11 Mar

Logistics: Computer project part 1 Feedback and solutions

part 2 due 24 March

Recap:

Grand-canonical ensemble fixes μ, T

Chemical potential $\mu = -T \left. \frac{\partial S}{\partial N} \right|_E < 0$

Replica trick

$$Z_g(\beta, \gamma)$$

Taking the derivative of the resulting entropy with respect to E_{tot}, keeping N_{tot} fixed, gives the temperature from Eq. 22. Thanks to Eqs. 70 and 71, the result should simplify in a pleasant way:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E_{\text{tot}}}\right|_{N_{\text{tot}}} = R\left(\underbrace{\frac{\partial \beta}{\partial E}\frac{\partial}{\partial \beta}\log Z_g}_{-E} + \underbrace{\frac{\partial \gamma}{\partial E}\frac{\partial}{\partial \gamma}\log Z_g}_{N}\right) + E\frac{\partial \beta}{\partial E} + \beta - N\frac{\partial \gamma}{\partial E}$$

$$= \frac{\partial \beta}{\partial E}(-E) + \frac{\partial \gamma}{\partial E}(N) + E\frac{\partial \beta}{\partial E} + \beta - N\frac{\partial \gamma}{\partial E} = \beta$$

$$\beta = \frac{1}{T}$$

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In the same way, the derivative with respect to N_{tot}, keeping E_{tot} fixed, gives the chemical potential with similar simplifications:

$$\mu = -T\left.\frac{\partial S}{\partial N_{\text{tot}}}\right|_{E_{\text{tot}}} = -TR\left(\underbrace{\frac{\partial \beta}{\partial N}\frac{\partial}{\partial \beta}\log Z_g}_{-E} + \underbrace{\frac{\partial \gamma}{\partial N}\frac{\partial}{\partial \gamma}\log Z_g}_{N}\right) - T\left(E\frac{\partial \beta}{\partial N} - \gamma + N\frac{\partial \gamma}{\partial N}\right)$$

$$= -T\left[\frac{\partial \beta}{\partial N}(-E) + \frac{\partial \gamma}{\partial N}(N) + E\frac{\partial \beta}{\partial N} - \gamma - N\frac{\partial \gamma}{\partial N}\right]$$

$$= \gamma T = \frac{\gamma}{\beta}$$

In the end you should find

$$\beta = \frac{1}{T} \qquad\qquad \gamma = \beta\mu = \frac{\mu}{T} \qquad\qquad (72)$$

and the desired result that all information about the particle reservoir has dropped out, with no remaining reference to R, E_{tot} or N_{tot}. This large external reservoir is still present to fix the temperature T and chemical potential μ that characterize the grand-canonical system Ω, but beyond that nothing about it is relevant (or even knowable) in the grand-canonical approach.

Every aspect of Ω can now be specified in terms of its fixed temperature T and chemical potential μ, starting with the parameters $\beta = 1/T$ and $\gamma = \mu/T$. In particular, the probability—in thermodynamic equilibrium—that Ω adopts micro-state ω_i with (non-conserved) internal energy E_i and particle number N_i is

$$p_i = \frac{1}{Z_g}e^{-\beta(E_i - \mu N_i)} = \frac{1}{Z_g}e^{-(E_i - \mu N_i)/T}. \qquad\qquad (73)$$

Since the particle number N_i is dimensionless, the combination $E_i - \mu N_i$ that appears here reflects our observation below Eq. 67 that the chemical potential μ has dimensions of energy.

These micro-state probabilities are normalized by the **grand-canonical partition function**

$$Z_g(T, \mu) = \sum_{i=1}^{M} e^{-\beta(E_i - \mu N_i)} = \sum_{i=1}^{M} e^{-(E_i - \mu N_i)/T}. \tag{74}$$

Analogously to the canonical partition function, this Z_g is a fundamental quantity in the grand-canonical ensemble, from which many other derived quantities can be obtained.

6.3 The grand-canonical potential, internal energy, entropy, and particle number

The development of the grand-canonical ensemble we have seen so far closely resembles our earlier work setting up the canonical ensemble. We have generalized the thermal reservoir to a particle reservoir that allows both the internal energy and particle number of the system Ω to vary, while keeping its temperature T and chemical potential μ fixed. By adapting the replica ansatz to this setup, we determined the micro-state probabilities p_i and grand-canonical partition function Z_g, and found them to be independent of the details of the particle reservoir.

We now continue by considering a similar set of derived quantities for the grand-canonical ensemble in thermodynamic equilibrium. In addition to the expectation value of the internal energy introduced in Section 3.2, the fluctuations of the particle number mean that we also need to consider its expectation value,

$$\langle E \rangle (T, \mu) = \sum_{i=1}^{M} E_i \, p_i = \frac{1}{Z_g} \sum_{i=1}^{M} E_i \, e^{-\beta(E_i - \mu N_i)}$$

$$\langle N \rangle (T, \mu) = \sum_{i=1}^{M} N_i \, p_i = \frac{1}{Z_g} \sum_{i=1}^{M} N_i \, e^{-\beta(E_i - \mu N_i)}.$$

Looking back to Eqs. 70 and 71, we can expect both of these derived quantities to be related to derivatives of the logarithm of the grand-canonical partition function. In Section 3.3, similar relations led us to define the Helmholtz free energy for the canonical ensemble, which we can also generalize to the grand-canonical case.

We define **grand-canonical potential** of a grand-canonical ensemble to be

$$\Phi(T, \mu) = -T \log Z_g(T, \mu) = -\frac{\log Z_g(\beta, \mu)}{\beta}, \tag{75}$$

where Z_g is the grand-canonical partition function of the ensemble. In terms of this free energy, Eqs. 73 and 74 are

$$Z_g = e^{-\Phi/T} \qquad\qquad p_i = e^{(\Phi - E_i + \mu N_i)/T}.$$

The grand-canonical potential is sometimes called the *Landau free energy*, named after Lev Landau, to highlight its similarity with the Helmholtz free energy. As mentioned above, we want to consider derivatives of the grand-canonical potential, the simplest of which is with respect to the chemical potential,

$$\frac{\partial}{\partial \mu}\Phi(\beta,\mu) = -\frac{1}{\beta}\frac{\partial}{\partial \mu}\log Z_g = \frac{-1}{\beta Z_g}\sum_i \frac{\partial}{\partial \mu}e^{-\beta(E_i - \mu N_i)}$$

$$= \frac{-\beta}{\beta Z_g}\sum_i N_i\, e^{-\beta(E_i - \mu N_i)}$$

$$= -\frac{1}{\cancel{\beta}}\cancel{\beta} - \sum_i N_i\, p_i = -\langle N\rangle$$

$$p_i = \frac{1}{Z_g}e^{-\beta(E_i - \mu N_i)}$$

The derivative with respect to the temperature is a little messier, but can be simplified by recalling $\frac{\partial}{\partial T} = -\beta^2 \frac{\partial}{\partial \beta}$ from Eq. 35. As in Section 3.3, it involves $\frac{\partial}{\partial T}\log Z_g$, which is again worth collecting in advance,

$$-\frac{\partial}{\partial T}\left[\frac{\Phi(T,\mu)}{T}\right] = \frac{\partial}{\partial T}\log Z_g(T,\mu) = -\beta^2\frac{1}{Z_g}\sum_i \frac{\partial}{\partial \beta}e^{-\beta(E_i - \mu N_i)}$$

$$= \frac{\beta^2}{Z_g}\sum_i \left(E_i - \mu N_i\right)e^{-\beta(E_i - \mu N_i)}$$

$$= \frac{\langle E_i\rangle - \mu\langle N\rangle}{T^2}$$

$$\frac{\partial}{\partial T}\Phi(T,\mu) = \frac{\partial}{\partial T}\left(-T\log Z_g\right) = -\log Z_g - T\left(\frac{\langle E\rangle - \mu\langle N\rangle}{T^2}\right)$$

$$= -\log Z_g - \beta\langle E\rangle + \beta\mu\langle N\rangle$$

$$\Phi = -T\log Z_g$$

$$= \frac{\Phi - \langle E\rangle + \mu\langle N\rangle}{T}$$

You should find

$$\frac{\partial \Phi}{\partial T} = \frac{\Phi - \langle E \rangle + \mu \langle N \rangle}{T} = -\log Z_g - \beta \langle E \rangle + \beta \mu \langle N \rangle,$$

which we can connect to the entropy by inserting the probabilities p_i from Eq. 73 into the general definition of the entropy from Eq. 20:

$$p_i = \frac{1}{Z_g} e^{-\beta(E_i - \mu N_i)}$$

$$S(T, \mu) = -\sum_{i=1}^{M} p_i \log p_i = -\sum_i p_i \left(-\log Z_g - \beta E_i + \beta \mu N_i \right)$$

$$= \log Z_g + \beta \langle E \rangle - \beta \mu \langle N \rangle$$

$$= -\frac{\partial \Phi}{\partial T}$$

From this work we can read off the following relations involving the grand-canonical potential $\Phi(T, \mu)$:

$$\langle N \rangle (T, \mu) = -\frac{\partial}{\partial \mu} \Phi \tag{76}$$

$$S(T, \mu) = -\frac{\partial}{\partial T} \Phi \tag{77}$$

$$\langle E \rangle (T, \mu) = -T^2 \frac{\partial}{\partial T} \left[\frac{\Phi}{T} \right] + \mu \langle N \rangle \tag{78}$$

$$\Phi(T, \mu) = -T S + \langle E \rangle - \mu \langle N \rangle \tag{79}$$

Finally, the connections between the energy, entropy and particle number provided by these relations motivate a further extension of the general first law of thermodynamics we derived in Eq. 63. To make the notation less cumbersome here, we write $\langle E \rangle$ and $\langle N \rangle$ as E and N, keeping in mind that these are properties of the system's thermodynamic macro-state rather than its fluctuating micro-state. In this notation, Eq. 63 reads $dE = T\,dS - P\,dV$, and relates any changes in the internal energy of a canonical system to changes in its entropy (heat) or volume (work).

Extending this to the grand-canonical ensemble, we can express the entropy as a function of the internal energy, volume and particle number, $S(E, V, N)$, and consider the change in entropy due to changes in each of these three parameters,

$$dS = \left. \frac{\partial S}{\partial E} \right|_{V,N} dE + \left. \frac{\partial S}{\partial V} \right|_{E,N} dV + \left. \frac{\partial S}{\partial N} \right|_{V,E} dN = \frac{1}{T} dE + \left. \frac{\partial S}{\partial V} \right|_{E,N} dV - \frac{\mu}{T} dN.$$

We can interpret the remaining partial derivative by considering Eq. 63 in the case of fixed internal energy E. This equation already incorporates the fixed particle

number N, since it was derived in the framework of the canonical ensemble:

$$dE = 0 = T\, dS - P\, dV \qquad \Longrightarrow \qquad \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T}.$$

Putting things together, we obtain the generalized thermodynamic identity

$$dE = T\, dS - P\, dV + \mu\, dN. \tag{80}$$

Due to this result, the term $\mu\, dN$ is sometimes referred to as "chemical work", in analogy to the mechanical work $W = -P\, dV$ done on a system by changing its volume. This thermodynamic identity provides a convenient way to remember (or derive) relations between the internal energy, entropy, volume and particle number in thermodynamic equilibrium, by considering processes in which any two of these are fixed. For example, fixing N and V gets us back to Eq. 22 for the temperature,

$$dE = T\, dS \qquad \Longrightarrow \qquad \frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V},$$

while fixing N and S gives Eq. 55 for the pressure,

$$dE = -P\, dV \qquad \Longrightarrow \qquad P = -\left.\frac{\partial E}{\partial V}\right|_{N,S}.$$

If we fix the entropy S and volume V, we end up with another way of understanding the chemical potential,

$$dE = \mu\, dN \qquad \Longrightarrow \qquad \mu = \left.\frac{\partial E}{\partial N}\right|_{S,V}. \quad < 0 \tag{81}$$

That is, the chemical potential is the change in the internal energy when we change the number of particles in the system, without changing its entropy or volume. If we consider adding particles to the system, $\Delta N > 0$, we argued below Eq. 67 that we should generically expect an increase in the entropy. In order to keep the entropy fixed in this process, we therefore need the change in the energy to decrease the entropy by the corresponding amount. For natural systems with positive temperatures, this requires decreasing the energy, $\Delta E < 0$. Similarly, keeping the entropy fixed as we decrease N would require increasing E, so that Eq. 81 confirms our earlier finding that for natural systems the chemical potential is negative in general.