# 4.8: The Grand Canonical Ensemble in the Thermodynamic Limit

This section uncovers results that are of interest in their own right, but it also serves as an example of a mathematically rigorous argument in statistical mechanics.

**Definitions**. The grand partition function is

$$\Xi(T,V,\alpha)=\sum_{N=0}^{\infty}e^{-\alpha N}Z(T,V,N),\tag{4.8.1}$$

the Helmholtz free energy is

$$F(T,V,N)=-k_BT\ln Z(T,V,N),\tag{4.8.2}$$

and the chemical potential is

$$\mu(T,V,N)=\frac{\partial F(T,V,N)}{\partial N})_{T,V}.\tag{4.8.3}$$

**Theorem**. *Consider a grand canonical ensemble of hard-core particles at equilibrium with a bath of temperature T and "number control parameter" α. There is a "most probable value of N", called $\hat{N}$ (a function of T, V , and α), satisfying*

$$\alpha=-\frac{\mu(T,V,\hat{N})}{k_BT},\tag{4.8.4}$$

*such that, in the thermodynamic limit,*

$$-k_BT\ln\Xi(T,V,\alpha)\to-\mu(T,V,\hat{N})\hat{N}+F(T,V,\hat{N}).\tag{4.8.5}$$

**Strategy**. The theorem assumes hard-core particles so that there will be a maximum number of particles in any given volume, whence the sum (4.45) is finite rather than infinite, and convergence questions do not arise. (Less restrictive conditions—e.g. that the repulsion between two nearby particles increases rapidly enough as they are brought together—may be used instead of the hard-core condition, but then the proof becomes more technical and less insightful.) The proof works by establishing both upper and lower bounds on sum (4.45), and then showing that, in the thermodynamic limit, these two bounds are equal.

**Proof**. Assume that each hard-core particle has volume $v_0$. Then the maximum number of particles that can fit into a container of volume $V$ is $N^* \le V/v_0$. Thus the sum in equation (4.45) does not go to ∞, but stops at $N^*$.

We will need a trivial mathematical result, called "the method of the maximum term": If $f_N$ is a sequence of positive terms, $N = 0, 1, \ldots N^*$, and if the maximum element of the sequence is $\max\{f_N\}$, then

$$\max\{f_N\}\le\sum_{N=0}^{N^*}f_N\le(N^*+1)\max\{f_N\}.\tag{4.8.6}$$

Applying this result to the sum (4.45), we obtain

$$\max\{e^{-\alpha N}Z_N\}\le\Xi\le(N^*+1)\max\{e^{-\alpha N}Z_N\},\tag{4.8.7}$$

where $Z_N$ is shorthand for $Z(T, V, N)$. Taking the logarithm of each side, and realizing that $\ln\max\{f\} = \max\{\ln f\}$, gives

$$\max\{-\alpha N+\ln Z_N\}\le\ln\Xi\le\ln(N^*+1)+\max\{-\alpha N+\ln Z_N\}.\tag{4.8.8}$$

To prepare for taking the thermodynamic limit, we divide both sides by $V$ and employ the definition $F_N = -k_BT\ln Z_N$, resulting in

$$\max\left\{-\alpha\frac{N}{V}-\frac{F_N}{k_BTV}\right\}\le\frac{\ln\Xi}{V}\le\frac{\ln(N^*+1)}{V}+\max\left\{-\alpha\frac{N}{V}-\frac{F_N}{k_BTV}\right\}.\tag{4.8.9}$$

Consider the difference between these upper and lower bounds. It is clear that

$$0\le\frac{\ln(N^*+1)}{V}\le\frac{\ln(V/v_0+1)}{V}.\tag{4.8.10}$$

In the limit as $V\to\infty$, the right hand side above approaches 0, so

$$\frac{\ln(N^*+1)}{V} \to 0. \tag{4.8.11}$$

Thus in the thermodynamic limit the lower bound approaches the upper bound, and

$$\frac{\ln \Xi}{V} \to \max\left\{-\alpha\frac{N}{V} - \frac{F_N}{k_B TV}\right\}. \tag{4.8.12}$$

Now we need to find the maximum of the quantity in curly brackets above. The maximum is located at $N = \hat{N}$, which we find by taking the partial derivative with respect to $N$ and setting it equal to zero:

$$\frac{\alpha}{V} = -\frac{1}{k_B TV}\frac{\partial F_N}{\partial N}\Big]_{N=\widehat{N}}. \tag{4.8.13}$$

Using the definition (4.47), the equation for $\hat{N}$ becomes

$$\alpha = -\frac{\mu(T,V,\hat{N})}{k_B T}. \tag{4.8.14}$$

Returning to equation (4.56), this location of $\hat{N}$ implies that, for sufficiently large values of $V$,

$$\frac{\ln \Xi}{V} = -\frac{\mu(T,V,\hat{N})}{k_B T}\frac{\hat{N}}{V} - \frac{F_{\hat{N}}}{k_B TV}, \tag{4.8.15}$$

from which the final result (4.49) follows immediately.

**Resume**. The system under study can exchange energy and particles with a heat bath that has "energy control parameter" $\beta = 1/k_B T$ and "number control parameter" $\alpha$. The probability that the system contains exactly N particles is

$$P_N = \frac{e^{-\alpha N} Z(\beta,V,N)}{\Xi(\beta,V,\alpha)}. \tag{4.8.16}$$

The proof shows that, in the thermodynamic limit, there is one particular value of $N$, namely \(\hat{N}\, for which $P_N$ approaches 1. All the other $P_N$ 's, of course, approach 0. The condition for locating \(\hat{N}\ is just that it gives the maximum value of $P_N$ . . . this condition gives rise to equation (4.48). Once $\hat{N}\, is located, the result$\($P_{\hat{N}}$ → 1 becomes equation (4.49).