Semiclassical Statistical Mechanics

from Statistical Physics using Mathematica

A classical ensemble is represented by a distribution of points in phase space. Two important theorems, equipartition and virial, are derived from this concept. However, finite classical entropy requires discretization of the phase space using a volume obtained by comparison with quantum mechanical results for prototypical systems. Applications are made to harmonic oscillators, ideal gases, and gases of diatomic molecules.

Classical phase space

A classical system with f degrees of freedom is described by generalized coordinates $q_i[t]$ and momenta $p_i[t]$ which satisfy the equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

where $H = H[q_1, p_1, \cdots, q_f, p_f, t]$ is the Hamiltonian function. Each point in the $2f$ dimensional *phase space* represents a different microstate of the system. It is useful to let $\xi = \{q_1, p_1, \cdots, q_f, p_f\}$ represent a point in phase space such that $\xi[t]$ represents the motion of the system, its trajectory, through phase space. Suppose that $A = A[\xi, t]$ is some property of the system that depends upon the phase-space variables and may also depend explicitly upon time as well. The total time rate of change for this property is then

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial t} + \sum_{i=1}^{f}\left(\frac{\partial A}{\partial q_i}\dot{q}_i + \frac{\partial A}{\partial p_i}\dot{p}_i\right) = \frac{\partial A}{\partial t} + \sum_{i=1}^{f}\left(\frac{\partial A}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial H}{\partial q_i}\right)$$

Thus, if we define the *Poisson bracket* $[A, H]$ as

$$[A, H] = \sum_{i=1}^{f}\left(\frac{\partial A}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial H}{\partial q_i}\right)$$

we obtain the time dependence

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial t} + [A, H]$$

Therefore, if we assume that the Hamiltonian does not depend explicitly upon time,

$$\frac{\partial H}{\partial t} = 0 \implies \frac{\mathrm{d}H}{\mathrm{d}t} = 0$$

we immediately find that the energy $E = H[\,\xi[0]\,]$ is a constant of the motion for conservative systems. States of specified energy are confined to a $2f-1$ dimensional hypersurface embedded in the $2f$ dimensional phase space.

A classical ensemble consists of a set of points in phase space, with each point representing a system in a specified microstate. The number of points in a region of phase space near ξ in a volume $d\Gamma = \prod_{i=1}^{f} dq_i\, dp_i$ is given by $\rho[\xi, t]\, d\Gamma$, where the phase-space density $\rho[\xi, t]$ is the classical analog of the quantum mechanical density operator. As each member of the ensemble moves through phase space along a trajectory specified by Hamilton's equations of motion, the phase space density evolves in time. Consider a simply-connected volume Γ bounded by a surface σ. The number of systems within Γ is given by

$$N_\Gamma = \int_\Gamma d\Gamma\, \rho[\xi, t]$$

Using the divergence theorem, the rate at which members of the ensemble leave volume Γ can be expressed in terms of the flux through the surface σ as

$$\int_\sigma d\vec{\sigma} \cdot \vec{j} = \int_\Gamma d\Gamma\, \nabla \cdot \vec{j}$$

where $\vec{j} = \rho\, \vec{v}$ is the current based upon phase velocity $\vec{v} = \{\dot{q}_1, \cdots, \dot{p}_f\}$. Thus, recognizing that members of the ensemble are neither created nor destroyed, the phase-space density must satisfy a continuity equation of the form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0$$

The two contributions to the divergence

$$\nabla \cdot (\rho\, \vec{v}) = \vec{v} \cdot \nabla \rho + \rho\, \nabla \cdot \vec{v}$$

can be simplified using Hamilton's equations of motion

$$\vec{v} \cdot \nabla \rho = \sum_{i=1}^{f} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial q_i}{\partial t} + \frac{\partial \rho}{\partial p_i} \frac{\partial p_i}{\partial t} \right) = [\rho, H]$$

$$\nabla \cdot \vec{v} = \sum_{i=1}^{f} \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = \sum_{i=1}^{f} \left(\frac{\partial^2 H}{\partial q_i\, \partial p_i} - \frac{\partial^2 H}{\partial p_i\, \partial q_i} \right) = 0$$

Therefore, *Liouville's theorem*

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \vec{v} \cdot \nabla \rho = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

states that the local density in the phase-space neighborhood of a representative point is conserved. In fluid mechanics, the total derivative $\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \vec{v} \cdot \nabla \rho$, known as a convective derivative, measures the time dependence of the density for a moving parcel of fluid viewed from a point that moves with that parcel, rather than from a fixed location. According to Liouville's theorem, the phase-space density for a system obeying Hamilton's equations of motion behaves like an incompressible fluid. Therefore, as a classical ensemble evolves its location and shape in phase space may change but its volume is conserved.

The ensemble average of property A which depends upon the phase-space variables is

$$\langle A \rangle = \frac{\int d\Gamma\, \rho[\xi, t]\, A[\xi, t]}{\int d\Gamma\, \rho[\xi, t]}$$

where the integral spans the entire phase space. Note that Liouville's theorem ensures that the denominator is constant. In order to obtain a stationary expectation value we normally require that neither A nor ρ depend explicitly upon time, but this condition is not sufficient because as the phase point moves along the trajectories specified by their equations of motion the density $\rho[\xi, t]$ evolves. Equilibrium requires

$$\text{equilibrium} \Longrightarrow \frac{\partial \rho}{\partial t} = 0 \Longrightarrow [\rho, H] = 0$$

and is most simply achieved using an ensemble $\rho = \rho[H]$ based upon the Hamiltonian. The canonical ensemble

$$\text{canonical ensemble}: \quad \rho \propto \text{Exp}[-\beta H]$$

clearly satisfies this condition and, hence, is stationary. Alternatively, the microcanonical ensemble consisting of all states within the volume of phase space within a specified range of energy

$$\text{microcanonical ensemble}: \; \rho = \Gamma^{-1}\, \Theta[\delta E - | E - H[\xi] |]$$

is also stationary.

Counting states in classical phase space

If classical microstates were to correspond to mathematical points in phase space, the total number of states compatible with finite intervals of energy and volume would be infinite for most systems. Thus, the calculation of entropy, or other thermodynamic potentials, is problematical in classical statistical mechanics. Sensible enumeration of classical microstates requires that a $2 f$ dimensional phase space be divided into cells with finite volume δ^f where δ has dimensions $dq\, dp$. Although we might envision a classical limit $\delta \to 0$, such a limiting procedure would yield infinite entropies. Fortunately, quantum mechanics provides a natural discretization of the phase space — the uncertainty principle limits the precision with which conjugate coordinates and momenta can be specified. Thus, we expect that δ must be closely related to Planck's constant. Furthermore, if the parameter δ is to remain small and finite it must be a universal constant so that entropies can be added meaningfully for systems of different types. Hence, we are free to evaluate this constant by comparison with any convenient quantum system. The two examples below both suggest that $\delta = h$. Therefore, we normalize the differential phase-space volume element

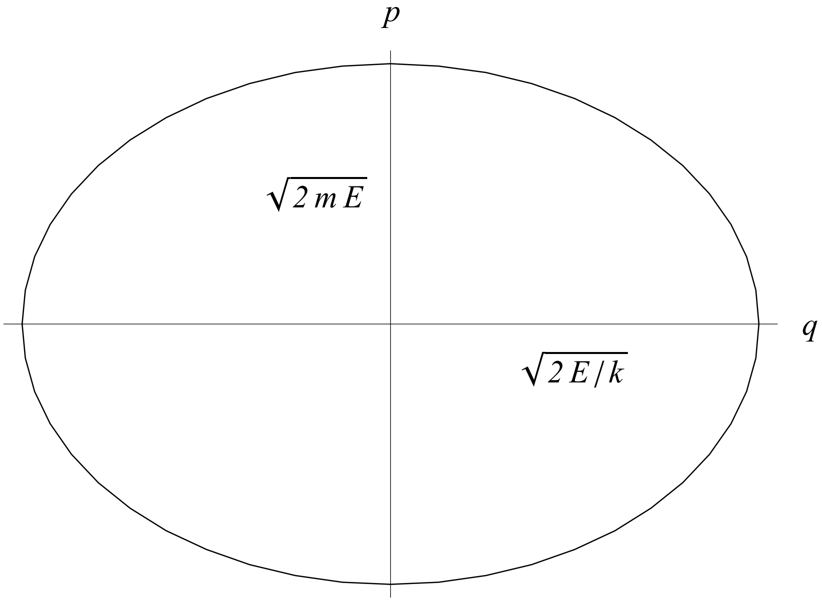
$$d\Gamma = \prod_{i=1}^{f} \frac{dq_i\, dp_i}{h}$$

using a factor h^{-1} for each degree of freedom.

This analysis is based upon an *inverse correspondence principle*. In quantum mechanics one often use correspondence with classical physics to determine the form of the Hamiltonian, but here we use quantum mechanics to determine the normalization factor for the phase-space density. Similarly, we sometimes mix classical descriptions for some aspects with quantum mechanical descriptions of other degrees of freedom. For example, when we study the heat capacity for noninteracting gases with internal rotational and vibrational degrees of freedom we will employ a classical description for the center of mass but quantum mechanical descriptions for the internal excitations of each molecule. These types of mixed models are described as *semiclassical*. It is interesting to observe that quantum statistics is usually easier than classical statistics and that classical statistics usually does not make sense unless quantum mechanics is used to obtain finite entropy.

■ Example: harmonic oscillator

Consider a one-dimensional harmonic oscillator with Hamiltonian $H = \frac{p^2}{2m} + \frac{1}{2} k q^2$.



States with energy E are found on an ellipse with axes $\pm\sqrt{2E/k}$ in q and $\pm\sqrt{2mE}$ in p. The microcanonical ensemble of systems with energy E is then the set of points on the ellipse, which is infinite in number. To obtain finite results, we discretize the set and claim that the multiplicity $\Omega[E]$ is proportional to the circumference of the ellipse. Similarly, the number of states $\Sigma[E]$ with energies $E' \leq E$ is proportional to the area of the ellipse. Thus, we claim

$$\Sigma = \frac{\pi}{\Sigma_0} \sqrt{\frac{2E}{k}} \sqrt{2mE} = \frac{2\pi E}{\Sigma_0} \sqrt{\frac{m}{k}} = 2\pi \frac{E}{\omega \Sigma_0}$$

where Σ_0 is the area of an elementary cell in phase space and where we have used the harmonic oscillator frequency $\omega = \sqrt{k/m}$. Classical physics does not specify the cell size — because classical physics claims that it is possible, at least in principle, to specify coordinates and momenta with arbitrary precision, it would appear that one should take the limit $\Sigma_0 \to 0$. Thus, in that limit entropy becomes infinite because there are an infinite number of states compatible with the definition of the ensemble. However, quantization of energy requires there to be a minimum volume of phase space surrounding each of the finite number of states in a specified energy range. The simplest method for obtaining this cell size is to examine the density of states

$$g = \frac{\partial \Sigma}{\partial E} = \frac{2\pi}{\omega \Sigma_0}$$

and to use the quantization of energy

$$g = \frac{1}{\hbar \omega} \implies \Sigma_0 = 2\pi\hbar = h$$

to recognize that the cell size is governed by Planck's constant.

■ Example: particle in a box

Consider a cubical box with volume $V = L^3$ containing N noninteracting particles with mass m. Single-particle wave functions take the form

$$\psi(x, y, z) \propto \text{Sin}[k_x x]\,\text{Sin}[k_y y]\,\text{Sin}[k_z z]$$

where the requirement that ψ vanishes upon the walls imposes the quantization condition

$$k_i = \frac{n_i \pi}{L} \qquad i \in \{x, y, z\}$$

where the n_i must be integers. Thus, we find that the spacing between adjacent wave numbers is π / L such that each quantum state occupies a cell in k-space with volume $(\pi / L)^3$. Assuming that nonrelativistic kinematics applies, the single-particle energies become

$$\varepsilon_k = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m} = n^2 \varepsilon_0$$

where

$$\varepsilon_0 = \frac{\pi^2 \hbar^2}{2 m L^2} = \frac{h^2}{8 m L^2}$$

is the basic unit of energy and

$$n^2 = {n_x}^2 + {n_y}^2 + {n_z}^2$$

represents a dimensionless excitation variable. Note that $n \geq 1$ but need not be an integer.

The states available to a particle in the box can be represented by points on a three-dimensional lattice in the space $\{k_x, k_y, k_z\}$. All distinct states are represented by points with the octant with all $n_i \geq 0$; negative integers merely change the sign of the wave function and are redundant. The total number of states in the spherical shell with radius between k and $k + dk$ is then the volume of one octant of a spherical shell divided by the cell volume, such that

$$d\Gamma = \frac{1}{8} \frac{4 \pi k^2 \, dk}{(\pi / L)^3} = \frac{V}{2 \pi^2} k^2 \, dk$$

Although this derivation was made for a cube, it can be shown that for a sufficiently large volume V the result is independent of the shape of the enclosure. Therefore, it is convenient to express $d\Gamma$ in the more general form

$$d\Gamma = \frac{d^3 r \, d^3 p}{(2 \pi \hbar)^3} = \rho_1[\xi] \, d\xi \implies \rho_1[\xi_1] = (2 \pi \hbar)^{-3}$$

where $\xi = \{\vec{r}, \vec{p}\}$ are the coordinates of a single particle and ρ_1 is the classical phase-space density for a single particle.

Therefore, the volume δ for an elementary cell in classical phase space is identified as being Planck's constant, $h = 2 \pi \hbar$. This result is obviously related to the Heisenberg uncertainty principle, which states that there is a finite precision with which a pair of conjugate variables can be known simultaneously.

Equipartition theorem

A powerful theorem of classical statistical mechanics concerns the equipartition of energy among the harmonic degrees of freedom. Suppose that the energy $E = E[q_1, \cdots, q_f, p_1, \cdots, p_f]$ can be separated in the form

$$E = \varepsilon_i[\xi_i] + E'[q_1, \cdots, p_f]$$

where ξ_i is any coordinate or momentum which does not appear in E'. Further, suppose that $\varepsilon_i = b\,\xi_i^{\alpha}$. Normally $\alpha = 2$ for a harmonic coordinate or momentum. If α is even, the integration extends over $-\infty < \xi_i < \infty$, but for odd or nonintegral α the range of ξ_i must be limited to ensure a convergent integral.

The mean value of ε_i in the canonical distribution is

$$\overline{\varepsilon_i} = \frac{\int d\Gamma\, \mathrm{Exp}[-\beta\,\varepsilon_i]\, \mathrm{Exp}[-\beta\, E']\, \varepsilon_i}{\int d\Gamma\, \mathrm{Exp}[-\beta\,\varepsilon_i]\, \mathrm{Exp}[-\beta\, E']} = \frac{\int d\xi\, \mathrm{Exp}[-\beta\,\varepsilon_i]\, \varepsilon_i}{\int d\xi\, \mathrm{Exp}[-\beta\,\varepsilon_i]} = -\frac{\partial}{\partial\beta} \mathrm{Log}\Big[\int d\xi\, \mathrm{Exp}[-\beta\,\varepsilon_i]\Big]$$

If we now let

$$y^{\alpha} \equiv \beta\,\xi^{\alpha} \implies d\xi = \beta^{-1/\alpha}\, dy$$

we find

$$\int d\xi\, \mathrm{Exp}[-\beta\, b\,\xi^{\alpha}] = \beta^{-1/\alpha} \int dy\; \mathrm{Exp}[-b\, y^{\alpha}]$$

Assuming that the limits of integration with respect to y do not depend upon β, *viz.* the limits of ξ are $(0,\infty)$ or $(-\infty, \infty)$, we obtain

$$\mathrm{Log}\Big[\int d\xi\, \mathrm{Exp}[-\beta\,\varepsilon]\Big] = -\alpha^{-1}\,\mathrm{Log}[\beta] + \mathrm{Log}\Big[\int dy\; \mathrm{Exp}[-b\, y^{\alpha}]\Big] \implies \frac{\partial}{\partial\beta}\mathrm{Log}\Big[\int d\xi\, \mathrm{Exp}[-\beta\,\varepsilon]\Big] = -\frac{k_B\, T}{\alpha}$$

Thus, the mean value of ε_i reduces to $k_B\, T/\alpha$. Therefore, the equipartition theorem states:

> The mean energy $\overline{\varepsilon_i}$ contributed by each separable coordinate or momentum ξ_i whose contribution to the Hamiltonian is proportional to ξ_i^{α} is $\overline{\varepsilon_i} = k_B\, T/\alpha$.

For example, consider an ideal gas consisting of nonrelativistic particles with no internal degrees of freedom. The total energy is then a sum of $3\,N$ quadratic contributions to the kinetic energy arising from the three independent momentum components for each particle. Hence, the equipartition theorem predicts $U = \frac{3}{2}\, N\, k_B\, T$ for a nonrelativistic ideal gas.

The equipartition theorem also applies to internal degrees of freedom. For example, consider a diatomic molecule. Harmonic vibrations along the separation between the two atoms contribute two quadratic terms to the energy, one for the internal potential and one for the internal kinetic energy. Hence, the equipartition theorem predicts an additional contribution of $2\,(N\, k_B\, T/2)$ to the internal energy of the gas. Furthermore, diatomic molecules possess two degrees of freedom corresponding to rotations about axes perpendicular to the symmetry axis. Note that rotations about a symmetry axis are forbidden by quantum mechanics because the physical state is unchanged. According to the equipartition theorem, these rotations contribute $k_B\,T$ for each molecule. Therefore, we predict that the specific heat for a gas of diatomic molecules should be

$$\text{diatomic} \Longrightarrow C_V = \frac{7}{2} R$$

based upon equipartition among translational, rotational, and vibrational degrees of freedom.

Although equipartition of the energy among independent degrees of freedom is an important property of classical statistical mechanics, uncritical application of the theorem can lead to absurd results. According to the theorem, the contribution of each independent degree of freedom to the internal energy appears to be independent of the amplitude of the motion associated with that coordinate. Consider a gas of diatomic molecules for which the internal spring constant is enormous. Unless the kinetic energies are large enough for collisions to excite this stiff spring, the molecules might as well be rigid. However, the equipartition theorem predicts that the contribution to the internal energy of the gas is the same for small T as for high T whether or not the spring can be excited with appreciable amplitude. This contribution remains even as we make the spring infinitely stiff.

This prediction of classical statistical mechanics leads to a serious paradox. Any classical system can be subdivided into arbitrarily small components interacting with each other. The binding of adjacent parts can be described by potential and kinetic contributions to the total energy. Each of these degrees of freedom contributes equally to the specific heat even if the binding forces are so strong that these parts are rigidly bound. Therefore, classical statistical mechanics predicts the absurd result that all specific heats are infinite!

The resolution of this paradox again lies in quantum mechanics. Because microscopic motions are quantized, these motions can be excited in discrete quantities only, not with amplitudes related to the excitation energy. Unless sufficient energy is available, some degrees of freedom will be dormant and will not contribute to the specific heat. Only when $k_B\,T$ is much larger than the spacing between energy levels is classical equipartition among available degrees of freedom achieved. Nevertheless, the theorem does provide limiting values that are useful when the number of active degrees of freedom can be enumerated.

■ Example: harmonic oscillators

Consider a collection of N independent classical harmonic oscillators with the same frequency ω governed by the Hamiltonian

$$H = \sum_{i=1}^{N} H_i = \sum_{i=1}^{N} \left(\frac{p_i^2}{2\,m} + \frac{1}{2}\, m\,\omega^2\, q_i^2 \right)$$

The separability of the energy permits factorization of the canonical partition function, $Z = Z_1^N$, where

$$Z_1 = \int \frac{dq\,dp}{h} \operatorname{Exp}\left[-\beta \left(\frac{p^2}{2\,m} + \frac{1}{2}\, m\,\omega^2\, q^2 \right) \right] = \frac{k_B\,T}{\hbar\,\omega}$$

Thus, the principal thermodynamic functions become

$$\begin{aligned}
F &= -N\,k_B\,T \operatorname{Log}\left[\frac{k_B\,T}{\hbar\,\omega} \right] \\
U &= -\frac{\partial \ln Z}{\partial \beta} = N\,k_B\,T \quad \Longrightarrow \quad C_V = N\,k_B \\
S &= \frac{U-F}{T} = N\,k_B \left(1 + \operatorname{Log}\left[\frac{k_B\,T}{\hbar\,\omega} \right] \right) = N\,k_B \left(1 + \operatorname{Log}\left[\frac{U}{N\,\hbar\,\omega} \right] \right) \\
\mu &= -T \left(\frac{\partial S}{\partial N} \right)_U = -\,k_B\,T \operatorname{Log}\left[\frac{k_B\,T}{\hbar\,\omega} \right]
\end{aligned}$$

The pressure vanishes because in this simple model there are no interactions between oscillators and no dependence of the oscillator frequency upon the volume or density of the system.

The internal energy is consistent with the classical equipartition theorem which assigns $\frac{1}{2} k_B T$ to each harmonic coordinate or momentum that appears in the Hamiltonian. In the high-temperature limit the entropy per oscillator is proportional to average number of quanta of excitation, $U / N \hbar \omega$, which according to the equipartition theorem is equal to $k_B T / \hbar \omega$. Similarly, at high temperature the chemical potential is large and negative. However, the low temperature limit remains problematical because the entropy appears to become negative for $k_B T / \hbar \omega \le e^{-1}$. Therefore, the classical enumeration of microstates fails as the average number of quanta per degree of freedom falls below unity. Clearly, we must employ quantum mechanics in the low temperature limit where the thermal energy $k_B T$ becomes comparable to the spacing between energy levels. The limiting value $C_V = N k_B$ applies to high temperatures but the heat capacity is suppressed at low temperature where insufficient energy is available to excite the modes counted by the equipartition theorem.

Virial theorem

We now consider a generalization of the equipartition theorem for classical systems. The proof is usually presented using the microcanonical ensemble but is much easier using the canonical ensemble. Hence, we choose the latter confident that the results are independent of ensemble in the thermodynamic limit.

The virial theorem is a generalization of the familiar work-energy theorem in Newtonian mechanics that applies in Hamiltonian mechanics to generalized coordinates and forces. To motivate this generalization, consider the time dependence of $\sum \vec{r}_i \cdot \vec{p}_i$ for a collection of N nonrelativistic classical particles with coordinates $\vec{r}_i$ and momenta $\vec{p}_i$, such that

$$\frac{d}{dt} \sum_{i=1}^{N} \vec{r}_i \cdot \vec{p}_i = \sum_{i=1}^{N} \left(\vec{r}_i \cdot \frac{d\vec{p}_i}{dt} + \vec{p}_i \cdot \frac{d\vec{r}_i}{dt} \right) = \sum_{i=1}^{N} \left(\vec{r}_i \cdot \vec{F}_i + 2 K_i \right)$$

where $\vec{F}_i$ is the force acting on particle i and $K_i = \frac{p^2}{2m} = \frac{1}{2} \vec{p}_i \cdot \frac{d\vec{r}_i}{dt}$ is its kinetic energy. Since the ensemble average of $\sum \vec{r}_i \cdot \vec{p}_i$ must be constant in equilibrium, we find

$$\left\langle \frac{d}{dt} \sum_{i=1}^{N} \vec{r}_i \cdot \vec{p}_i \right\rangle = \frac{d}{dt} \left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{p}_i \right\rangle = 0 \implies \mathcal{V} = \left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \right\rangle = -2 K$$

where $K = \langle \sum_i K_i \rangle$ is the average kinetic energy and $\mathcal{V}$ is known as the *Clausius virial*. Alternatively, for any particle we can evaluate the long-term time average of $\vec{r}_i \cdot \vec{F}_i$ using

$$\overline{\vec{r}_i \cdot \vec{F}_i} = \frac{1}{\mathcal{T}} \int_o^{\mathcal{T}} dt \, \vec{r}_i(t) \cdot \vec{F}_i(t) = \frac{1}{\mathcal{T}} (\vec{r}_i \cdot \vec{p}_i)_0^{\mathcal{T}} - \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt \, m v_i^2$$

where $\mathcal{T}$ is the observation period. Making the perfectly reasonable assumption that the coordinates and momenta remain finite, the integrated term must vanish in the limit $\mathcal{T} \to \infty$, such that

$$\overline{\vec{r}_i \cdot \vec{F}_i} = -2 \overline{K_i} \implies \overline{\left\langle \sum_i \vec{r}_i \cdot \vec{F}_i \right\rangle} = -2 \overline{K}$$

Therefore, we obtain the same virial theorem $\mathcal{V} = -2 K$ from either temporal or ensemble averaging.

This theorem can be generalized to Hamiltonian mechanics by replacing the coordinate r_i with the generalized coordinate or momentum ξ_i and replacing the force by the generalized force $\partial H / \partial \xi_j$. Thus, we seek to evaluate the ensemble average

$$\left\langle \xi_i \frac{\partial H}{\partial \xi_j} \right\rangle = \frac{\int d\Gamma\, e^{-\beta H}\, \xi_i \frac{\partial H}{\partial \xi_j}}{\int d\Gamma\, e^{-\beta H}}$$

where ξ_i represents any of the generalized coordinates or momenta that appear in the Hamiltonian H. The numerator can be integrated by parts with respect to ξ_j, such that

$$\int d\Gamma\, e^{-\beta H}\, \xi_i \frac{\partial H}{\partial \xi_j} = -\frac{1}{\beta} \int d\Gamma'_j \left((\xi_i\, e^{-\beta H})_{\xi_j} - \int d\xi_j\, e^{-\beta H} \frac{\partial \xi_i}{\partial \xi_j} \right)$$

where $d\Gamma'_j$ excludes $d\xi_j$ and where the integrated portion (surface terms) must be evaluated for the extreme values of ξ_j. We assume that the surface terms vanish for extreme values of ξ_j. For example, if ξ_j is a position coordinate for a system confined to a finite volume the extreme values are on the walls where the confinement potential is infinite and the Boltzmann factor vanishes. Similarly, if ξ_j is a momentum the extreme values represent infinite kinetic energies for which the surface terms also vanish. Thus, we are left with

$$\int d\Gamma\, e^{-\beta H}\, \xi_i \frac{\partial H}{\partial \xi_j} = k_B T \int d\Gamma\, e^{-\beta H} \frac{\partial \xi_i}{\partial \xi_j} = \delta_{i,j}\, k_B T \int d\Gamma\, e^{-\beta H}$$

Therefore, we obtain the *virial theorem* in the more general form

$$\left\langle \xi_i \frac{\partial H}{\partial \xi_j} \right\rangle = \delta_{i,j}\, k_B T$$

The virial theorem includes the equipartition theorem as a special case. Suppose that the Hamiltonian can be separated in the form $H = \varepsilon_j + H'_j$ where $\varepsilon_j = b\, \xi_j^{\alpha}$ and where H'_j is independent of ξ_j. We then obtain

$$\xi_j \frac{\partial H}{\partial \xi_j} = \alpha\, \varepsilon_j \implies \overline{\varepsilon_j} = \frac{k_B T}{\alpha}$$

as before. More generally, using

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = -\langle q_i\, \dot{p}_i \rangle = k_B T$$

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = \langle p_i\, \dot{q}_i \rangle = k_B T$$

we find

$$\left\langle \sum_{i=1}^{3N} p_i\, \dot{q}_i \right\rangle = 3 N k_B T$$

$$\left\langle -\sum_{i=1}^{3N} q_i\, \dot{p}_i \right\rangle = 3 N k_B T$$

for N particles in three dimensions without having to assume that the Hamiltonian is separable.

■ Example: quadratic forms

Suppose that the Hamiltonian can be expressed in the form

$$H = \sum_j (A_j p_i^2 + B_j q_j^2)$$

by means of an appropriate canonical transformation. Clearly,

$$\sum_j \left(p_j \frac{\partial H}{\partial p_j} + q_j \frac{\partial H}{\partial q_j} \right) = 2 H$$

for this homogeneous second-order function. Thus, the virial theorem takes the form

$$\langle H \rangle = \frac{1}{2} f k_B T$$

where f is the total number of harmonic contributions to the Hamiltonian (coordinates + momenta). Note that this result is independent of the coefficients, A_j or B_j.

More generally, consider a Hamiltonian of the general quadratic form

$$H = \frac{1}{2} \sum_{i,j} \xi_i \mathcal{M}_{i,j} \xi_j$$

where each ξ_i is a generalized coordinate or momentum and $\mathcal{M}_{i,j}$ is an f-dimensional square matrix with positive eigenvalues. Using the virial theorem we again find

$$\sum_j \xi_j \frac{\partial H}{\partial \xi_j} = 2 H \implies \langle H \rangle = \frac{1}{2} f k_B T$$

where f is the number of *active* degrees of freedom. This result can be applied to the rotational Hamiltonian for a rigid rotor

$$H_{\text{rot}} = \frac{1}{2} \sum_{i,j} \omega_i I_{i,j} \omega_j \implies \langle H_{\text{rot}} \rangle = \frac{3}{2} k_B T$$

where $I_{i,j}$ is the rotational inertia tensor and ω_i are the three components of angular velocity with respect to the center of mass.

However, one must always exercise care in application of classical equipartition or virial theorems. Consider a diatomic molecule composed of two ions surrounded by an electron cloud. The moments of inertia about axes perpendicular to the separation between the ions are equal, $I_1 = I_2 = I$, but the moment of inertia about the symmetry axis $I_3 \ll I$ is much smaller because essentially all of the mass is concentrated in the ions and the nuclear radii, r_N, are smaller than interatomic separations, R, by a factor of order 10^{-5}, such that

$$\frac{I_3}{I_1} \sim \frac{m_e R^2 + m_N r_N^2}{m_N R^2} = \frac{m_e}{m_N} + \left(\frac{r_N}{R} \right)^2 \sim 10^{-3} + 10^{-10}$$

Hence, the energy scale for classical rotation about the separation axis is about a factor of 10^3 higher than the energy for the orthogonal axes. Recognizing that high energy modes are "frozen out" unless the temperature is high enough to permit full participation, we expect to obtain a rotational contribution to the heat capacity of R for modest temperatures and an increase to $\frac{3}{2} R$ for high temperatures. Furthermore, there is a more rigorous quantum mechanical argument that excludes rotations about the symmetry axis. Quantum mechanically, rotation about a symmetry axis may change the phase of a wave function but does not lead to a new state of the system — the rotated state is indistinguishable from the original. Thus, there is no dynamical variable associated with rotations about a symmetry axis and no associated contribution to the internal energy or heat capacity. Therefore, in the absence of an electronic excitation which breaks the rotational symmetry, there are only two active rotational degrees of freedom for a diatomic molecule.

■ Example: nonrelativistic ideal gas

We can evaluate Clausius' virial explicitly for an ideal gas in which the only forces which act on the particles are the confinement forces at the walls. Since those forces act only at the walls and are responsible for the pressure p upon the gas, we can write

$$\left\langle \sum_i \vec{r}_i \cdot \vec{F}_i^{\text{wall}} \right\rangle = -p \int d\vec{A} \cdot \vec{r}$$

where $d\vec{A}$ is an outward element of surface area and $\vec{r}$ is the coordinate vector for a particle at the surface of the container. The surface integral can be evaluated using Gauss' law

$$\int d\vec{A} \cdot \vec{r} = \int d^3 r \, \nabla \cdot \vec{r} = 3\, V$$

so that

$$\left\langle \sum_i \vec{r}_i \cdot \vec{F}_i^{\text{wall}} \right\rangle = -3\, p\, V = -2\, U \implies p\, V = \frac{2}{3}\, U = N\, k_B\, T$$

for an ideal nonrelativistic gas for which $U = K$.

■ Example: ultrarelativistic ideal gas

Consider a dilute gas that is so hot that the ultrarelativistic limit, $\varepsilon_i = p_i\, c$, applies. Although the Hamiltonian does not separate in a convenient manner for use of the equipartition theorem, we can apply the virial theorem to each component α of the momentum $\vec{p}_i$ for particle i

$$H = \sum_{i=1}^{N} p_i\, c = c \sum_{i=1}^{N} \left(p_{i,x}{}^2 + p_{i,y}{}^2 + p_{i,z}\right)^{1/2} \implies \frac{\partial H}{\partial p_{i,\alpha}} = \frac{c\, p_{i,\alpha}}{p_i} \implies \left\langle p_{i,\alpha} \frac{\partial H}{\partial p_{i,\alpha}} \right\rangle = k_B\, T$$

such that the summation over components gives the mean single-particle energy as

$$\langle \varepsilon_i \rangle = \left\langle \sum_\alpha p_{i,\alpha} \frac{\partial H}{\partial p_{i,\alpha}} \right\rangle = 3\, k_B\, T$$

Therefore, the internal energy of an ultrarelativistic gas becomes

$$U = 3\, N\, k_B\, T \implies C_V = 3\, N\, k_B$$

which is larger by a factor of two than the corresponding nonrelativistic result.

Maxwell velocity distribution

Consider a gas that is sufficiently dilute that intermolecular interactions may be neglected. The single-particle energy may then be expressed in the form

$$\varepsilon = \frac{p^2}{2\,m} + \varepsilon_s + V[\vec{r}]$$

where ε_s is the internal excitation for state s and $V[\vec{r}]$ is an external potential. Internal modes of excitation may include rotational or vibrational motions within a molecule or excitations of electrons. The external potential includes the confinement potential, defined to vanish within the enclosure and to become infinite at its walls, and may include the gravitational potential or interactions with an applied electromagnetic field.

The probability $P_s[\vec{r}, \vec{p}]\, d^3 r\, d^3 p$ for a molecule in internal state s to be found within a small volume $d^3 r$ at position $\vec{r}$ and with momentum in a volume $d^3 p$ centered on $\vec{p}$ is then expressed in the canonical distribution as

$$P_s[\vec{r}, \vec{p}]\, d^3 r\, d^3 p \;\propto\; \text{Exp}\left[-\frac{\beta\, p^2}{2\,m}\right] \text{Exp}[-\beta\, \varepsilon_s]\, \text{Exp}[-\beta\, V[\vec{r}]\,]\, d^3 r\, d^3 p$$

It is important to recognize that since the three contributions to the energy are separable, the probability is factorizable, such that

$$P_s[\vec{r}, \vec{p}]\, d^3 r\, d^3 p \;=\; (P_p[\vec{p}]\, d^3 p)\; (P_r[\vec{r}]\, d^3 r)\, P_s$$

where

$$P_p[\vec{p}]\, d^3 p \;\propto\; \text{Exp}\left[-\frac{\beta\, p^2}{2\,m}\right] d^3 p$$

governs the momentum distribution,

$$P_r[\vec{r}]\, d^3 r \;\propto\; \text{Exp}[-\beta\, V[\vec{r}]\,]\, d^3 r$$

governs the density, and

$$P_s \;\propto\; \text{Exp}[-\beta\, \varepsilon_s]$$

governs the spectrum of internal molecular excitations.

First, consider a free monatomic gas for which $\varepsilon_s = 0$ and for which $V[\vec{r}]$ vanishes within the enclosure but is essentially infinite at the walls so that there is no possibility for escape. The density is then independent of position and $P_r = V^{-1}$ such that the position probability integrated over volume is normalized to unity. The normalization of P_p is determined by the integral

$$\int_{-\infty}^{\infty} d p\, \text{Exp}\left[-\frac{\beta\, p^2}{2\,m}\right] \;=\; (2\,\pi\, m\, k_B\, T)^{1/2} \;=\; p_B$$

Therefore, the basic probability distribution for momentum is

$$P_p[\vec{p}]\, d^3 p \;=\; \text{Exp}\left[-\frac{\beta\, p^2}{2\,m}\right] \frac{d^3 p}{{p_B}^3}$$

It is often useful to express this distribution in several equivalent forms. If we are interested only in the magnitude of the momentum, we can use isotropy to replace the cartesian form $d^3 p$ by the spherical form

$$d^3 p \to 4\,\pi\, p^2\, d p \;\Longrightarrow\; P_p[p]\, d p \;=\; \text{Exp}\left[-\frac{\beta\, p^2}{2\,m}\right] \frac{4\,\pi\, p^2\, d p}{{p_B}^3}$$

and thus to determine the probability $P[p]\, d p$ that the magnitude of the momentum vector is found in the interval $(p,\ p + d p)$. Alternatively, we define $f[v]\, d v$ to be the mean number of molecules per unit volume whose velocities are found in the interval $(v,\ v + d v)$, such that

$$f[v]\,dv \;=\; n\,P_p[p]\,dp$$

where $n = N/V$ is the particle density and $p = m\,v$ is the nonrelativistic momentum. Therefore, the customary form for the *Maxwell velocity distribution* becomes

$$f[v]\,dv \;=\; n\,\mathrm{Exp}\left[-\frac{m\,v^2}{2\,k_B\,T}\right]\frac{4\,\pi\,v^2\,dv}{{v_B}^3}$$

where $v_B = (2\,\pi\,k_B\,T/m)^{1/2}$ is a scale parameter for the thermal distribution of velocities. Finally, if we define dimensionless variables

$$u = \frac{v}{v_B} \qquad\qquad \rho = \frac{p}{p_B}$$

the various distribution functions may be expressed in the following dimensionless forms.

$$\begin{aligned} P[\vec{\rho}]\,d^3\rho &= \mathrm{Exp}[-\pi\,\rho^2]\,d^3\rho & f[\vec{u}]\,du &= n\,\mathrm{Exp}[-\pi\,u^2]\,d^3u \\ P[\rho]\,d\rho &= \mathrm{Exp}[-\pi\,\rho^2]\,4\,\pi\,\rho^2\,d\rho & f[u]\,du &= n\,\mathrm{Exp}[-\pi\,u^2]\,4\,\pi\,u^2\,du \\ P[\rho_x]\,d\rho_x &= \mathrm{Exp}[-\pi\,{\rho_x}^2]\,d\rho_x & f[u_x]\,du_x &= n\,\mathrm{Exp}[-\pi\,{u_x}^2]\,du_x \end{aligned}$$

The Maxwell velocity distribution is sketched below. A few important characteristics of this distribution are the most probable speed $\tilde{u}$, the mean speed $\overline{u}$, and the rms speed $u_{\mathrm{rms}} = \langle u^2\rangle^{1/2}$. The most probable velocity is determined by

$$f'[\tilde{u}] == 0 \;\;\Longrightarrow\;\; \tilde{u} \;=\; \pi^{-1/2}$$

The mean and rms speeds are determined by the moments

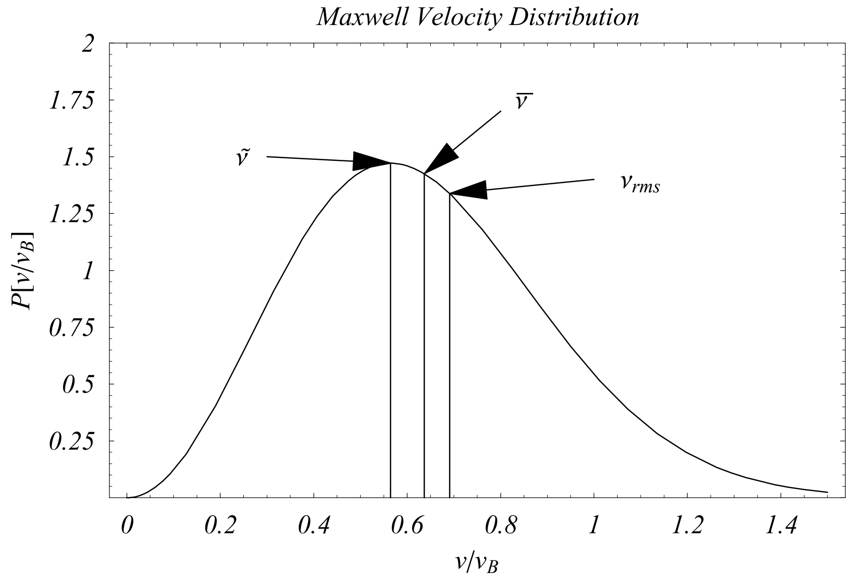
$$\overline{u} \;=\; n^{-1}\int_0^\infty u\,f[u]\,du \;=\; \frac{2}{\pi}$$

$${u_{\mathrm{rms}}}^2 \;=\; n^{-1}\int_0^\infty u^2\,f[u]\,du \;=\; \frac{3}{2\,\pi}$$

such that

$$\tilde{u} \;=\; 0.564\,, \quad \overline{u} \;=\; 0.637\;, \quad u_{\mathrm{rms}} \;=\; 0.691$$

Due to the asymmetric shape of the speed distribution and its long tail extending to relatively large speeds, the mean speed is about 13% larger than the most probable speed and the rms speed is 22% larger than $\tilde{u}$. Successive moments with higher powers of u progressively increase due to their increasing emphasis of the tail of the distribution. Finally, the width of the distribution can be gauged by its rms deviation, $\sigma_u = (\langle u^2\rangle - \langle u\rangle^2)^{1/2} = 0.48\,\tilde{u}$. Thus, the spread of speeds is clearly a large fraction of the most probable speed.



Inserting the scale parameter $v_B = \sqrt{2\pi k_B T/m}$, we find that the moments of the speed distribution

$$\tilde{v} = \sqrt{2 k_B T/m} \quad \Longrightarrow \quad \frac{1}{2} m \tilde{v}^2 = k_B T$$

$$\overline{v} = \sqrt{\frac{8}{\pi} k_B T/m} \quad \Longrightarrow \quad \frac{1}{2} m \overline{v} = \frac{4}{\pi} k_B T$$

$$v_{\text{rms}} = \sqrt{3 k_B T/m} \quad \Longrightarrow \quad \frac{1}{2} m {v_{\text{rms}}}^2 = \frac{3}{2} k_B T$$

are all of order $\sqrt{k_B T/m}$ and the corresponding momenta are of order $\sqrt{m k_B T}$. The average kinetic energy

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_B T$$

corresponds to $\frac{1}{2} k_B T$ for each of the three independent translational degrees of freedom. (Note that the average kinetic energy is obtained from v_{rms} and is larger that the most probably kinetic energy.) The internal energy of the gas is then the number of molecules times the average kinetic energy per molecule, so that

$$U = \frac{3}{2} N k_B T \quad \Longrightarrow \quad C_V = \frac{3}{2} N k_B$$

independent of species or pressure. Obviously the molar gas constant is given by $R = N_A k_B$ where Avogadro's number N_A is the number of molecules per mole and k_B is Boltzmann's constant.

Using $k_B T \approx \frac{1}{40}$ eV at room temperature, we estimate that the average kinetic energy for an ideal gas near 300 K is about 0.037 eV independent of species. For N_2, with a molecular weight $m c^2 \sim 28 \times 10^3$ MeV, the rms velocity is about $v_{\text{rms}} \sim 2 \times 10^{-6} c \sim 600\ m/s$. It is no coincidence that this speed is about twice the velocity of sound in air, since molecular speed sets the scale of velocity for mechanical disturbances.

Entropy of a classical ideal gas

Neglecting interactions among the constituents of a dilute ideal gas, the energy of any state separates into N independent kinetic contributions of the form

$$E = \sum_{i=1}^{N} \varepsilon_i \qquad \varepsilon_i = \frac{\vec{p}_i^{\,2}}{2\,m}$$

where N is the number of particles. We also neglect possible internal excitation energies within the constituents. Hence, the partition function reduces to $Z = Z_1{}^N$ where the single-particle partition function

$$Z_1 = V\left(\int_{-\infty}^{\infty} \frac{dp}{2\,\pi\,\hbar}\,\mathrm{Exp}\left[-\frac{\beta\,p^2}{2\,m}\right]\right)^3 = V\left(\frac{m\,k_B\,T}{2\,\pi\,\hbar^2}\right)^{3/2} = V\,\lambda_B{}^{-3}$$

is obtained by summing over cells of volume $(2\,\pi\,\hbar)^3$ in classical phase space. Because the three cartesian momenta, $\{p_x,\,p_y,\,p_z\}$ provide three independent contributions of the same form, Z_1 also factors such that $Z_1 = Z_{1\,x}\,Z_{1\,y}\,Z_{1\,z} = (Z_{1\,x})^3$. It is useful to define the Boltzmann wavelength

$$\lambda_B = \frac{h}{p_B} \qquad p_B = (2\,\pi\,m\,k_B\,T)^{1/2}$$

as the de Broglie wavelength for a particle that carries a typical thermal momentum (Boltzmann momentum) p_B, such that

$$\lambda_B = \left(\frac{2\,\pi\,\hbar^2}{m\,k_B\,T}\right)^{1/2} = \frac{h}{(2\,\pi\,m\,k_B\,T)^{1/2}}$$

It is also useful to define a corresponding de Broglie or thermal density as $n_B = \lambda_B{}^{-3}$. When the particle density becomes comparable to the de Broglie density, the wave packets of neighboring particles overlap significantly, on average, and quantum effects become important. Thus, it is useful to define a quantum concentration

$$n_Q = \frac{N}{V}\,\lambda_B{}^3 = \frac{n}{n_B}$$

as a guide to the relative importance of quantum effects for specified temperature and density. Clearly, for equal temperature and particle density, quantum effects are more important for lighter particles because $\lambda_B \propto m^{-1/2} \Longrightarrow n_Q \propto m^{-3/2}$.

We can now evaluate the Helmholtz free energy as

$$F = -N\,k_B\,T\,\mathrm{Log}[V\,\lambda_B{}^{-3}]$$

The mechanical equation of state is determined by evaluating the pressure, such that

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \Longrightarrow p\,V = N\,k_B\,T$$

as expected. Similarly, the internal energy and heat capacity

$$U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V = -N\left(\frac{\partial \ln Z_1}{\partial \beta}\right)_V = \frac{3}{2} N k_B T$$
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B$$

are also in agreement with results familiar from classical thermodynamics. (Note that here N is the number of particles rather than the number of moles, so that the molar gas constant is simply $R = N_A k_B$ where N_A is Avogadro's number.)

The entropy is obtained by differentiating the free energy with respect to temperature, whereby

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N k_B \left(\text{Log}[V \lambda_B{}^3] + \frac{3}{2}\right) \qquad \text{(incorrect)}$$

Although this theory has predicted both the mechanical equation of state and the heat capacity correctly, the free energy and entropy suffer from the serious flaw that neither is extensive. Suppose that the volume is divided into two equal halves by an imaginary wall. Each half contains half the particles and contributes entropy

$$V \to \frac{V}{2},\; N \to \frac{N}{2} \implies S \to \frac{S}{2} - \frac{1}{2} N k_B \ln 2$$

Therefore, this calculation suggests that the entropy of the gas is reduced by the amount $N k_B \ln 2$ upon introduction of an imaginary wall. This absurd result is known as the *Gibbs paradox*.

Examination of our expressions for entropy and free energy reveals that the Gibbs paradox could be avoided if the volume were to be replaced by V / N under the logarithm. A similar result can be obtained by subtracting $k_B \text{Log}[N!] = k_B (N \text{Log}[N] - N)$, whereby

$$S \to S - k_B \text{Log}[N!] \implies S = N k_B \left(\text{Log}\left[\frac{V}{N \lambda_B{}^3}\right] + \frac{5}{2}\right)$$

is known as the *Sackur-Tetrode formula* after the people who first used Planck's constant to discretize the phase space. This revised entropy is now extensive in the sense that S scales with N and V according to

$$V \to \alpha V,\; N \to \alpha N \implies S \to \alpha S$$

The physical origin of the Gibbs paradox concerns the indistinguishability of identical particles. Suppose that a microstate is described by the set of occupation numbers $\xi = \{n_i\}$ where i labels a cell in the phase space for a single particle and n_i is the number of particles whose momentum and position are found within that cell. The total number of permutations of N particles among the states belonging to the configuration $\{n_i\}$ suggests the multiplicity function

$$g_\xi = \frac{N!}{\prod_i n_i!}$$

where the numerator is the total number of permutations of the N particles and the denominator represents the indistinguishable permutations among the particles within each cell of phase space. If we assume that it is possible, at least in principle, to distinguish among these various states, then the configuration ξ should be assigned multiplicity g_ξ. On the other hand, if we assume that it is impossible, even in principle, to distinguish between identical particles, the configuration ξ should be assigned multiplicity 1.

The Gibbs prescription consists of reducing the number of distinct states by the overall factor $N!$. However, the actual factor g_ξ depends upon the occupation numbers. Evidently, the Gibbs prescription is applicable when the density is small and the temperature high enough for the average occupation number $\langle n_i \rangle \ll 1$ to be small, such that

$$n_i \ll 1 \implies \frac{N!}{\prod_i n_i!} \approx N!$$

Thus, the Gibbs prescription for a classical partition function for N identical noninteracting particles reads

$$n_Q \ll 1 \implies Z_N = \frac{Z_1^N}{N!}$$

With this prescription we find

$$S = N k_B \left(\mathrm{Log}\left[\frac{V}{N \lambda_B^3}\right] + \frac{5}{2}\right) = N k_B \left(\frac{5}{2} - \ln n_Q\right)$$
$$F = -N k_B T \left(\mathrm{Log}\left[\frac{V}{N \lambda_B^3}\right] + 1\right) = -N k_B T (1 - \ln n_Q)$$

provided that $n_Q \ll 1$. Thus, the Gibbs prescription is valid when the quantum concentration is small and fails when n_Q approaches unity. When $n_Q \sim 1$, we must employ a correct quantum mechanical treatment for the wave function of N identical particles with due regard to the proper particle-exchange symmetry of that wave function. Finally, we note that the chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \,\mathrm{Log}\left[\frac{V}{N \lambda_B^3}\right] = k_B T \ln n_Q$$

is large and negative for a classical ideal gas with small quantum concentration. Recall that *fugacity* z is defined by $\mu = k_B T \,\mathrm{Log}[z]$. Thus, the fugacity for a classical ideal gas

$$z = \mathrm{Exp}\left[\frac{\mu}{k_B T}\right] = n_Q$$

reduces to the quantum concentration and is small and positive at high temperatures where the classical approximation applies.

More generally, using the Gibbs prescription for the partition function for N identical indistinguishable particles, the free energy and chemical potential take the forms

$$Z_N = \frac{Z_1^N}{N!} \implies F = -N k_B T \left(\mathrm{Log}\left[\frac{Z_1}{N}\right] + 1\right), \quad \mu = -k_B T \,\mathrm{Log}\left[\frac{Z_1}{N}\right]$$

such that

$$F = -N k_B T \left(1 - \frac{\mu}{k_B T}\right)$$

If we assume that the translational degrees of freedom can be factored out, such that $Z_1 = V \lambda_B^{-3} \zeta[T]$ where $\zeta[T]$ represents the partition function for internal degrees of freedom, then

$$Z_1 = V \lambda_B^{-3} \zeta[T] \implies \mu = -k_B T \,\mathrm{Log}\left[\frac{V \zeta[T]}{N \lambda_B^3}\right]$$

Thus, the fugacity takes the form

$$z = \frac{N \lambda_B^3}{V \zeta[T]}$$

For an ideal gas one assumes that the density is small compared with $\zeta[T] / \lambda_B^3$ such that the chemical potential is large and negative and the fugacity is small. If the density is large, the fugacity appears to be large and the chemical potential to be positive, but caution must be exercised with respect to both the classical approximation of nonoverlapping wave packets and the assumption of negligible interactions. When we treat translational degrees of freedom classically and internal degrees of freedom ($\zeta[T]$) quantum mechanically, the model can be described as *semiclassical*. For example, for a gas of elementary particles with spin s, the internal partition function reduces to $\zeta \to g = 2 s + 1$, where g is the degeneracy of a single-particle momentum state, and is independent of temperature. The quantum concentration is then generalized to read

$$n_Q = \frac{N \lambda_B{}^3}{g V}$$

However, for a gas of atoms or molecules with more complicated internal structure, the internal partition function depends upon temperature. Thus, $\zeta[T]$ is a measure of the number of active internal degrees of freedom.

Ideal gas of diatomic molecules

Consider a gas of noninteracting diatomic molecules. These molecules consist of two massive ions surrounded by a cloud of much lighter electrons. Due to the difference in mass between the ions and the electrons, the motion of the electrons is much faster than that of the ions. Hence, the electron cloud can adjust rapidly to any ion motion. Therefore, we can approximate interactions with the electronic cloud by an effective potential that depends upon the separation between the ions. To a first approximation, this potential is harmonic for small-amplitude vibrations about the equilibrium separation between the ions. Alternatively, the system can rotate as a rigid object with moment of inertia $I \approx m R^2$ where m is the ion mass and R their separation.

The rotational energy ε_ℓ can be estimated by assuming that the rotational inertia is approximately

$$I \approx m R^2 \implies \varepsilon_\ell \approx \frac{\ell (\ell + 1) \hbar^2}{2 m R^2}$$

where m is the atomic mass, R is the equilibrium separation between ions, and ℓ is the rotational angular momentum. Thus, for N_2 we obtain

$$\varepsilon_1 \approx \frac{2 \, (1973 \text{ eV Å})^2}{2 \, (28 \times 10^9 \text{ eV}) \, (1 \text{ Å})^2} \approx 0.7 \times 10^{-4} \text{ eV}$$

This energy is quite small, so we might expect rotational degrees of freedom to reach the equipartition limit even for temperatures as low as a few tens of kelvins.

The characteristic energy of molecular vibrations is much larger, typically in the neighborhood of 0.5 eV. Electronic excitations are generally characterized by energies of several eV. Thus, the characteristic temperature for excitation of the electron cloud is much larger than the energy of ionic vibrations, which in turn is very much larger than the energy of rotations. Therefore, we may assume that, to a good approximation, these modes are decoupled from one another, such that

$$H = H_p + H_{\text{rot}} + H_{\text{vib}} + H_e \implies Z_1 = Z_p \, Z_{\text{rot}} \, Z_{\text{vib}} \, Z_e$$

where H_p, H_{rot}, H_{vib}, and H_e represent independent translational, rotational, vibrational, and electronic degrees of freedom. The partition function, $Z = Z_1{}^N / N!$ can then be factored. The partition function for translational motion has already been developed for the ideal gas. In the remainder of this section we present simple approximations for the rotational and vibrational factors, Z_{rot} and Z_{vib}.

■ Rotations

We assume that rotations of a diatomic molecule can be adequately described by the rigid rotor model with constant rotational inertia and that electronic motions are sufficiently fast that azimuthal symmetry is maintained. The energy levels of a rigid rotor are then

$$\varepsilon_\ell \approx \frac{\ell(\ell+1)\hbar^2}{2I}$$

where I is the rotational inertia and ℓ is a nonnegative integer describing the orbital angular momentum. The projection of angular momentum upon any axis is restricted to integer values between $-\ell$ and $+\ell$. Hence, the degeneracy of energy level ε_ℓ is $g_\ell = 2\ell + 1$. If the two ions are different (heteronuclear molecule), then ℓ can assume any nonnegative integral value, but if the two ions are identical the values of ℓ are restricted to either even or odd integers by the requirements of exchange symmetry. For simplicity we consider here the heteronuclear case and relegate the homonuclear cases to the exercises. The partition function for rotations of a heteronuclear molecule can now be written in the form

$$Z_{\text{rot}} = \sum_{\ell=0}^{\infty} (2\ell+1)\,\text{Exp}\!\left[-\ell(\ell+1)\frac{T_{\text{rot}}}{T}\right]$$

where $k_B T_{\text{rot}} = \hbar^2/2I$ determines the temperature scale relevant to rotational degrees of freedom.

In the low temperature limit the molecules are found near the ground state with overwhelming probability because the Boltzmann factor is a rapidly decreasing function of ℓ. Thus, only a few contributions to the partition function are relevant and we may approximate the rotational partition function by

$$T \ll T_{\text{rot}} \Longrightarrow Z_{\text{rot}} \approx 1 + 3\,\text{Exp}[-2T_{\text{rot}}/T]$$

The rotational contributions to the internal energy and heat capacity are then approximately

$$T \ll T_{\text{rot}} \Longrightarrow U_{\text{rot}} = -N\frac{\partial \ln Z_{\text{rot}}}{\partial \beta} \approx 3Nk_B T\,\frac{2T_{\text{rot}}}{T}\,\frac{e^{-2T_{\text{rot}}/T}}{1+3e^{-2T_{\text{rot}}/T}}$$

$$T \ll T_r \Longrightarrow C_{\text{rot}} = 3Nk_B\left(\frac{2T_{\text{rot}}}{T}\right)^2\frac{e^{-2T_{\text{rot}}/T}}{(1+3e^{-2T_{\text{rot}}/T})^2}$$

This system shares the low-temperature $y^2 e^{-y}$ behavior characteristic of any two-state system because at low temperature the spacing between quantum levels reduces the system to binary form, where here $y = 2T_{\text{rot}}/T$.

In the high temperature limit

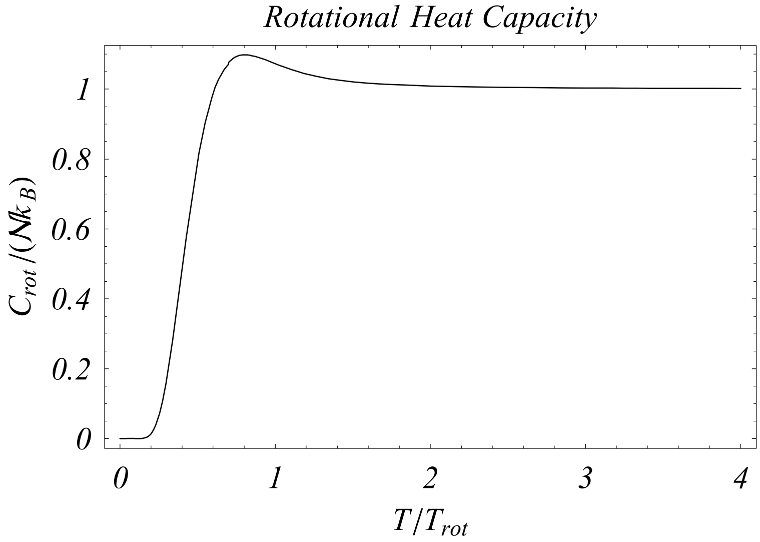
$$T \gg T_{\text{rot}} \Longrightarrow Z_{\text{rot}} \approx \int_0^\infty d\ell\,\frac{\partial \varepsilon_\ell}{\partial \ell}\,\text{Exp}[-\beta\varepsilon_\ell] = \frac{T}{T_{\text{rot}}}$$

the spacing between levels is much smaller than the energy of thermal fluctuations such that the spectrum is effectively continuous and the sum may be replaced by an integral. Thus, we find the essentially classical result

$$T \gg T_{\text{rot}} \Longrightarrow U_{\text{rot}} = Nk_B T \Longrightarrow C_{\text{rot}} = Nk_B$$

This result could have been obtained from the equipartition theorem provided that quantum symmetry principles are respected in counting the degrees of freedom. Each rotational degree of freedom make a quadratic contribution to the energy and hence yields a contribution of $k_B/2$ to the heat capacity. Classically, we might have expected there to be three rotational degrees of freedom per molecule. However, the preceding result suggests that only two degrees of freedom are active even in the high temperature limit. The difference is due to the fact that rotations about a symmetry axis do not produce observable changes of the quantum state and hence do not correspond to true dynamical degrees of freedom. Therefore, an axially symmetric rotor possesses only two rotational degrees of freedom.

The analysis of the intermediate temperature range, $T \sim T_{\rm rot}$, is more complicated because the summation cannot be performed in closed form. The figure below is taken from *rotvib.nb* where numerical summation of the rotational partition function is performed for a heteronuclear diatomic molecule. Interestingly, we find that the heat capacity overshoots the equipartition value and approaches the limit from above.



■ Vibrations

We have already analyzed the vibrational partition function several times. Expressing the vibrational energy as $\hbar\,\omega = k_B\,T_{\rm vib}$, we find

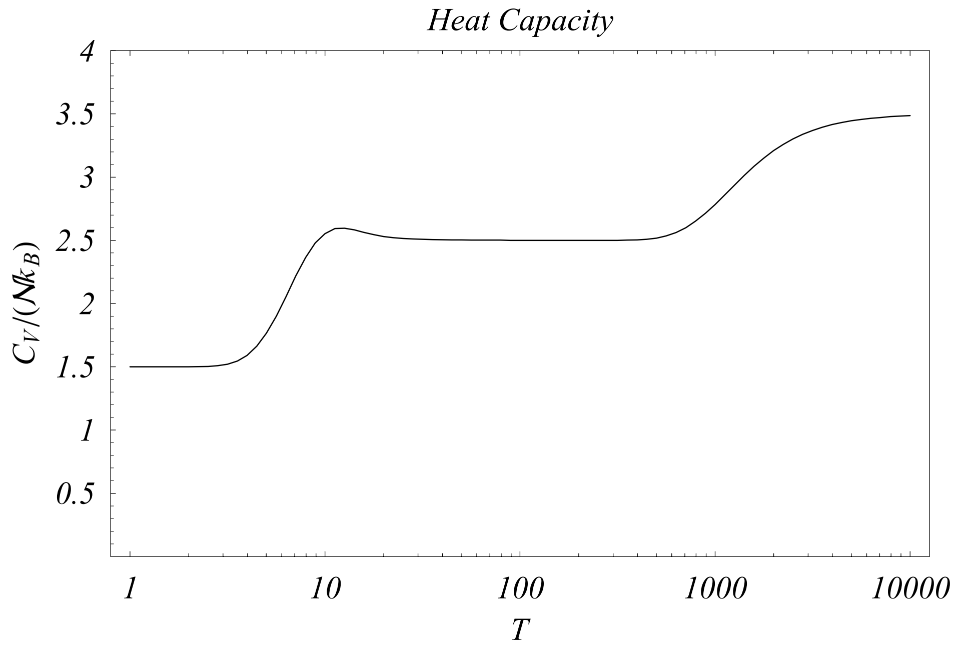
$$
\begin{aligned}
Z_{\rm vib} &= \sum_{n=0}^{\infty} e^{-n\,T_{\rm vib}/T} = \frac{1}{1-e^{-T_{\rm vib}/T}} \\
U_{\rm vib} &= \frac{N\,k_B\,T_{\rm vib}}{e^{T_{\rm vib}/T}-1} \\
C_{\rm vib} &= N\,k_B\left(\frac{T_{\rm vib}}{T}\right)^2 \frac{e^{-T_{\rm vib}/T}}{(1-e^{-T_{\rm vib}/T})^2}
\end{aligned}
$$

with limiting behaviors

$$
\begin{aligned}
T \gg T_{\rm vib} &\Longrightarrow C_{\rm vib} \approx N\,k_B \\
T \ll T_{\rm vib} &\Longrightarrow C_{\rm vib} \approx N\,k_B\left(\frac{T_{\rm vib}}{T}\right)^2 e^{-T_{\rm vib}/T}
\end{aligned}
$$

■ Heat capacity

The figure below, taken from *rotvib.nb*, shows the combined translational, rotational, and vibrational heat capacities, $C_V = \frac{3}{2}\,N\,k_B + C_{\rm rot} + C_{\rm vib}$, using $T_{\rm rot} = 15$ and $T_{\rm vib} = 4130$ kelvin for HCl. Note that a logarithmic temperature scale is need because the rotational and vibrational temperatures differ by more than two orders of magnitude. Thus, for room temperature we expect the molar heat capacity to be about $\frac{5}{2}\,R$, representing equipartition among translational and rotational modes, but vibrational excitations are frozen out. Full participation of vibrational modes requires temperatures above about 10^4 kelvin.



Problems

▼ Invariance of the phase-space volume

Prove that $\prod_i dq_i\, dp_i$ is invariant with respect to canonical transformations of the generalized coordinates and momenta.

▼ Semiclassical internal entropy

Consider a system of N identical indistinguishable noninteracting particles and assume that the single-particle partition function can be expressed in the form $Z_1 = V \lambda_B{}^{-3} \zeta[T]$ where $\lambda_B = (2\pi\hbar^2/m k_B T)^{1/2}$ is the thermal wavelength and $\zeta[T]$ is the partition function for internal excitations. Evaluate the entropy and discuss the internal contribution. Express the low temperature behavior of the internal entropy in terms of the energies and degeneracies of the lowest few levels.

▼ Langmuir adsorption theorem

Consider a plane crystal surface which contains N_s sites at which a molecule from the surrounding gas can be adsorbed. The crystal, which has negligible volume itself, is placed at the bottom of a container of volume V which contains a gas at temperature T consisting of N_g molecules of mass m. We seek to determine the equilibrium fraction, N_b / N_s, of the available sites that hold an adsorbed molecule, where N_b is the total number of molecules adsorbed onto the surface. We assume that only one molecule may occupy each site and that the energy which binds a molecule to a site is ε_b, which is independent of the concentration of filled sites.

a) Recall that the free energy for an ideal gas is given by

$$F_g = N_g k_B T \left(\text{Log}\left[\frac{N_g \lambda^3}{V} \right] - 1 \right) \quad \text{with} \quad \lambda = \left(\frac{h^2}{2 \pi m k_B T} \right)^{1/2}$$

and determine the chemical potential of the gas, μ_g, as a function of its pressure and temperature.

b) Determine the canonical partition function, $Z_b[N_b, T]$, that governs the adsorbed molecules, taking care to account to the number of ways that N_b molecules may be distributed among N_s sites.

c) Calculate the free energy, $F[N_b, T]$, for the adsorbed molecules. You may assume that both N_b and N_s are very large, but do not assume that $N_b \ll N_s$. Then compute the chemical potential, μ_b, for the bound gas.

d) State the equilibrium condition and from it derive the Langmuir adsorption theorem,

$$\frac{N_b}{N_s} = \frac{p}{p + p_0[T]}$$

and determine $p_0[T]$.

e) Alternatively, obtain the grand partition function, $\mathcal{Z}_b[T, \mu]$, for the system of adsorption sites and deduce the mean number of adsorbed molecules, $\overline{N}_b$. Show that both canonical and grand canonical methods yield the same result.

▼ Relativistic ideal gas

The classical Hamiltonian for an ideal relativistic gas takes the form

$$H = \sum_{i=1}^{N} m c^2 \left(\sqrt{1 + \left(\frac{p_i}{m c} \right)^2} - 1 \right)$$

where m is the rest mass and where the rest energy has been subtracted so that the Hamiltonian represents the total kinetic energy of N particles.

a) Show that the single-particle partition function takes the form

$$Z_1 \propto \text{Exp}[x] \, f[x]$$

where $x = m c^2 / k_B T$ is the ratio between rest and thermal energies and where

$$f[x] = \int_0^\infty dp\, p^2\, \mathrm{Exp}\left[-x\sqrt{1+p^2}\,\right]$$

Although *Mathematica* 4.0 cannot evaluate the definite integral for $f[x]$ directly, the change of variables $p \to \sqrt{y^2-1}$ provides immediate gratification.

b) Derive the mechanical equation of state.

c) Derive symbolic expressions for the internal energy and isochoric heat capacity. Use *Mathematica* to produce a log-linear plot of $C_V[x]$ and interpret the low and high temperature limits.

▼ Morse potential

The potential energy between the atoms of a hydrogen molecule can be approximated by a Morse potential of the form

$$V(r) = V_0\,(\,\mathrm{Exp}[-2\,(r-r_0)/a_0] - 2\,\mathrm{Exp}[-(r-r_0)/a_0]\,)$$

where r is the distance between nuclei, $V_0 = 4.4$ eV, $r_0 = 0.8$ Å, and $a_0 = 0.5$ Å. Sketch the potential and calculate the characteristic rotational and vibrational temperatures. Also estimate the temperature for which anharmonic effects become important.

▼ Gas with quartic interaction

An ideal nonrelativistic gas consists of N identical molecules in volume V. Each molecule has one active internal mode of excitation described by the single-particle Hamiltonian

$$H_i = \frac{\vec{P}_i^{\,2}}{2M} + \frac{p_i^{\,2}}{2\mu} + \gamma\, x_i^{\,4}$$

where M is the mass, $\vec{P}_i$ is the center-of-mass momentum, p_i is the internal momentum conjugate to the internal displacement variable x_i, and where μ and γ are positive constants. Use semiclassical statistics.

a) Compute the Helmholtz free energy and evaluate the mechanical equation of state.

b) Evaluate the internal energy and isochoric heat capacity. How does this result compare with a harmonic internal potential?

c) Calculate the entropy for this system and provide a qualitative explanation of its dependencies upon the parameters of the single-particle Hamiltonian.

Recall:

$$\Gamma[z] = \int_0^\infty dt\, e^{-t}\, t^{z-1}$$

▼ Classical rigid rotor

The Hamiltonian for a rigid rotor is

$$H_{\text{rot}} = \sum_{i=1}^{3} \frac{L_i^2}{2 I_i}$$

where $L_i = I_i \omega_i$ is the angular momentum about a principal axis with moment of inertia I_i. The orientation of the body relative to a space-fixed frame is described by three Euler angles (ϕ, θ, ψ), where $0 \le \phi \le 2\pi$ is a rotation about the $\hat{z}$ axis, $0 \le \theta \le \pi$ is a rotation about the $\hat{y}'$ axis, and $0 \le \psi \le 2\pi$ is a rotation about the $\hat{z}''$ axis. One can show that the angular velocities take the form

$$\begin{aligned}
\omega_1 &= \dot{\theta}\,\text{Sin}[\psi] - \dot{\phi}\,\text{Sin}[\theta]\,\text{Cos}[\psi] \\
\omega_2 &= \dot{\theta}\,\text{Cos}[\psi] + \dot{\phi}\,\text{Sin}[\theta]\,\text{Sin}[\psi] \\
\omega_3 &= \dot{\psi} + \dot{\phi}\,\text{Cos}[\theta]
\end{aligned}$$

a) Deduce the canonical momenta $\{p_\theta, p_\phi, p_\psi\}$ and express H_{rot} in canonical form.

b) Evaluate the rotational partition function, entropy, and internal energy for N independent rigid rotors assuming that all orientations are distinguishable.

c) Suppose that for an integer $n > 1$ rotation through an angle $2\pi/n$ about some axis produces an indistinguishable state for a body with n-fold symmetry about that axis. For example, the H_2O molecule has a 2-fold symmetry. How are the entropy and heat capacity affected by discrete symmetries?

▼ Heat capacity for polyatomic gases

Suppose that a gas consists of N identical noninteracting molecules which each contain n atoms.

a) Separate the $3n$ degrees of freedom per molecule into translational, rotational, and vibrational modes and determine their contributions to the classical heat capacity. You will need to distinguish linear molecules with axial symmetry from other structures without axial symmetry.

b) Write a general expression for the semiclassical partition function for methane, CH_4, in terms of the principal moments of inertia, I_i, and vibrational frequencies, ω_j. Be sure to consider the discrete symmetries for this tetrahedral structure.

▼ Ortho- and para-hydrogen

A proper treatment of the rotational thermodynamics of an ideal gas of homonuclear molecules must carefully consider the exchange symmetry of the nuclear part of the wave function. Suppose that the two identical nuclei are fermions, as in the H_2 molecule. Since the nuclear wave function must then be antisymmetric with respect to exchange, antisymmetric spin must be combined with symmetric spatial wave functions and symmetric spin must be combined with antisymmetric spatial wave functions. The spatial wave function is even or odd with respect to exchange according to whether the orbital angular momentum ℓ is even or odd.

a) Show that there are $s_A(2 s_A + 1)$ antisymmetric and $(s_A + 1)(2 s_A + 1)$ symmetric spin wave functions for two identical nuclei with spin s_A. Thus, demonstrate that the rotational partition function for a homonuclear diatomic molecule with fermion nuclei is

$$Z_r^{\text{FD}} = s_A (2 s_A + 1) Z_{\text{even}} + (s_A + 1)(2 s_A + 1) Z_{\text{odd}}$$

where

$$Z_{\text{even}} = \sum_{\ell \text{ even}} (2\ell + 1) \exp\left[-\ell(\ell+1) \frac{T_{\text{rot}}}{T}\right]$$

$$Z_{\text{odd}} = \sum_{\ell \text{ odd}} (2\ell + 1) \exp\left[-\ell(\ell+1) \frac{T_{\text{rot}}}{T}\right]$$

are the rotational partition functions separated into contributions for even and odd spatial wave functions. What is the corresponding expression for the rotational partition function, Z_r^{BE}, that applies when the nuclei are bosons?

b) The gas can be described as a mixture of two components in thermal equilibrium with each other described by the even and odd partition functions. It is conventional to assign the component with greater statistical weight a prefix *ortho-* and the lesser *para-*. For example, since $s_A = \frac{1}{2}$ for H_2, ortho-hydrogen is governed by Z_{odd} and para-hydrogen by Z_{even}. Because the nuclear spin is only very weakly coupled to the outside world, the equilibration time for the nuclear degrees of freedom is quite large, on the order of a year for hydrogen. Therefore, it is possible to prepare a sample with any desired mixture of ortho- and para- components and to determine the heat capacities for those components separately. Construct a plot which compares C_{even} with C_{odd}.

c) Deduce the equilibrium ratio, $R[T] = \frac{N_{\text{ortho}}}{N_{\text{para}}}$, between the ortho- and para- concentrations and evaluate the high and low temperature limits. Thus, show that at high temperature the rotational heat capacity of hydrogen should be

$$C_r^{\text{FD}} = \frac{s_A}{2 s_A + 1} C_{\text{even}} + \frac{s_A + 1}{2 s_A + 1} C_{\text{odd}}$$

in equilibrium. Therefore, if a sample is prepared in equilibrium at high temperature and cooled, approximately the same weighting is expected at lower temperature before the nuclear spin distribution has had time to relax to its equilibrium value of $R[T]$ at the lower temperature. Make a figure which compares this C_r^{FD} with the equilibrium heat capacity and discuss your results.

▼ Voltage fluctuations in LC circuit

An interesting thermometer can be made by observing the voltage fluctuations in a circuit consisting of an ideal inductor L connected in parallel to an ideal capacitor C. The circuit is in thermal contact with a heat reservoir at temperature T.

a) By considering the energy stored in this circuit, show that this system is a harmonic oscillator with appropriate analogs of mass and spring constant. What is the natural frequency?

b) Deduce the root-mean-square voltage, V_{rms}, using classical statistical mechanics.

c) Using the quantum states of a harmonic oscillator, deduce the temperature dependence of V_{rms}.

d) Evaluate the low and high T behavior of V_{rms} and compare with the classical result. Under what conditions might such a circuit serve as a thermometer?

▼ Settling rate for pollutants

We wish to study the long-term behavior of a spherical particle undergoing Brownian motion in air. A simple model for the equation of motion of such a particle is provided by the Langevin equation

$$m \frac{d\vec{v}}{dt} == -\alpha \vec{v} + \vec{F}_{\text{ext}} + \vec{\mathcal{F}}$$

where m is the mass of the particle, $\vec{v}[t]$ is its velocity at time t, α is a friction coefficient, $\vec{F}_{\text{ext}}$ is an external force, and $\vec{\mathcal{F}}[t]$ is the rapidly fluctuating force exerted by air molecules colliding with the particle. Assume that the external force is independent of time. Although the collision force varies rapidly in a random fashion, simple physical arguments suggest that it satisfies the conditions

$$\left\langle \vec{\mathcal{F}}[t] \right\rangle = 0$$
$$\langle \mathcal{F}_i[t]\, \mathcal{F}_j[t'] \rangle \approx A\, \delta_{i,j}\, \delta[t - t']$$

where the angle brackets represent ensemble averages, $\delta_{i,j}$ is the Kronecker delta symbol, and A is a temperature-dependent function of the properties of the system.

a) Show that the formal solution to the Langevin equation has the form

$$\vec{v}[t] = \text{Exp}[-t/\tau]\left(\vec{v}_0 + \int_0^t \text{Exp}[t'/\tau]\, \vec{a}[t']\, dt' \right)$$

and determine τ and $\vec{a}[t']$.

b) Obtain general expressions for the long-term ensemble averages:

$(i)\ \lim_{t\to\infty} \langle \vec{v}[t] \rangle$ and $(ii)\ \lim_{t\to\infty} \langle \vec{v}[t] \cdot \vec{v}[t] \rangle$

c) Use equipartition arguments to obtain a relationship between A, α, and temperature for the case $\vec{F}_{\text{ext}} = 0$.

d) Next consider the Brownian motion of a particle in the atmosphere subject to gravity and assume that A is not affected by this additional force. Determine the long-term values of

$(i)\ \langle \vec{v} \rangle$ and $(ii)\ \left\langle (\vec{v} - \langle \vec{v} \rangle)^2 \right\rangle$

e) If the particle in question were a pollutant, under what conditions would we expect pollution to remain suspended in air for a long time rather than settling on the ground?

▼ Laser cooling

An ensemble of neutral atoms can be cooled and trapped using lasers tuned slightly below the resonant frequency for an atomic transition between the ground state and an excited state. In this problem we explore a few of the basic properties of this process.

a) Consider an atom at rest illuminated by a laser tuned to the resonant frequency $\omega = \omega_0$. Write an expression for the average force F upon the atom in terms of the transition rate $B\,u$ for absorbing a photon, where B is the Einstein coefficient for absorption and the spectral density $u[\omega]$ is the energy density per unit frequency interval. Neglect Doppler shifts at this stage.

b) Now suppose that an atom with velocity $\vec{v}$ is illuminated by two beams in opposite directions that are also parallel to $\vec{v}$. Demonstrate that if the laser frequency ω is slightly smaller than ω_0, the net force exerted by the pair of beams is dissipative, such that

$$\vec{F} = -\alpha\,\vec{v}$$

Find an expression for the friction coefficient α assuming that

$$\frac{du}{d\omega} \approx \frac{u[\omega_0]}{\gamma} = -\frac{u_0}{\gamma}$$

where u_0 is the peak spectral density and γ is the laser linewidth.

c) Recall that the Einstein A and B coefficients for spontaneous and stimulated emission are related by

$$B = \frac{c^3}{4\,\hbar\,{\omega_0}^3}\,A$$

and that $A = \tau^{-1}$ where τ is the natural lifetime for the excited state. Also, recognizing that the laser intensity is $I = c\,u_0\,\gamma$, express α in terms of I, ω, γ, and τ. Given that $\omega_0 = 3.19\times 10^{15}$ radian/s and $\tau = 16.1$ ns for sodium atoms, evaluate α for a laser intensity of $100\,\mathrm{mW}/\mathrm{cm}^2$ and a linewidth of 10 MHz.

d) Show that isotropic illumination leads to cooling and develop an expression for the cooling rate dT/dt assuming that the velocity distribution remains approximately Maxwellian. Evaluate the cooling rate for sodium atoms with mass $m = 3.8\times 10^{-23}\,g$.