

Unit 2-14: A Note About the Proper Choice of Coordinates

We can write the partition functions as:

$$\text{microcanonical : } \Omega(E, V, N) = \int_{\substack{\text{all degrees} \\ \text{of freedom}}} \delta(E - \mathcal{H}) \quad (2.14.1)$$

$$\text{canonical : } Q_N(T, V) = \int_{\substack{\text{all degrees} \\ \text{of freedom}}} e^{-\beta \mathcal{H}}$$

where the integral is meant as an integral over all the degrees of freedom that characterize the system. If the degrees of freedom are continuous, then the integration should include an appropriate factor (like h^{-3N} for the gas of N classical particles) so that the partition function is a dimensionless quantity.

For *classical* systems, with continuous degrees of freedom, it is **essential** that the degrees of freedom one integrates over be a set of Hamiltonian *canonically conjugate* coordinate-momenta pairs (q_i, p_i) . The reason is Liouville's theorem, discussed in Notes 2-3. To describe equilibrium the probability density for the system to be at a particular point in phase space should not vary with time, i.e. $\partial \rho / \partial t = 0$. According to Liouville's theorem, this will be the case whenever all states of a given energy E are equally likely, i.e. $\rho(\{q_i, p_i\}) = \rho(\mathcal{H}[\{q_i, p_i\}])$. But Liouville's theorem only applies if we are labeling the states by a set of Hamiltonian canonically conjugate coordinate-momenta pairs – recall, we had to use Hamilton's equations of motion to derive Liouville's theorem.

If $\{q_i, p_i\}$, $i = 1$ to $3N$, are such canonically conjugate degrees of freedom, then we have for the canonical partition function,

$$Q_N(T, V) = \frac{C}{h^{3N}} \int dq_1 dq_2 \cdots dq_{3N} \int dp_1 dp_2 \cdots dp_{3N} e^{-\beta \mathcal{H}[q_1, \dots, q_{3N}, p_1, \dots, p_{3N}]} \quad (2.14.2)$$

where $C = 1/N!$ if the particles are indistinguishable, and $C = 1$ if the particles are distinguishable.

Now sometimes it might be convenient to label states by some other set of coordinates, for example $\{q_i, \dot{q}_i\}$. In that case, one can compute the partition function in terms of the convenient coordinates *provided* one makes the correct transformation of the variables of integration,

$$Q_N(T, V) = \frac{C}{h^{3N}} \int dq_i dp_i e^{-\beta \mathcal{H}[q_i, p_i]} = \frac{C}{h^{3N}} \int dq_i d\dot{q}_i J e^{-\beta \mathcal{H}[q_i, \dot{q}_i]} \quad (2.14.3)$$

where J is the *Jacobian* of the transformation from $\{q_i, p_i\}$ to $\{q_i, \dot{q}_i\}$. It is *crucial* to include this Jacobian factor to get the correct result for the partition function.

If one goes from a set of variables $\{y_1, y_2, \dots, y_M\}$ to a new set of variables $\{x_1, x_2, \dots, x_M\}$, then the Jacobian is given by,

$$J = \det \begin{bmatrix} \frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} & \cdots \\ \frac{\partial y_2}{\partial x_1} & \frac{\partial y_2}{\partial x_2} & \cdots \\ \vdots & \vdots & \ddots \\ \vdots & \vdots & \ddots \end{bmatrix} \quad \text{where "det" means the determinant of the matrix} \quad (2.14.4)$$

Then one has,

$$\prod_{i=1}^M \int dy_i = \prod_{i=1}^M \int dx_i J \quad (2.14.5)$$

Example:

Consider a classical gas of N non-interacting charged particles, each with charge q , in an external magnetic field. Although it might seem strange to assume that the charged particles do not interact with each other, this turns out not to be a bad approximation for electrons in a metal (take PHY 512!). We will, however, take the charged particles to interact with the magnetic field.

From mechanics you know that the Hamiltonian for such a system is,

$$\mathcal{H} = \sum_{i=1}^N \frac{1}{2m} \left| \mathbf{p}_i - \frac{q}{c} \mathbf{A}(\mathbf{r}_i) \right|^2 \quad \text{where } \mathbf{A}(\mathbf{r}) \text{ is the magnetic vector potential.} \quad (2.14.6)$$

The particle's velocity \mathbf{v}_i , in terms of the canonical momentum \mathbf{p}_i , is given by,

$$\mathbf{v}_i = \frac{\mathbf{p}_i - \frac{q}{c} \mathbf{A}(\mathbf{r}_i)}{m} \quad (2.14.7)$$

At first glance it might seem that we could *not* compute the average total energy $E = \langle \mathcal{H} \rangle$ using the equipartition theorem, since \mathcal{H} couples \mathbf{p}_i to \mathbf{r}_i via $\mathbf{A}(\mathbf{r}_i)$.

However, if we directly compute the single-particle partition function Q_1 ,

$$Q_1 = \frac{1}{h^3} \int d^3r \int d^3p e^{-\beta |\mathbf{p} - \frac{q}{c} \mathbf{A}(\mathbf{r})|^2 / 2m} \quad (2.14.8)$$

we can do the following trick. Doing the integration over \mathbf{p} first and the integration over \mathbf{r} last, then since \mathbf{r} is a fixed quantity when we do the \mathbf{p} integration, then as far as the \mathbf{p} integration is concerned, $\frac{q}{c} \mathbf{A}(\mathbf{r})$ is just some fixed constant \mathbf{p}_0 . So we can make a transformation of variables in the integration from \mathbf{p} to $\mathbf{p}' = \mathbf{p} - \mathbf{p}_0$, and since the limits of integration for \mathbf{p}' remain $\pm\infty$, we can write,

$$Q_1 = \frac{1}{h^3} \int d^3r \int d^3p' e^{-\beta |\mathbf{p}'|^2 / 2m} \quad (2.14.9)$$

This now gives exactly the same Q_1 as for a gas of particles that is *not* in a magnetic field! Hence we can conclude that the total energy of the gas in the magnetic field is the same as the gas in zero field, $E = \frac{3}{2} N k_B T$.

We can view this result in terms of a coordinate transform, like we discussed above. Instead of writing the partition function in terms of the canonical coordinates $\{\mathbf{r}_i, \mathbf{p}_i\}$, with $\mathbf{p}_i = m\mathbf{v}_i + \frac{q}{c} \mathbf{A}(\mathbf{r}_i)$ the canonical momentum, we could instead use the coordinates $\{\mathbf{r}_i, \mathbf{v}_i\}$. We then would have,

$$Q_1 = \frac{1}{h^3} \int d^3r \int d^3v J e^{-\beta m |\mathbf{v}|^2 / 2} \quad (2.14.10)$$

Here $J = m^3$ is the Jacobian of the transformation from $\{\mathbf{r}, \mathbf{p}\}$ to $\{\mathbf{r}, \mathbf{v}\}$. We can now do the integration over \mathbf{v} and get the same result for Q_1 as in the case with no magnetic field. The thing that makes this work simply in this case is that the Jacobian J is just a *constant*, and *not* some function of \mathbf{r} and \mathbf{v} .

Warning! Our result, that the energy $E = \frac{3}{2} N k_B T$ for a gas of non-interacting charged particles in a magnetic field is the same as when the field is zero, holds only for a system of *classical* particles. When we treat the particles quantum mechanically, this will no longer be true.