to thermodynamics: Compare the expressions for $f(\beta, n)$ and $p(\beta, \mu)$ with Eqs (??) and (??). These are indeed the free energy and the pressure of thermodynamics!

Here we view the formulæ for S, F, and p, as three aspects of a unique notion that finds its motivation in Boltzmann entropy. Physicists tend to consider these situations to be different, and they have named them "ensembles". The *microcanonical ensemble* is a system with fixed energy, volume, and number of particle. The *canonical ensemble* is a system where volume and number of particles are fixed, but energy is allowed to fluctuate; the probability for a given state $\{p_i, q_i\}$ is weighed with the "Gibbs factor" $\mathrm{e}^{-\beta H(\{p_i,q_i\})}$. And in the *grand-canonical ensemble*, the number of particles is also allowed to fluctuate with weight $\mathrm{e}^{\beta\mu}$. Theorem I is then known as "equivalence of ensembles" since it shows that the three paths from the microscopic world to the macroscopic one are equivalent.

PROOF OF THEOREM I (a). Let us introduce the notation $s_D(u, n) = \frac{1}{|D|}S(|D|u, D, |D|n)$ and $f_D(\beta, n) = \frac{1}{|D|}F(\beta, D, |D|n)$. We have

$$f_D(\beta, n_D) = -\frac{1}{\beta|D|} \log\Big[\beta|D| \int_{-\infty}^{\infty} \mathrm{e}^{-|D|[\beta u - s_D(u,n_D)]}\,\mathrm{d}u\Big]. \tag{3.6}$$

We define $f(\beta, n)$ as the Legendre transform of $s(u, n)$. Now we show that

$$\limsup_{D\nearrow\mathbb{R}^d} f_D(\beta, n_D) \leqslant f(\beta, n). \tag{3.7}$$

Given $\varepsilon > 0$, there exists an interval (a, b) where $u - \frac{1}{\beta}s(u, n) < f(\beta, n) + \frac{1}{2}\varepsilon$ for all $u \in (a, b)$. And because of $s_D(u, n)$ converges uniformly to $s(u, n)$ on compact sets, we have, for D large enough, $u - \frac{1}{\beta} s_D(u, n_D) < f(\beta, n) + \varepsilon$ for all $u \in (a, b)$. Then

$$\begin{aligned} f_D(\beta, n_D) &\leqslant -\frac{1}{\beta|D|} \log\Big[\beta|D| \int_a^b \mathrm{e}^{-\beta|D|[u - \frac{1}{\beta} s_D(u,n_D)]} \,\mathrm{d}u\Big] \\ &\leqslant -\frac{1}{\beta|D|} \log\Big[\beta|D|(b-a)\,\mathrm{e}^{-\beta|D|[f(\beta,n)+\varepsilon]}\Big] \\ &= -\frac{1}{\beta|D|} \log\Big[\beta|D|(b-a)\Big] + f(\beta, n) + \varepsilon. \end{aligned} \tag{3.8}$$

Taking the limits $D \nearrow \mathbb{R}^d$ and $\varepsilon \to 0$ yields the result.

We now control the liminf in the same manner. Recall that $s(u, n) = -\infty$ if $u < -Bn$, and that $s_D(u, n)$ is less than the entropy of the ideal gas with energy $u + Bn$ (see the exercise). Then, for any parameter A,

$$f_D(\beta, n_D) = -\frac{1}{\beta|D|} \log\Big\{\beta|D| \Big[\underbrace{\int_{-Bn}^{A} \mathrm{e}^{-|D|[\beta u - s_D(u,n_D)]} \,\mathrm{d}u}_{\leqslant (A+Bn)\,\mathrm{e}^{-\beta|D|[f(\beta,n)-\varepsilon]}} + \underbrace{\int_{A}^{\infty} \mathrm{e}^{-|D|[\beta u - s_D(u,n_D)]} \,\mathrm{d}u}_{\leqslant \int_A^\infty \mathrm{e}^{-\frac{1}{2}\beta|D|u} \,\mathrm{d}u}\Big]\Big\}. \tag{3.9}$$

The bound for the second integral follows from $s(u, n) \leqslant \frac{3}{2} n \log(u + Bn) + \text{const}$ (the constant depends on n). It holds provided A is large enough. We obtain

$$f_D(\beta, n_D) \geqslant f(\beta, n) - \varepsilon - \frac{1}{\beta|D|} \log\Big\{\beta|D|\Big[A + Bn + \mathrm{e}^{\beta|D| f(\beta,n)} \frac{1}{\frac{1}{2}\beta|D|}\,\mathrm{e}^{-\frac{1}{2}\beta|D|A}\Big]\Big\}. \tag{3.10}$$

For given β and n, we can choose A large enough so that the product of exponentials is less than 1. The contribution of the logarithmic term vanishes in the limit $D \nearrow \mathbb{R}^d$. As $\varepsilon \to 0$, we get a lower bound for the liminf that complements (3.7). □

The proof of the second claim is essentially the same.

Proof of Theorem I (b). Let us define the pressure by the equivalent expression

$$-p(\beta, \mu) = \inf_{u,n} \big[u - \mu n - \tfrac{1}{\beta} s(u, n)\big]. \tag{3.11}$$

The proof for

$$\liminf_{D \nearrow \mathbb{R}^d} \frac{1}{\beta|D|} \log Z(\beta, D, \mu) \geqslant p(\beta, \mu) \tag{3.12}$$

can be established as the one for the limsup of f_D, by using uniform convergence of s_D on compact domains, and by restricting the integral over u and the sum over N on a domain around the infimum of $u - \mu n - \frac{1}{\beta} s(u, n)$. For the lower bound for the liminf, recall that $s(u, n) = -\infty$ for $u < -Bn$ or $n < 0$. Then

$$p_D(\beta, \mu) = \frac{1}{\beta|D|} \log\Big[\beta|D| \sum_{N \geqslant 0} \int_{-Bn}^{\infty} \mathrm{d}u\; \mathrm{e}^{-\beta|D|[u - \mu n - \frac{1}{\beta} s_D(u,n)]}\Big]. \tag{3.13}$$

We set $n = \frac{N}{|D|}$. Thanks to the upper bound involving the entropy of the ideal gas, we have

$$\begin{aligned} \beta u - \beta\mu n - s_D(u, n) &\geqslant \beta u - \beta\mu n - \tfrac{3}{2} n \log(u + Bn) + \tfrac{5}{2} n \log n + \text{const}\, n \\ &\geqslant \tfrac{1}{2}\beta u + \beta n. \end{aligned} \tag{3.14}$$

The last inequality is true provided either u or n is large enough. We estimate the exponential in (3.13) using (3.11) if $0 \leqslant N < K$ and $-Bn < u < A$, where K and A are some fixed parameters. When either $N \geqslant K$ or $u > A$ we use (3.14). We obtain

$$p_D(\beta,\mu) \leqslant \frac{1}{\beta|D|} \log\Big\{\beta|D| \Big[K(A+BK)\,\mathrm{e}^{\beta|D|[p(\beta,\mu)+\varepsilon]} + \sum_{N\geqslant 0} \int_{-Bn}^{\infty} \mathrm{d}u\, 1\!\!1_{\{N>K \text{ or } u>A\}}\, \mathrm{e}^{-\beta|D|[\frac{1}{2}u+n]} \Big]\Big\}. \tag{3.15}$$

If K and A are large, the last term is less than $\mathrm{e}^{\beta|D|p(\beta,\mu)}$ for all D. Then

$$p_D(\beta,\mu) \leqslant p(\beta,\mu) + \varepsilon + \frac{1}{\beta|D|} \log\big[\beta|D| 2K(A+BK)\big]. \tag{3.16}$$

Taking the limits $D \nearrow \mathbb{R}^d$ and $\varepsilon \to 0$ give the result. □

Exercise 3.1. Show that the expressions (3.2) and (3.4) for the canonical partition function are equivalent.

Exercise 3.2. Suppose that $U(q)$ is stable with constant B. Show that $S(U,D,N)$ is less than the entropy of the ideal gas with energy $U+BN$ instead of U.

Exercise 3.3. State precisely and prove **Laplace principle**:

$$\lim_{N\to\infty} \frac{1}{N} \log \int \mathrm{e}^{Nf(x)}\, \mathrm{d}x = \sup_x f(x).$$

Exercise 3.4. Links with the theory of large deviations. Recall that a sequence of random variables X_n satisfy a *principle of large deviations* if there exists a *rate function* $I : \mathbb{R} \to [0,\infty]$ such that for any Borel set B,

$$\lim_{n\to\infty} \frac{1}{n} \log \operatorname{Prob}(X_n \in B) = -\inf_{x\in B} I(x).$$

Comments between the similarities between large deviations and the equivalence of ensembles.