Statistical Physics

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6 Grand canonical ensemble

We repeat much of our discussion of Chapter 2, with the new flexibility of allowing the particle number to fluctuate about an average.

6.1 Grand partition function

As before we consider A replicas of system $\mathcal{S}$. We count the number of replicas in state $|i\rangle$ and denote that number by a_i. Note that each microstate corresponds to a definite, but not common, particle number

$$\begin{aligned} \hat{H}|i\rangle &= E_i|i\rangle \\ \hat{N}|i\rangle &= N_i|i\rangle \,. \end{aligned} \tag{6.1.1}$$

Recall the spin system introduced in Chapter 2, Eqn. (2.1.2). In the grand canonical ensemble, we might have ensembles like

$$\begin{aligned} \mathcal{E}^{(1)} &= \{|+\rangle, |--\rangle, |+\rangle, |+--\rangle, |-\rangle\} \\ \mathcal{E}^{(2)} &= \{|-+\rangle, |-+++\rangle, |-\rangle, |+-\rangle, |-+-\rangle\} \end{aligned} \tag{6.1.2}$$

where the particle number fluctuates between snapshots. Then we have a much larger space of allowed microstates $|i\rangle$. We again look at our ensemble and count how many times a_i a given microstate occurs.

We will again find those $\{a_i\}$ which can be realised in the largest number of ways, subject to the constraints of conservation of number of replicas (A), of energy fluctuations about a mean system energy (E), and of particle number fluctuations about a mean particle number (N)

$$\sum_i a_i = A \tag{6.1.3}$$

$$\sum_i a_i E_i = AE \tag{6.1.4}$$

$$\sum_i a_i N_i = AN \,. \tag{6.1.5}$$

Hence we need to introduce 3 Lagrange multipliers to solve

$$\frac{\partial}{\partial a_j}\left(\log W \;-\; \alpha\sum_i a_i \;-\; \beta\sum_i a_i E_i \;-\; \gamma\sum_i a_i N_i\right) \;=\; 0 \tag{6.1.6}$$

where

$$W \;=\; \frac{A!}{\prod_i a_i!} \,. \tag{6.1.7}$$

Hence

$$\frac{\partial}{\partial a_j}\left(-a_i\log a_i \;-\; \alpha a_i \;-\; \beta a_i E_i \;-\; \gamma a_i N_i\right) \;=\; 0 \tag{6.1.8}$$

or

$$\log a_j \;+\; 1 \;+\; \alpha \;+\; \beta E_j \;+\; \gamma N_j \;=\; 0 \qquad (6.1.9)$$

$$a_j \;=\; e^{-(1+\alpha)}\, e^{-\beta E_j}\, e^{-\gamma N_j} \qquad (6.1.10)$$

$$a_j \;=\; e^{-(1+\alpha)}\, e^{-\beta(E_j - \mu N_j)} \qquad (6.1.11)$$

which defines the **chemical potential** $\mu = -\gamma/\beta$. Thus we write down the statistical distribution function for the grand canonical ensemble, also called the **Gibbs distribution**,

$$\boxed{\rho_i \;=\; \frac{a_i}{A} \;=\; \frac{1}{\mathcal{Z}}\, e^{-\beta(E_i - \mu N_i)}} \qquad (6.1.12)$$

where the normalisation factor

$$\boxed{\mathcal{Z} \;=\; \sum_i e^{-\beta(E_i - \mu N_i)}} \qquad (6.1.13)$$

is called the **grand canonical partition function**.

As usual,

$$\langle E \rangle \;\equiv\; E \;=\; \sum_i \rho_i E_i \qquad (6.1.14)$$

but also

$$\langle N \rangle \;\equiv\; N \;=\; \sum_i \rho_i N_i \qquad (6.1.15)$$

The chemical potential and the inverse temperature play similar roles: just as the inverse temperature β is a Lagrange multiplier constraining the energy to fluctuate narrowly about a mean energy, the chemical potential μ constrains the particle number to fluctuate about a mean particle number. As with β, there is only one μ which characterises a system, or subsystems, in equilibrium.

6.2 Thermodynamics

Taking derivatives of the grand partition function (6.1.13) we find

$$N \;=\; \frac{1}{\beta}\,\frac{\partial}{\partial \mu} \log \mathcal{Z}\bigg|_{\beta,V} \qquad (6.2.1)$$

and

$$E \;-\; \mu N \;=\; -\,\frac{\partial}{\partial \beta} \log \mathcal{Z}\bigg|_{\mu,V} \;. \qquad (6.2.2)$$

Now to derive the first law of thermodynamics from the grand canonical ensemble, we recall from (3.2.5) that $S = -k \sum_i \rho_i \log \rho_i$ and from subsequent discussion that

$$\mathrm{d}S \;=\; -\,k \sum_i \mathrm{d}\rho_i\, \log \rho_i \qquad (6.2.3)$$

which, for the grand canonical ensemble, implies

$$\mathrm{d}S \;=\; \frac{1}{T} \sum_i \mathrm{d}\rho_i\, (E_i \;-\; \mu N_i)\,. \qquad (6.2.4)$$

From the product rule

$$\sum_i \mathrm{d}\rho_i\, E_i \;=\; \mathrm{d}E \;-\; \sum_i \rho_i\, \mathrm{d}E_i \tag{6.2.5}$$

$$\sum_i \mathrm{d}\rho_i\, N_i \;=\; \mathrm{d}N \;-\; \sum_i \rho_i\, \mathrm{d}N_i \tag{6.2.6}$$

we find

$$T\mathrm{d}S \;=\; \mathrm{d}E \;-\; \mu\, \mathrm{d}N - \sum_i \rho_i(\mathrm{d}E_i \;-\; \mu\, \mathrm{d}N_i)\,. \tag{6.2.7}$$

The pressure is

$$P \;=\; \frac{1}{\beta}\,\frac{\partial \log \mathcal{Z}}{\partial V}\bigg|_{\beta,\mu} \tag{6.2.8}$$

$$\;=\; -\sum_i \rho_i \left(\frac{\partial E_i}{\partial V} \;-\; \mu\,\frac{\partial N_i}{\partial V}\right) \tag{6.2.9}$$

Therefore, (6.2.7) becomes, after rearrangement,

$$\boxed{\begin{aligned} \mathrm{d}E \;&=\; T\mathrm{d}S \;-\; P\,\mathrm{d}V \;+\; \mu\,\mathrm{d}N \\ &=\; đQ \;+\; đW_{\text{mech}} \;+\; đW_{\text{chem}}\,. \end{aligned}} \tag{6.2.10}$$

We see an additional contribution to the **first law**. In addition to energy change from heat and mechanical work, there is a new possibility of chemical work done by adding or subtracting particles. We can see from (6.2.10)

$$\mu = \frac{\partial E}{\partial N}\bigg|_{S,V}\,. \tag{6.2.11}$$

In addition to a modified expression for an infinitesimal change in energy, we see the other thermodynamic potentials also receive contributions due to particle number fluctuations

$$\mathrm{d}F \;=\; \mathrm{d}(E \;-\; TS) \;=\; -S\,\mathrm{d}T \;-\; P\,\mathrm{d}V \;+\; \mu\,\mathrm{d}N \tag{6.2.12}$$

$$\mathrm{d}G \;=\; \mathrm{d}(F \;+\; PV) \;=\; -S\,\mathrm{d}T \;+\; V\mathrm{d}P \;+\; \mu\,\mathrm{d}N \tag{6.2.13}$$

$$\mathrm{d}H \;=\; \mathrm{d}(E \;+\; PV) \;=\; T\mathrm{d}S \;+\; V\mathrm{d}P \;+\; \mu\,\mathrm{d}N \tag{6.2.14}$$

The entropy in the grand canonical ensemble is given by

$$S \;=\; -\,k\sum_i \rho_i \log \rho_i \tag{6.2.15}$$

Inserting the distribution (6.1.12)

$$S \;=\; -\,k\sum_i \rho_i \left[-\beta\,(E_i - \mu N_i) \;-\; \log \mathcal{Z}\right] \tag{6.2.16}$$

$$\;=\; \frac{1}{T}\,(E - \mu N) \;+\; k \log \mathcal{Z} \tag{6.2.17}$$

We can do some repackaging to find

$$S = \frac{1}{T}\left(-\frac{\partial}{\partial\beta}\log\mathcal{Z}\right)_{\mu,V} + k\log\mathcal{Z} \tag{6.2.18}$$

$$= kT\frac{\partial}{\partial T}\log\mathcal{Z}\bigg|_{\mu,V} + k\log\mathcal{Z} \tag{6.2.19}$$

$$= \frac{\partial}{\partial T}\left(kT\log\mathcal{Z}\right)_{\mu,V}. \tag{6.2.20}$$

6.3 Grand potential

Along with the usual thermodynamic potentials, we can define another as the Legendre transform of F as

$$\boxed{\Omega = F - \mu N} \tag{6.3.1}$$

so that

$$\mathrm{d}\Omega = -S\,\mathrm{d}T - P\,\mathrm{d}V - N\mathrm{d}\mu. \tag{6.3.2}$$

We thought about scale transformations when earlier, with a scale factor of 2. Now let us scale the volume, and other extensive quantities, by a factor λ: $V \to \lambda V$ and $N \to \lambda N$. E, which is a function of independent variables S, V, and N, must also scale like λ

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N). \tag{6.3.3}$$

Differentiating with respect to λ and then setting $\lambda = 1$, we find

$$E = \frac{\partial E}{\partial S}\bigg|_{V,N} S + \frac{\partial E}{\partial V}\bigg|_{S,N} V + \frac{\partial E}{\partial N}\bigg|_{S,V} N \tag{6.3.4}$$

$$= TS - PV + \mu N \tag{6.3.5}$$

where the coefficients of S, V and N can be read off from (6.2.10). Similarly, the free energy $F = F(T, V, N)$ must be extensive, so

$$F(T, \lambda V, \lambda N) = \lambda F(T, V, N) \tag{6.3.6}$$

(remember that T is intensive). Consequently,

$$F = \frac{\partial F}{\partial V}\bigg|_{T,N} V + \frac{\partial F}{\partial N}\bigg|_{T,V} N \tag{6.3.7}$$

$$= -PV + \mu N. \tag{6.3.8}$$

The latter line (6.3.8) follows from (6.2.12). Another derivation follows from (6.3.5) and the definition $F = E - TS$.

We can either use extensivity

$$\Omega(T, \lambda V, \mu) = \lambda\Omega(T, V, \mu) \tag{6.3.9}$$

(μ is intensive) or (6.3.1) to show that

$$\Omega = -PV. \tag{6.3.10}$$

Applying $F = E - TS$ and (6.2.17) to (6.3.1) we find

$$\begin{aligned} \Omega &= E - TS - \mu N \\ &= E - (E - \mu N + kT \log \mathcal{Z}) - \mu N \\ &= -kT \log \mathcal{Z} \,. \end{aligned} \tag{6.3.11}$$

Thus Ω plays the role in the grand canonical ensemble that F played in the canonical ensemble. Explicitly putting subscripts in to denote the different partition functions:

$$\mathcal{Z}_{\text{GCE}} = e^{-\beta\Omega} \,, \qquad Z_{\text{CE}} = e^{-\beta F} \,. \tag{6.3.12}$$

Further reading

1. F Mandl, *Statistical Physics*, (Wiley & Sons, 1988), Chapter 9.