Classical Monatomic Ideal Gas

Equipartition Principle

• Statement: The equipartition principle is a statement about classical systems with quadratic Hamiltonians. It states that any canonical variable ξ (a q or a p) that appears in H only in a quadratic additive term of the form $\kappa \xi^2$, where κ is a constant, and whose range of values can be considered to be $(-\infty, \infty)$, contributes a term $\frac{1}{2}k_{\rm B}T$ to the mean energy of the system, or $\frac{1}{2}k_{\rm B}$ to the heat capacity. In particular, the mean energy of a system of N non-interacting particles (distinguishable or not), each of which contributes f quadratic terms in the positions and/or momenta to the total Hamiltonian is $\bar{E} = \frac{1}{2} f N k_{\rm B} T$.

• Proof: Suppose the Hamiltonian is of the form $H = \tilde{H}(\tilde{q}, \tilde{p}) + \kappa \xi^2$, where κ and ξ are as described above and the variables (\tilde{q}, \tilde{p}) do not include ξ . Then the partition function and mean energy can be calculated as

$$Z_{\rm c} = \int_{\Gamma} \mathrm{d}\Omega \,\mathrm{e}^{-\beta H(q,p)} = \tilde{Z} \int_{-\infty}^{+\infty} \mathrm{d}\xi \,\mathrm{e}^{-\beta\kappa\,\xi^2} = \tilde{Z} \sqrt{\frac{\pi}{\beta\kappa}} \,, \qquad \bar{E} = -\frac{\partial}{\partial\beta} \,\ln Z_{\rm c} = \tilde{E} + \frac{1}{2} \,\frac{\partial}{\partial\beta} \ln\beta = \tilde{E} + \frac{1}{2} k_{\rm B} T \,,$$

where \tilde{Z} and \tilde{E} are the parts of Z_c and \bar{E} that contain the contribution from the variables (\tilde{q}, \tilde{p}) , and we have used the well-known Gaussian integral $\int_{-\infty}^{+\infty} dx e^{-ax^2} = \sqrt{\pi/a}$.

Classical Monatomic Ideal Gas Thermodynamics

• Setup: As a first example of application of the equipartition principle, consider a monatomic ideal gas. The Hamiltonian is a sum of terms from individual non-interacting particles; if the particles are single atoms and T is low enough that their internal, electronic or nuclear degrees of freedom are not excited, then each term in the Hamiltonian is just the particle's translational kinetic energy, $H(q, p) = \sum_{i=1}^{N} \vec{p}_i^2/2m$.

• Canonical partition function: For a single particle, using again the Gaussian integral,

$$Z_1 = \frac{1}{h^3} \int_V d^3 x \left(\int_{-\infty}^{+\infty} dp \, e^{-\beta p^2/2m} \right)^3 = \frac{V}{h^3} \left(\sqrt{\frac{\pi}{\beta/2m}} \right)^3 = \frac{V}{\lambda_T^3} ,$$

where $\lambda_T := \sqrt{h^2 \beta / 2 \pi m}$ is the thermal wavelength. For N particles, since the particles are non-interacting $(H = H_1 + ... + H_N)$ the partition function is the product of N single-particle ones. If the particles are identical, however, one must take into account the fact that any permutation of the N particles leads to an indistinguishable state, even classically. This *Boltzmann statistics* leads to the N-particle particle particle of function.

$$Z_{\rm c} = \frac{1}{N!} Z_1^N = \frac{V^N}{N! \, \lambda_T^{3N}}$$

• Mean energy: We can obtain the mean energy directly from the equipartition principle, or as a result of a short calculation,

$$\bar{E} = -\frac{\partial}{\partial\beta} \, \ln \frac{V^N}{N!} \left(\frac{2\pi m}{h^2\beta}\right)^{3N/2} = \frac{3}{2} \, N k_{\rm\scriptscriptstyle B} T \; , \label{eq:E}$$

an expression that agrees with what we expect from the kinetic theory of ideal gases.

 \bullet Helmholtz free energy: Using the partition function $Z_{\rm c}$ above for a monatomic ideal gas, we find

$$F = -k_{\rm\scriptscriptstyle B}T\,\ln Z_{\rm\scriptscriptstyle c} = -k_{\rm\scriptscriptstyle B}T\,\ln \frac{V^N}{N!\,\lambda_T^{3N}} = -k_{\rm\scriptscriptstyle B}T\,(\ln V^N - \ln N! - \ln \lambda_T^{3N})\;. \label{eq:F}$$

This expression can now be used to obtain the pressure p, entropy S and chemical potential μ using definitions obtained from the fundamental identity of thermodynamics for F.

• Pressure: The ideal gas pressure equation of state can be obtained from the free energy,

$$p = -\frac{\partial F}{\partial V}\Big|_{T,N} = k_{\rm\scriptscriptstyle B}T\,\frac{\rm d}{{\rm d}V}\,\ln V^N = Nk_{\rm\scriptscriptstyle B}T\,\frac{1}{V}\;,\qquad {\rm or}\qquad pV = Nk_{\rm\scriptscriptstyle B}T\;.$$

(Alternatively, from $S(E, V) = k_{\rm B} \ln \Omega = k_{\rm B} \ln (V^N f(E))$ and $dS = \delta Q/T = (dE + pdV)/T$ we get that $p/T = \partial S/\partial V|_E = Nk_{\rm B}/V$.)

• Entropy: Using the fact that $S = T^{-1}(\bar{E} - F)$ and defining the number density $\rho := N/V$ we get

$$S = \frac{3}{2} N k_{\rm B} + k_{\rm B} \left(\ln V^N - \ln N! - \ln \lambda_T^{3N} \right) \approx N k_{\rm B} \left[-\ln(\rho \lambda_T^3) + \frac{5}{2} \right] = N k_{\rm B} \left\{ \ln \left[\frac{V}{N} \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \right] + \frac{5}{2} \right\}.$$

This expression, obtained using the Stirling approximation $\ln N! \approx N \ln N - N$, is the Sackur-Tetrode formula. Notice that, had we not had the N! factor in the denominator of Z, the $\ln N!$ term would have been absent in the first expression above (\bar{E} would not have changed, nor the pressure equation of state). As a result, the entropy would not have been additive (extensive), leading to the Gibbs paradox.

• Chemical potential: Using the expression of μ as a derivative of the Helmholtz free energy, we get

$$\mu := \frac{\partial F}{\partial N}\Big|_{T,V} = \frac{\partial}{\partial N} \Big[-k_{\rm B} T \left(\ln V^N - \ln N! - \ln \lambda_T^{3N} \right) \Big] \approx k_{\rm B} T \ln(\rho \lambda_T^3)$$

where we have again approximated $\ln N!$ using the Stirling formula. Alternatively, we can use

$$\mu = G/N = (E - TS + pV)/N .$$

Second-Order Quantities and Fluctuations

• Remark: As our system is in a canonical state, we were able to derive expressions for all thermodynamic variables above just using the partition function Z_c instead of having to use the full $\rho(q, p)$. Second-order thermodynamic quantities can also be calculated using ony Z_c , because they are derivatives of first-order ones, and some fluctuations of phase-space functions can be reduced to second-order quantities.

• Heat capacity: There is a simple expression for any system in a canonical state. Using $(\partial/\partial\beta)Z_{\rm c} = -Z_{\rm c}\bar{E}$,

$$C_V = \frac{\partial \bar{E}}{\partial T}\Big|_{V,N} = \frac{\mathrm{d}\beta}{\mathrm{d}T} \frac{\partial}{\partial\beta} \Big(\frac{1}{Z_{\mathrm{c}}} \sum_s H(s) \,\mathrm{e}^{-\beta H(s)} \Big) = -\frac{1}{k_{\mathrm{B}}T^2} \left[\frac{1}{Z_{\mathrm{c}}^2} (Z_{\mathrm{c}}\bar{E})^2 - \frac{1}{Z_{\mathrm{c}}} \sum_s H^2(s) \,\mathrm{e}^{-\beta H(s)} \right] = \frac{(\Delta E)^2}{k_{\mathrm{B}}T^2} \,.$$

This is a special case of a general result known as the fluctuation-dissipation theorem. Notice that it is always positive, $C_V > 0$. For the classical monatomic ideal gas in particular, we can calculate $C_V = \partial \bar{E} / \partial T = \frac{3}{2} N k_{\rm B}$, as we already knew from kinetic theory.

• Compressibility: The isothermal compressibility is $\kappa_T = -(1/V) (\partial V/\partial p)_{T,N} = 1/p$, as we also had found before. (And, like other response functions for any system in a canonical ensemble, it is always positive.)

• Energy fluctuations: The variance of the distribution of values of the energy can be obtained from the general relation $(\Delta E)^2 = k_{\rm B}T^2C_V$ for any system in thermal equilibrium. Then, in our case of the monatomic ideal gas, $(\Delta E)^2 = \frac{3}{2}N(k_{\rm B}T)^2 = \bar{E}^2/(\frac{3}{2}N)$, and the relative energy fluctuation is $(\Delta E)/\bar{E} = \sqrt{2/(3N)}$.

The Maxwell Speed Distribution

To find the probability distribution of particle speeds we actually need to know the full distribution function $\rho(q, p)$ for the system. Since the probability density that a particle have momentum \vec{p} is $h^{-3} \int_V d^3r \,\rho(\vec{r}, \vec{p})$, we get that the probability density for the magnitude v of the velocity is

$$f(v) = \frac{m^3 v^2}{h^3} \int \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi \int_V \mathrm{d}^3 r \,\rho(\vec{r},\vec{p}) = \frac{4\pi \,m^3 v^2}{h^3 Z_1} \int_V \mathrm{d}^3 r \,\mathrm{e}^{-\beta H_1(\vec{r},\vec{p})} = \left(\frac{m}{2\pi \,k_{\rm\scriptscriptstyle B} T}\right)^{3/2} 4\pi v^2 \,\mathrm{e}^{-mv^2/2k_{\rm\scriptscriptstyle B} T} \,,$$

the Maxwell speed distribution for particles in a classical ideal gas.

Reading

• Course textbook: Kennett, § 4.5.

• Other books: Halley, pp 150–154; Mattis & Swendsen, § 2.2; Pathria & Beale, §§ 3.9 (classical) and 8.2 (quantum); Plischke & Bergersen, —; Reif, §§ 6.3 (classical) and 7.8 (quantum); Schwabl, §§ 6.3–6.4.