

Physics 127a: Class Notes

Lecture 9: Grand Canonical Ensemble

This describes a system in contact with a reservoir with which it can exchange *energy* and *particles*. The equilibrium is characterized by the reservoir *temperature* T and *chemical potential* μ . As for the canonical ensemble, we can derive properties of the grand canonical ensemble by treating system plus reservoir as an isolated system together described by the microcanonical ensemble. The results are:

- Probability for the system to have N particles and be in state j with energy $E_j^{(N)}$ is

$$P_{j,N} \propto e^{-\beta(E_j^{(N)} - \mu N)}. \quad (1)$$

(remember this comes from counting the number of states in the *reservoir*)

- Define the *grand canonical partition function*

$$\mathcal{Q} = \sum_N \sum_j e^{-\beta(E_j^{(N)} - \mu N)}, \quad (2)$$

and the corresponding *grand potential*

$$\Omega = -kT \ln \mathcal{Q}. \quad (3)$$

- For a macroscopic system we can replace the sums by integrals

$$\mathcal{Q} \simeq \int dN \int \frac{dE}{\Delta} e^{-\beta(E - \mu N - TS(E,N))} \quad (4)$$

where $e^{S/k}$ is the number of states in the energy shell Δ . For large N the integrand is dominated by $E \simeq \bar{E}$ and $N \simeq \bar{N}$ which minimize $E - \mu N - TS$ given by differentiation

$$\mu = T \left(\frac{\partial S}{\partial N} \right)_E, \quad (5)$$

$$1 = T \left(\frac{\partial S}{\partial E} \right)_N. \quad (6)$$

These two equations implicitly give \bar{E} , \bar{N} , and tell us the physical result that the temperature and chemical potential of the system are given by the results of the isolated system at the most probable E and N . Furthermore in evaluating $\ln \mathcal{Q}$ only the value of the integrand at its maximum contributes at $O(N)$

$$\Omega \simeq U - TS - \mu N \quad (7)$$

(strictly we should use the most probable values \bar{E} , \bar{N} , but can replace them by the means U , N since the distribution is so narrow).

- Differentiating and using $dU = TdS - PdV + \mu dN$ gives the thermodynamic identity in the form

$$d\Omega = -SdT - Nd\mu - PdV. \quad (8)$$

- Making a system at T, μ, V by adding little volumes dV at the same T, P gives us (since then $dT = d\mu = 0$)

$$\Omega = -PV. \quad (9)$$

Grand Potential for the Classical Ideal Gas

We can write

$$\mathcal{Q} = \sum_N z^N \mathcal{Q}_N \quad (10)$$

with $z = e^{\beta\mu}$ known as the fugacity and \mathcal{Q}_N the *canonical partition function* for N particles. Also, for the classical ideal gas

$$\mathcal{Q}_N = \frac{(Q_1)^N}{N!}, \quad (11)$$

so that

$$\mathcal{Q} = \sum_N \frac{(zQ_1)^N}{N!} = e^{zQ_1}. \quad (12)$$

Thus

$$-\frac{\Omega}{kT} = \frac{PV}{kT} = \ln \mathcal{Q} = zQ_1. \quad (13)$$

For a monatomic gas we found

$$Q_1 = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}. \quad (14)$$

This is the ideal gas law—but in terms of μ rather than N . Normally we would eliminate μ in terms of the mean N using

$$N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V}. \quad (15)$$

From Eq. (13) we see that the only μ dependence of Ω is in the fugacity $z = e^{\beta\mu}$, and differentiating gives

$$N = zQ_1 \quad (16)$$

which with Eq. (14) gives the same expression for $\mu(N, T, V)$ as we found before, and with Eq. (13) gives the ideal gas law in the familiar form.

Number fluctuations

In the grand canonical ensemble, the probability of finding N particles in the system is

$$P(N) = \frac{\sum_j e^{-\beta(E_j^{(N)} - \mu N)}}{\sum_N \sum_j e^{-\beta(E_j^{(N)} - \mu N)}} = \frac{z^N \mathcal{Q}_N}{\mathcal{Q}}. \quad (17)$$

For the ideal gas

$$\mathcal{Q}_N = \frac{(Q_1)^N}{N!} \quad (18)$$

and

$$P(N) = z^N \mathcal{Q}_1^N e^{-zQ_1}. \quad (19)$$

As we have seen $\langle N \rangle = zQ_1$ (this can of course be derived as $\sum_N N P(N)$ from equation (19)), so that for the ideal gas the number fluctuations are described by the *Poisson distribution*

$$P(N) = \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!}. \quad (20)$$