Equivalence of microcanonical and canonical ensemble

There are many partition functions, but how are their results related? If the usual formal derivation, e.g., of the canonical formalism from the microcanonical formalism, works as designed, all ensembles should give us the same thermodynamics; thermodynamic potentials corresponding to various partition functions are related mutually by Legendre transformations. Therefore, for ordinary particle-particle interactions (e.g., not long-ranged and with a sufficiently hard core),[1] in the thermodynamic limit all the partition functions are expected to be equivalent in the sense that all give identical thermodynamic densities and fields. Here, let us demonstrate this *ensemble equivalence* of microcanonical and canonical ensembles.

Let us take a finite system with N particles. The canonical partition function is defined as

$$Z(T) = \sum_E w(E) e^{-\beta E}, \tag{0.0.1}$$

where the sum $\sum_E$ is the sum over all the shells of thickness δE. $w(E)$ is the microcanonical ensemble: the number of microstates whose energy is in $(E - \delta E, E]$. (0.0.1) is an infinite sum, but we assume it converges (if not, there is no thermodynamics[2]). Therefore, there is E_+ (which is of order N as shown in the fine lettered explanation below) beyond which the sum (0.0.1) is bounded by 1:

$$\sum_E w(E) e^{-\beta E} = Z(T) \le \sum_{E \le E_+} w(E) e^{-\beta E} + 1. \tag{0.0.2}$$

Let us write the largest value of the summand of (0.0.1) as $w(E^*)e^{-\beta E^*} = \max_E \left[w(E)e^{-\beta E}\right]$ $(\ge w(0) \ge 1)$. Obviously (see Fig. 1),

$$w(E^*)e^{-\beta E^*} \le Z(T) \le (E_+/\delta E) w(E^*) e^{-\beta E^*} + 1 \le 2(E_+/\delta E) w(E^*) e^{-\beta E^*}, \tag{0.0.3}$$

where $E_+/\delta E$ is the number of shells. Therefore,

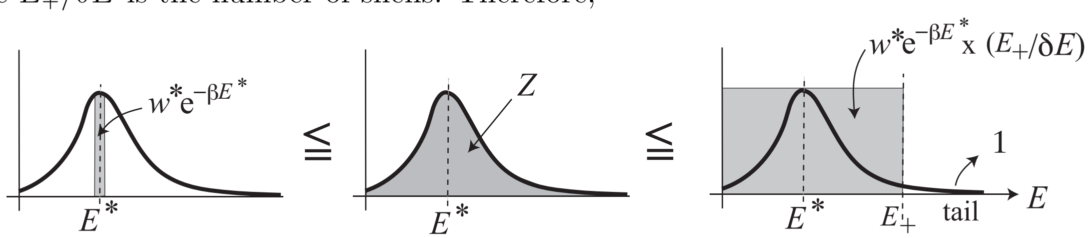


Fig. 1 The inequalities in (0.0.3) are illustrated. The gray areas respectively from left to right correspond to the three formulas in (0.0.3). E^* is the peak position, whose height is $w^* e^{-\beta E^*}$, where $w^* = w(E^*)$.

$$\sup_E \{S(E) - E/T\} \le -A/T \le \sup_E \{S(E) - E/T\} + k_B \log(2E_+) - k_B \log \delta E. \tag{0.0.4}$$

Recall that S is a monotonic function of E, we can rewrite the above result as

$$\sup_S \{ST - E\} \le -A \le \sup_S \{ST - E\} + k_B T \log(2E_+) - k_B T \log \delta E. \tag{0.0.5}$$

[1] as long as entropy is a concave function ($-S$ is a convex function) of all the extensive parameters.

[2] Its convergence is guaranteed if the interactions among particles are as mentioned above.

$\sup_S\{ST - E\}$ is an 'official' Legendre transformation giving $-A$. Notice that this A is the thermodynamically calculated from S obtained by Boltzmann's principle statistically mechanically.

Since E_+ is of order N and since we know $\langle E\rangle/N \ll \delta E \ll \langle E\rangle$, the above formula implies that the free energy per particle A/N obtained from the canonical partition function, and that 'indirectly' obtained thermodynamically from S due to Boltzmann's principle are identical, if $\log N/N$ is small enough.

Outline of evaluating $w(E)$ and a proof of $E_+ = O[N]$

Suppose the system with volume V has N particles and its Hamiltonian is

$$H = H_0 + \Phi, \tag{0.0.6}$$

where Φ is the interaction terms (the potential part of the Hamiltonian). Thus, H_0 is the purely kinetic 'ideal gas' portion. We assume that the system is stable (the total energy is bounded from below by an extensive lower bound:

$$\Phi \geq -BN \tag{0.0.7}$$

for some constant $B > 0$.

The proof consists of two steps. First, w is estimated for non-interacting systems (i.e., Φ turned off), and then we consider how the result is modified by interactions.

For non-interacting systems (with suffix I) we can compute entropy explicitly and know that the general form is:

$$w^I(E) = \exp[Vs(e)], \tag{0.0.8}$$

where e is the internal energy density. and s the entropy density.

Since $\Phi \geq -BN$ ($B > 0$),

$$H \geq H_0 - BN. \tag{0.0.9}$$

Here, the inequality implies that the expectation values with respect to any ket satisfy the inequality. We can generally show for the i-th excited state $|i\rangle$,

$$\langle i|H|i\rangle = E_i \geq E_i^I - BN. \tag{0.0.10}$$

where E_i^I is the ith the energy level of the corresponding ideal system, because

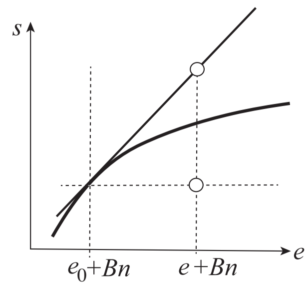
$$\langle i|H_0|i\rangle \geq E_i^I \tag{0.0.11}$$

thanks to the minimax principle (proved below). Notice that if $E \geq E'$, obviously $w^I(E) \geq w^I(E')$. Also $w(E_i) = w^I(E_i^I)$ (by definition). Since $E_i + BN \geq E_i^I$,

$$w(E) = w^I(E^I) \leq w^I(E + BN). \tag{0.0.12}$$

Combining this with (0.0.8), we get

$$w(E) \leq \exp[Vs(e + Bn)], \tag{0.0.13}$$



where n is the number density. Therefore,

$$w(E)e^{-\beta E} \le \exp[Vs(e + Bn) - \beta E]. \tag{0.0.14}$$

We know s is concave, so

$$s(e + Bn) \le s(e_0 + Bn) + \beta_0(e - e_0), \tag{0.0.15}$$

where β_0 is the slope at e_0, but choosing e_0 appropriately, we can choose β_0 freely as long as it is positive. Let us introduce

$$\tilde{s} = s(e_0 + Bn) - \beta_0 e_0 \tag{0.0.16}$$

and choose $\beta_0 = \beta/2$ to obtain

$$w(E)e^{-\beta E} \le \exp[V\tilde{s} + \beta V e/2 - \beta E] = \exp[V\tilde{s} - \beta E/2]. \tag{0.0.17}$$

Thus,

$$\sum_{E \ge E_+} w(E)e^{-\beta E} \le \sum_{E \ge E_+} \exp[V\tilde{s} - \beta E/2] = \frac{2}{\beta} e^{V\tilde{s}} e^{-\beta E_+/2}. \tag{0.0.18}$$

We wish to bound this with 1, so we require

$$\frac{\beta E_+}{2} + \log\frac{\beta}{2} > V\overline{s}. \tag{0.0.19}$$

That is, $E_+ \ge (2k_BT)[V\tilde{s} + \log(2k_BT)]$ is required. Therefore, when T is given, if the volume is sufficiently large, we have only to choose E_+/V slightly larger than $2k_BT\tilde{s}$. Indeed, $E_+ = O[V] = O[N]$.

The minimax principle for eigenvalues[3]

Let A be a self-adjoint operator defined on a vector space V. Let us arrange the eigenvalues of A in increasing order and number them (with their multiplicity taken into account), writing the k-th eigenvalue as $\mu(k)$. There is a variational principle for $\mu(k)$. In particular, there is a variational principle for the ground state $\mu(1)$.

[**Minimax principle**][4] For an arbitrary finite dimensional subspace $\mathcal{M}$ of V, let us compute

$$\lambda(\mathcal{M}) = \max_{|\varphi\rangle \in \mathcal{M}, \langle\varphi|\varphi\rangle = 1} \langle\varphi|A|\varphi\rangle. \tag{0.0.20}$$

[3] D. Ruelle, *Statistical Mechanics* Section 2.5 (World Scientific, 1999; original 1969). This is a copy of the same item found in Appendix: Introduction to Mechanics.

[4] In the following, precisely speaking, instead of min and max we should use inf and sup.

The minimum value of $\lambda(\mathcal{M})$ with $\mathcal{M}$ restricted to k-subspace is the k-th eigenvalue:

$$\mu(k) = \lambda(k) \equiv \min_{dim\mathcal{M}=k} \lambda(\mathcal{M}). \tag{0.0.21}$$

[Proof] Write the orthonormal basis corresponding to $\{\mu(k)\}$ as $\{|k\rangle\}$. First of all, $\lambda(k) \leq \mu(k)$ is obvious.[5*] Thus, we have only to show $\lambda(k) \geq \mu(k)$.

Since $\mathcal{M}$ is a finite dimensional vector space, it must be contained in a subspace spanned by $\{|1\rangle, \cdots, |N\rangle\}$ for a sufficiently large N (recall our numbering of the eigenvectors of A: $A|k\rangle = \mu(k)|k\rangle$). Take a subspace $\mathcal{V}$ spanned by $\{|k\rangle, \cdots, |N\rangle\}$ (that is, the orthogonal complement of the $(k-1)$-dimensional subspace spanned by $\{|1\rangle, \cdots, |k-1\rangle\}$). Since $\mathcal{M}$ is with dimension k, $\mathcal{M}$ and $\mathcal{V}$ must share a vector which is not zero. Let us normalize it and call it $|0\rangle$. Since $\lambda(\mathcal{M})$ is defined through maximization,

$$\lambda(\mathcal{M}) \geq \langle 0|A|0\rangle, \tag{0.0.22}$$

but $|0\rangle = \sum_{i=k}^{N} |i\rangle\langle i|0\rangle$, so

$$\langle 0|A|0\rangle = \sum_{i=k}^{N} |\langle i|0\rangle|^2 \mu_i \geq \mu(k). \tag{0.0.23}$$

That is, for any k dimensional $\mathcal{M}$ we have $\lambda(\mathcal{M}) \geq \mu(k)$. This implies $\lambda(k) \geq \mu(k)$. Thus, we have shown that $\lambda(k) = \mu(k)$.

[5*] If we adopt the k-dimensional subspace spanned by $\{|1\rangle, \cdots, |k\rangle\}$ as $\mathcal{M}$, $\lambda(\mathcal{M}) = \mu(k)$, so the smallest value we look for by changing $\mathcal{M}$ cannot be larger than this value.