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09. Microcanonical Ensemble

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Abstract

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8. Kinetic Theory II

Classical Hamiltonian system [tln45]

Consider an autonomous classical dynamical system with $3N$ degrees of freedom (e.g. N particles in a 3D box with reflecting walls). The dynamics is fully described by $6N$ independent variables, e.g. by a set of *canonical coordinates* $q_1, \ldots, q_{3N}; p_1, \ldots, p_{3N}$.

The time evolution of these coordinates is specified by a *Hamiltonian function* $H(q_1, \ldots, q_{3N}; p_1, \ldots, p_{3N})$ and determined by the *canonical equations*:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}; \quad i = 1, \ldots, 3N$$

The time evolution of an arbitrary dynamical variable $f(q_1, \ldots, q_{3N}; p_1, \ldots, p_{3N})$ is determined by *Hamilton's equation of motion*:

$$\frac{df}{dt} = \sum_{i=1}^{3N} \left(\frac{\partial f}{\partial q_i}\dot{q}_i + \frac{\partial f}{\partial p_i}\dot{p}_i \right) = \sum_{i=1}^{3N} \left(\frac{\partial f}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial H}{\partial q_i} \right) \equiv \{f, H\}.$$

Conserved quantity: $\displaystyle\frac{df}{dt} = 0 \;\Leftrightarrow\; \{f, H\} = 0.$
Energy conservation is guaranteed: $\displaystyle\frac{dH}{dt} = 0$ because $\{H, H\} = 0$.

The microstate of the system is specified by one point in the $6N$-dimensional *phase space* (Γ-space): $\mathbf{X} \equiv (q_1, \ldots, q_{3N}; p_1, \ldots, p_{3N})$. As time evolves, this point traces a trajectory through Γ-space.

The conservation law $H(q_1, \ldots, q_{3N}; p_1, \ldots, p_{3N}) = \text{const}$ confines the motion of any phase point to a $6N - 1$-dimensional hypersurface in Γ-space. Other conservation laws, provided they exist, will further reduce the dimensionality of the manifold to which phase-space trajectories are confined.

Note: Within the framework of kinetic theory, the microstate of the same system was described by N points in the 6D space spanned the position and velocity coordinates of a single particle, $(x, y, z; v_x, v_y, v_z)$.

Our knowledge of the instantaneous microstate of the system is expressed by a probability density $\rho(\mathbf{X}, t)$ in Γ-space.

Normalization: $\displaystyle\int_\Gamma d^{6N}X\, \rho(\mathbf{X}, t) = 1.$

Instantaneous expectation value: $\displaystyle\langle f \rangle = \int_\Gamma d^{6N}X\, f(\mathbf{X})\rho(\mathbf{X}, t).$

Maximum knowledge about microstate realized for $\rho(\mathbf{X}, 0) = \delta(\mathbf{X} - \mathbf{X_0})$.

Classical Liouville operator [tln46]

To describe the time evolution of $\rho(\mathbf{X},t)$ we consider a volume V_0 with surface S_0 in Γ-space. The following equations relate the change of probability inside V_0 to the flow of probability through S_0 and use Gauss' theorem.

$$\frac{\partial}{\partial t}\int_{V_0} d^{6N}X\,\rho(\mathbf{X},t) = -\oint_{S_0} d\mathbf{s}\cdot\dot{\mathbf{X}}\rho(\mathbf{X},t) = -\int_{V_0} d^{6N}X\,\nabla_{\mathbf{X}}\cdot[\dot{\mathbf{X}}\rho(\mathbf{X},t)].$$

Balance equation: $\displaystyle\frac{\partial}{\partial t}\rho(\mathbf{X},t) + \nabla_{\mathbf{X}}\cdot[\dot{\mathbf{X}}\rho(\mathbf{X},t)] = 0.$

Use $\nabla_{\mathbf{X}}\cdot[\dot{\mathbf{X}}\rho] = \rho\nabla_{\mathbf{X}}\cdot\dot{\mathbf{X}} + \dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}\rho$ and $\nabla_{\mathbf{X}}\cdot\dot{\mathbf{X}} = 0.$

$$\Rightarrow\ \frac{\partial}{\partial t}\rho(\mathbf{X},t) + \dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}\rho(\mathbf{X},t) = 0.$$

Introduce convective derivative: $\displaystyle\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}.$

Liouville theorem: $\displaystyle\frac{d}{dt}\rho(\mathbf{X},t) = 0.$

Use $\displaystyle\dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}\rho = \sum_{i=1}^{3N}\left(\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i}\right) = \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right) = \{\rho, H\}.$

Liouville operator: $\displaystyle L \equiv i\{H,\ \} = i\sum_{i=1}^{3N}\left(\frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i} - \frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i}\right).$

Liouville equation: $\displaystyle i\frac{\partial\rho}{\partial t} = i\{H,\rho\} = L\rho.$

Formal solution: $\rho(\mathbf{X},t) = e^{-iLt}\rho(\mathbf{X},0).$

L is a Hermitian operator. Hence all its eigenvalues are real. Hence $\rho(\mathbf{X},t)$ cannot relax to equilibrium in any obvious way. The Liouville equation reflects the time reversal symmetry of the underlying microscopic dynamics. Obtaining the broken time reversal symmetry of irreversible processes from the Liouville equation is a central problem in statistical mechanics (topic of ergodic theory).

Nevertheless: the thermal equilibrium is described by a stationary (time-independent) probability density:

$$\frac{\partial\rho}{\partial t} = 0\ \Rightarrow\ L\rho = 0\ \Rightarrow\ \{H,\rho\} = 0.$$

A stationary ρ is an eigenfunction of L with eigenvalue zero. If $\rho = \rho(H)$ then $\{H,\rho\} = 0$. Hence ρ is time-independent.

Quantum Liouville operator [tln47]

The density operator $\rho(t)$ is a positive definite Hermitian operator. Like its classical counterpart, the phase-space density $\rho(\mathbf{X}, t)$, it describes what we know about the state of the system.

Normalization: $\mathrm{Tr}[\rho(t)] = 1$. Expectation value: $\langle A(t) \rangle = \mathrm{Tr}[A\rho(t)]$.

Diagonal representation: $\rho(t) = \sum_i p_i |\pi_i(t)\rangle\langle\pi_i(t)|$.

p_i: probability of finding the system in the state $|\pi_i(t)\rangle$.

$$\Rightarrow\ \langle A(t) \rangle = \sum_i p_i \langle \pi_i(t)|A|\pi_i(t)\rangle = \sum_{nn'} \langle n|A|n'\rangle\langle n'|\rho(t)|n\rangle.$$

$\{|n\rangle\}$: orthonormal basis. $\langle n'|\rho(t)|n\rangle$: elements of the density matrix.

Schrödinger equation: $H|\pi_i(t)\rangle = i\hbar \dfrac{\partial}{\partial t}|\pi_i(t)\rangle$.

$$\Rightarrow\ i\hbar\frac{\partial \rho}{\partial t} = \sum_i p_i \left[H|\pi_i(t)\rangle\langle\pi_i(t)| - |\pi_i(t)\rangle\langle\pi_i(t)|H\right] = H\rho - \rho H = [H, \rho].$$

Liouville operator: $L \equiv \dfrac{1}{\hbar}[H,\ ]$.

Liouville equation: $i\dfrac{\partial \rho}{\partial t} = \dfrac{1}{\hbar}[H, \rho] = L\rho$.

Formal solution: $\rho(t) = e^{-iLt}\rho(0) = e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}$.

Time evolution carried by density operator or by dynamical variable:

$$\langle A(t) \rangle = \mathrm{Tr}[Ae^{-iHt/\hbar}\rho e^{iHt/\hbar}] = \mathrm{Tr}[e^{iHt/\hbar}Ae^{-iHt/\hbar}\rho].$$

von Neumann equation: $i\hbar\dfrac{\partial \rho}{\partial t} = [H, \rho] \ \Rightarrow\ \rho(t) = e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}$.

Heisenberg equation: $i\hbar\dfrac{\partial A}{\partial t} = -[H, A] \ \Rightarrow\ A(t) = e^{iHt/\hbar}A(0)e^{-iHt/\hbar}$.

Density matrix in energy representation $H|\lambda\rangle = E_\lambda|\lambda\rangle$:

$$\rho_{\lambda\lambda'}(t) = \sum_{\lambda\lambda'} \langle\lambda|\rho|\lambda'\rangle e^{-i(E_\lambda - E_{\lambda'})t/\hbar}.$$

Stationarity of density operator: $i\hbar\dfrac{\partial \rho}{\partial t} = 0 \ \Rightarrow\ [H, \rho] = 0$.

$\Rightarrow$ ρ is diagonal in the energy representation: $\rho = \sum_\lambda p_\lambda |\lambda\rangle\langle\lambda|$.

Gibbs entropy [tln48]

At thermal equilibrium: $\partial\rho/\partial t = 0$. This condition is satisfied by $\rho = \rho(H)$.

Q: What is the functional dependence of ρ on H?
A: $\rho(H)$ must maximize the entropy $S(\rho)$ subject to the constraints related to whether the system is isolated, closed, or open.

Q: What is the functional dependence of S on ρ?
A: The Gibbs entropy can be motivated by Boltzmann's H-function and by Shannon's concept of uncertainty:

- classical system: $S = -k_B \int d^{6N}X\, \rho(\mathbf{X}) \ln[C_N \rho(\mathbf{X})]$,
- quantum system: $S = -k_B\, \mathrm{Tr}[\rho \ln \rho]$.

The additive constant C_N in the classical expression allocates a certain phase-space volume element to every microstate:

- distinguishable particles: $C_N = h^{3N}, \quad h \simeq 6.62 \times 10^{-34}\mathrm{Js}$,
- indistinguishable particles: $C_N = h^{3N} N!$.

The factor $N!$ is needed to compensate for overcounting indistinguishable permutations of identical particles. No correction is necessary in quantum mechanics, where microstates have definite permutation symmetries.

Q: Why does one microstate require a nonzero phase-space volume element?
A: The Heisenberg uncertainty principle, $\Delta q_i \Delta p_i \geq \frac{1}{2}\hbar$, must be satisfied to accommodate quantum mechanical microstates.

Q: What is the precise size of that volume needed for one microstate?
A: The volume element is h^{3N} for a system with $3N$ degrees of freedom.

Number of microstates in volume element $d^{6N}X$: $\displaystyle \frac{1}{h^{3N}} d^{6N}X = \prod_{i=1}^{3N} \left[\frac{1}{h} dq_i dp_i\right]$.

Illustration: harmonic oscillator (2D phase space).

Hamiltonian: $\displaystyle H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2 = \frac{h\omega}{2\pi}\left(n + \frac{1}{2}\right)$.

Classical trajectories are concentric ellipses with axes $2q_{max}, 2p_{max}$.

Energy quantization implies quantized amplitudes:

$$q_{max} = \sqrt{\frac{h}{\pi m\omega}\left(n + \frac{1}{2}\right)}, \quad p_{max} = \sqrt{\frac{hm\omega}{\pi}\left(n + \frac{1}{2}\right)}.$$

Area of ellipse: $A(n) = \pi q_{max} p_{max} = h(n + 1/2) \quad \Rightarrow A(n+1) - A(n) = h$.

Microcanonical ensemble [tln49]

Consider an isolated classical system (volume V, N particles, internal energy U). The goal is to determine the thermodynamic potential $U(S,V,N)$ pertaining to that situation, from which all other thermodynamic properties can be derived.

Maximize Gibbs entropy $S = -k_B \int_{U\leq H(\mathbf{X})\leq U+\Delta} d^{6N}X\,\rho(\mathbf{X})\ln[C_N\rho(\mathbf{X})]$

subject to the contraint $\int_{U\leq H(\mathbf{X})\leq U+\Delta} d^{6N}X\,\rho(\mathbf{X}) = 1$ (normalization).

Apply calculus of variation with one Lagrange multiplier:

$$\delta\int d^{6N}X\{-k_B\rho\ln[C_N\rho]+\alpha_0\rho\} = 0$$

$$\Rightarrow\quad \int d^{6N}X\,\delta\rho\{-k_B\ln[C_N\rho]-k_B+\alpha_0\} = 0.$$

$$\Rightarrow\quad \rho(\mathbf{X}) = \frac{1}{C_N}\exp\left(\frac{\alpha_0}{k_B}-1\right) = \text{const} = \begin{cases} \Omega_\Delta^{-1} & U\leq H(\mathbf{X})\leq U+\Delta \\ 0 & \text{otherwise,}\end{cases}$$

where $\Omega_\Delta(U,V,N) = \int_{U\leq H(\mathbf{X})\leq U+\Delta} d^{6N}X$ is the volume of the energy shell.

Thermodyn. potentials: $S(U,V,N) = k_B\ln\left[\frac{\Omega_\Delta(U,V,N)}{C_N}\right] \;\Rightarrow\; U(S,V,N)$.

The dependence of S or U on the energy width Δ is undesirable and can, in fact, be avoided. If we replace the shell volume $\Omega_\Delta(U,V,N)$ by the entire volume inside the shell, $\Omega(U,V,N)$, the resulting expression for $S(U,V,N)$ differs only by a term $\propto \ln N$, which is negligible in macroscopic systems.

$$\Rightarrow\quad S(U,V,N) = k_B\ln\left[\frac{\Omega(U,V,N)}{C_N}\right],\ \text{where}\ \Omega(U,V,N) = \int_{H(\mathbf{X})\leq U} d^{6N}X.$$

Consider an isolated quantum system: $H|n\rangle = E_n|n\rangle$.

Maximize $S = -k_B\sum_{E_n<U} p_n\ln p_n$ subject to the constraint $\sum_{E_n<U} p_n = 1$.

$$\Rightarrow\quad p_n = \frac{1}{N_<(U)}\ \text{where}\ N_<(U) = \sum_{E_n<U}.\qquad \Rightarrow\quad S = k_B\ln[N_<(U)].$$

[tex73] Classical ideal gas (microcanonical ensemble)

Consider a classical ideal gas of N atoms confined to an insulating box of volume V. The Hamiltonian of the system reflects the kinetic energy of $3N$ noninteracting degrees of freedom:

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}.$$

(a) Calculate the entropy $S(U, V, N)$ in the *microcanonical* ensemble. Show that the result is the Sackur-Tetrode equation:

$$S(U, V, N) = \frac{5}{2} N k_B + N k_B \ln \left[\frac{V}{N h^3} \left(\frac{4\pi m U}{3N} \right)^{3/2} \right].$$

(b) Derive the internal energy $U = \frac{3}{2} N k_B T$ and the equation of state $pV = N k_B T$ from $S(U, V, N)$.

Solution:

[tex74] Array of classical harmonic oscillators (microcanonical ensemble)

Consider an array of N 3-dimensional classical harmonic oscillators, representing a system of $3N$ uncoupled degrees of freedom:

$$H = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2} m\omega^2 q_i^2 \right).$$

(a) Calculate the entropy $S(U, V, N)$ of this system in the *microcanonical* ensemble.
(b) Derive the internal energy $U(T, V, N)$, and the heat capacity $C = (\partial U/\partial T)_{VN}$.

Solution:

[tex75] Quantum harmonic oscillators (microcanonical ensemble I)

Consider an array of N quantum harmonic oscillators:

$$H = \sum_{i=1}^{N} \left[\hbar\omega \left(n_i + \frac{1}{2} \right) \right], \quad n_i = 0, 1, 2, \ldots.$$

(a) Calculate the entropy $S(U,N)$ of this system in the *microcanonical* ensemble via combinatorics as follows: Set $U = U_0 + M\hbar\omega$, $U_0 = \frac{1}{2}N\hbar\omega$, $M = n_1 + \cdots + n_N$. Next determine the number $N_\Delta(M,N)$ of configurations $(n_1, \cdots, n_N)$ for fixed values of M, N. Then relate S to N_Δ.
(b) Derive the internal energy $U(T,N)$, and the heat capacity $C = (\partial U/\partial T)_N$ from $S(U,N)$.

Solution:

[tex126] Quantum harmonic oscillators (microcanonical ensemble II)

Consider an array of N quantum harmonic oscillators:

$$H = \sum_{j=1}^{N} \left[\hbar\omega \left(n_j + \frac{1}{2} \right) \right], \quad n_j = 0, 1, 2, \ldots.$$

(a) Calculate the entropy $S(U, N)$ of this system in the *microcanonical* ensemble via saddle point method as follows. Express the number of distinct microstate at energy U in the form $N_\Delta = \sum_{n_1} \cdots \sum_{n_N} \delta(U - H)$ with the δ-function replaced by its Fourier integral. Then use the asymptotic Laplace expression for the integral and evaluate it retaining only contributions that are significant in the thermodynamic limit.
(b) Derive the internal energy $U(T, N)$, and the heat capacity $C = (\partial U / \partial T)_N$ from $S(U, N)$.

Solution:

[tex127] Quantum paramagnet (microcanoncal ensemble)

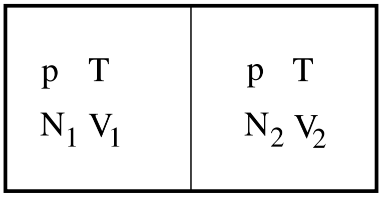
Consider an array of N noninteracting localized magnetic dipole moments $\mathbf{m}_i$ produced by localized electron spins in a paramagnetic insulator. In the presence of a magnetic field $\mathbf{H}$ pointing in z-direction, the Hamiltonian of this system represents the Zeeman energy:

$$\mathcal{H} = -\sum_{i=1}^{N} \mathbf{m}_i \cdot \mathbf{H} = -H \sum_{i=1}^{N} m_i^z = -h \sum_{i=1}^{N} \sigma_i.$$

where $h = H/2$ and $\sigma_i = 2m_i^z = \pm 1$.
(a) Calculate the entropy $S(E, h, N)$ of this system in the *microcanonical* ensemble via saddle point method as follows. Express the number of distinct microstate at enthalpy E in the form $N_\Delta = \sum_{\sigma_1} \cdots \sum_{\sigma_N} \delta(E - \mathcal{H})$ with the δ-function replaced by its Fourier integral. Then use the asymptotic Laplace expression for the integral and evaluate it retaining only contributions that are significant in the thermodynamic limit.
(b) Calculate from $S(E, h, N)$ an explicit expression for the enthalpy $E(T, h, N)$ and derive from it the magnetization $M(T, h, N)$.

Solution:

Entropy of mixing revisited [tln50]



Consider two dilute gases in a rigid and insulating box separated by a mobile conducting wall as in [tln25]: N_1 atoms on the left and N_2 atoms on the right.
At thermal equilibrium: $N_1/V_1 = N_2/V_2$.

The removal of the internal wall initiates the mixing of particles 1 and 2.

Is the process reversible or irreversible? The answer depends on whether particles 1 and 2 are of the same kind (indistinguishable) or of a different kind (distinguishable).

Mixing occurs without changes in any of the following quantities:

- total internal energy: $U = U_1 + U_2$,
- total volume: $V = V_1 + V_2$,
- total number of particles: $N = N_1 + N_2$.

Consider the Sackur-Tetrode formula for the entropy of an ideal gas [tex73]:

$$S(U,V,N) = \frac{5}{2}Nk_B + Nk_B \ln\left[\frac{V}{Nh^3}\left(\frac{4\pi mU}{3N}\right)^{3/2}\right].$$

Distinguishable particles: irreversible process

Initial entropy: $S_{init} = S(U_1,V_1,N_1) + S(U_2,V_2,N_2)$

Final entropy: $S_{fin} = S(U_1,V_1+V_2,N_1) + S(U_2,V_1+V_2,N_2)$

Entropy change: $\Delta S = N_1 k_B \ln\dfrac{V_1+V_2}{V_1} + N_2 k_B \ln\dfrac{V_1+V_2}{V_2} > 0.$

Indistinguishable particles: reversible process

Initial entropy: $S_{init} = S(U_1,V_1,N_1) + S(U_2,V_2,N_2)$

Final entropy: $S_{fin} = S(U_1+U_2,V_1+V_2,N_1+N_2)$

Entropy change: $\Delta S = 0.$