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10. Canonical Ensemble I

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Abstract

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Canonical Ensemble [tln51]

Consider a closed classical system (volume V , N particles, temperature T). The goal is to determine the thermodynamic potential $A(T, V, N)$ pertaining to that situation, from which all other thermodynamic properties can be derived.

Maximize Gibbs entropy $S = -k_B \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) \ln[C_N \rho(\mathbf{X})]$

subject to the constraints related to normalization and average energy:

$$\int_{\Gamma} d^{6N} X \rho(\mathbf{X}) = 1, \quad \int_{\Gamma} d^{6N} X H(\mathbf{X}) \rho(\mathbf{X}) = U.$$

Apply calculus of variation with two Lagrange multipliers:

$$\begin{aligned} \delta \int_{\Gamma} d^{6N} X \{ -k_B \rho \ln[C_N \rho] + \alpha_0 \rho + \alpha_U H \rho \} &= 0 \\ \Rightarrow \int_{\Gamma} d^{6N} X \delta \rho \{ -k_B \ln[C_N \rho] - k_B + \alpha_0 + \alpha_U H \} &= 0. \\ \Rightarrow \{ \dots \} = 0 \Rightarrow \rho(\mathbf{X}) &= \frac{1}{C_N} \exp \left(\frac{\alpha_0}{k_B} - 1 + \frac{\alpha_U}{k_B} H(\mathbf{X}) \right). \end{aligned}$$

Determine the Lagrange multipliers α_0 and α_U :

$$\int_{\Gamma} d^{6N} X \rho(\mathbf{X}) = 1 \Rightarrow \exp \left(1 - \frac{\alpha_0}{k_B} \right) = \frac{1}{C_N} \int_{\Gamma} d^{6N} X \exp \left(\frac{\alpha_U}{k_B} H(\mathbf{X}) \right) \equiv Z_N.$$

$$\int_{\Gamma} d^{6N} X \rho(\mathbf{X}) \{ \dots \} = 0 \Rightarrow S - k_B + \alpha_0 + \alpha_U U = 0.$$

$$\Rightarrow U + \frac{1}{\alpha_U} S = \frac{k_B}{\alpha_U} \ln Z_N. \text{ Compare with } U - TS = A \Rightarrow \alpha_U = -\frac{1}{T}.$$

Helmholtz free energy: $A(T, V, N) = -k_B T \ln Z_N$.

Canonical partition function: $Z_N = \frac{1}{C_N} \int_{\Gamma} d^{6N} X \exp(-\beta H(\mathbf{X}))$, $\beta = \frac{1}{k_B T}$.

Probability density: $\rho(\mathbf{X}) = \frac{1}{Z_N C_N} \exp(-\beta H(\mathbf{X}))$.

Canonical ensemble in quantum mechanics:

$$Z_N = \text{Tr} e^{-\beta H} = \sum_{\lambda} e^{-\beta E_{\lambda}}, \quad \rho = \frac{1}{Z_N} e^{-\beta H}, \quad A = -k_B T \ln Z_N.$$

[tex76] Classical ideal gas (canonical ensemble)

Consider a classical ideal gas of N atoms confined to a box of volume V in thermal equilibrium with a heat reservoir at temperature T . 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) Show that the canonical partition function is $Z_N = V^N / (N! \lambda_T^{3N})$, where $\lambda_T = \sqrt{h^2 / 2\pi m k_B T}$ is the thermal wavelength.
- (b) Derive from Z_N the Helmholtz free energy $A(T, V, N)$, the entropy $S(T, V, N)$, the pressure $p(T, V, N)$, the internal energy $U(T, N)$, and the chemical potential $\mu(T, V)$.
- (c) Show that the pressure is equal to two thirds of the energy density and that the adiabates satisfy $p^3 V^5 = \text{const}$.

Solution:

[tex77] Ultrarelativistic classical ideal gas (canonical ensemble)

Consider a classical ideal gas of N atoms confined to a box of volume V in thermal equilibrium with a heat reservoir at an extremely high temperature T . The Hamiltonian of the system,

$$H = \sum_{l=1}^N |\mathbf{p}_l|c,$$

where c is the speed of light, reflects the ultrarelativistic energy of N noninteracting particles:

- (a) Calculate the canonical partition function Z_N of this system.
- (b) Derive from Z_N the Helmholtz free energy $A(T, V, N)$, the entropy $S(T, V, N)$, the pressure $p(T, V, N)$, the internal energy $U(T, N)$, and the chemical potential $\mu(T, V)$.
- (c) Show that the pressure is equal to one third of the energy density and that the adiabates satisfy $p^3 V^4 = \text{const.}$

Solution:

[tex154] Ultrarelativistic classical ideal gas in two dimensions

Consider a classical ideal gas of N particles confined to a two-dimensional box of area V in thermal equilibrium at extremely high temperature T . Most particles are moving at speeds close to the speed of light c . We describe this system by a Hamiltonian of the form,

$$H = \sum_{l=1}^N \sqrt{p_x^2 + p_y^2} c.$$

(a) Show that the canonical partition function is

$$Z_N = \frac{1}{N!} \left[2\pi V \left(\frac{k_B T}{hc} \right)^2 \right]^N.$$

(b) Find the Helmholtz free energy $A(T, V, N)$, the entropy $S(T, V, N)$, the pressure $p(T, V, N)$, and the internal energy $U(T, N)$.

(c) Find the adiabat (for constant N) and express it in the form $p^\nu V = \text{const}$.

(d) Infer from the given canonical partition function $Z_N(T, V)$ an explicit expression for the grand partition function $Z(T, V, \mu)$, where $\mu = k_B T \ln z$ is the chemical potential and z is the fugacity.

Use $\int_0^\infty dx x^n e^{-ax} = n! a^{-n-1}$, $\ln n! \simeq n \ln n - n$, $\sum_{n=0}^\infty x^n / n! = e^x$.

Solution:

[tex78] Array of classical harmonic oscillators (canonical 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 canonical partition function Z_N for this model.
- (b) Derive from Z_N the Helmholtz free energy $A(T, N)$, the entropy $S(T, N)$, the internal energy $U(T, N)$, and the heat capacity $C \equiv (\partial U / \partial T)_N$.

Solution:

[tex136] Irreversible decompression

Consider an insulating box with two compartments. Each compartment initially contains N atoms of a monatomic classical ideal gas in equilibrium at initial pressures $p_1 \neq p_2$ and at the same initial temperature T . Gas atoms are then allowed to leak through a hole in the dividing wall.

- (a) Show that the temperature remains the same in the final equilibrium state.
- (b) Find the uniform pressure p in the final equilibrium state as a function of p_1 and p_2 .
- (c) Find the increase in total entropy, ΔS , between the initial and final equilibrium states.

Solution:

[tex137] Irreversible heat exchange

Consider an insulating box with two compartments. Each compartment initially contains N atoms of a monatomic classical ideal gas in equilibrium at initial temperatures $T_1 \neq T_2$ and at the same initial pressure p . Gas atoms are then allowed to leak through a hole in the dividing wall.

- (a) Find the uniform temperature T in the final equilibrium state as a function of T_1 and T_2 .
- (b) Show that the pressure remains the same in the final equilibrium state.
- (c) Find the increase in total entropy, ΔS , between the initial and final equilibrium states.

Solution:

[tex139] Reversible decompression

Consider a rigid, insulating box with two compartments of volumes V_1 and V_2 separated by an internal wall. Each compartment contains N atoms of a monatomic classical ideal gas [$pV = Nk_B T, C_V = \frac{3}{2}Nk_B$] in equilibrium at the same temperature T_{ini} .

(a) Find the maximum work, $\Delta W(T_{ini}, V_1, V_2, N)$, that can be extracted from this system by any means that keep the box rigid and insulating.

(b) Design a reversible process that employs the internal wall, which is movable by an external agent in a controlled manner and which can be switched between heat-conducting and insulating modes.

Solution:

[tex140] Reversible heat exchange

Consider a rigid, insulating box with two compartments of volumes V_1 and V_2 separated by an internal wall. Each compartment contains N atoms of a monatomic classical ideal gas [$pV = Nk_B T, C_V = \frac{3}{2}Nk_B$] in equilibrium at the same pressure.

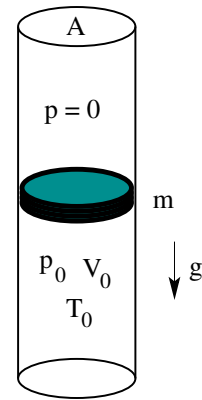
- (a) Find the maximum work, $\Delta W(T_1, T_2, N)$, that can be extracted from this system by any means that keep the box rigid and insulating.
- (b) Design a reversible process that employs the internal wall, which is movable by an external agent in a controlled manner and which can be switched between heat-conducting and insulating modes.

Solution:

[tex141] Heavy piston

A cylinder of cross section A with insulating walls has two compartments separated by a disk of mass m . The axis of the cylinder is vertical. A uniform gravitational field g is present. The disk is initially held at a fixed position by an external agent. The upper compartment is evacuated and the lower compartment contains 1 mol of a monatomic, classical, ideal gas [$pV = RT$, $C_V = \frac{3}{2}R$] at temperature T_0 , volume V_0 , and pressure p_0 . When the disk is released, it moves without (wall) friction and comes to rest at a lower position. Calculate the final values p_1, V_1, T_1 of pressure, volume, and temperature, respectively. The disk does not exchange heat. The only significant action of the gravitational field is on the disk.

Hint: Use energy conservation and Newton's third law. Assume thermal equilibrium for the initial and final states.



Solution:

Ensemble averages [tin52]

All thermodynamic quantities of a closed system can be inferred from the canonical partition function Z_N via the associated thermodynamic potential:

$$Z_N = \frac{1}{C_N} \int_{\Gamma} d^{6N} X \exp(-\beta H(\mathbf{X})), \quad \beta = \frac{1}{k_B T}.$$

Further properties of the system can be obtained from the canonical probability density $\rho(\mathbf{X})$ via equilibrium expectation values of arbitrary dynamical variables $f(\mathbf{X})$:

$$\langle f \rangle = \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) f(\mathbf{X}), \quad \rho(\mathbf{X}) = \frac{1}{Z_N C_N} \exp(-\beta H(\mathbf{X})).$$

From such expectation values, we can recover thermodynamic quantities and calculate fluctuations thereof, which are related to response functions, i.e. different thermodynamic quantities. Other expectation values, e.g. correlation functions, cannot be inferred directly from Z_N .

- Uncertainty about microstate and entropy:

$$S = -k_B \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) \ln[C_N \rho(\mathbf{X})].$$

- Average value H and internal energy:

$$\langle H \rangle = \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) H(\mathbf{X}) = \frac{1}{Z_N C_N} \int_{\Gamma} d^{6N} X H(\mathbf{X}) e^{-\beta H(\mathbf{X})}$$

$$\Rightarrow \langle H \rangle = -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z_N = \frac{\partial}{\partial \beta} (\beta A)$$

$$\text{Use } \frac{\partial}{\partial \beta} = \left(\frac{\partial T}{\partial \beta} \right) \frac{\partial}{\partial T} = -k_B T^2 \frac{\partial}{\partial T} \quad \Rightarrow \quad \langle H \rangle = A - T \frac{\partial A}{\partial T} = A + TS = U.$$

- Energy fluctuations and heat capacity:

$$\langle H^2 \rangle - \langle H \rangle^2 = \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} - \left[\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \right]^2 = \frac{\partial}{\partial \beta} \left[\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \right]$$

$$\Rightarrow \langle H^2 \rangle - \langle H \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Z_N = -\frac{\partial U}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T} = k_B T^2 C_V.$$

Classical virial theorem [tln83]

Classical Hamiltonian system: $\mathcal{H} = \mathcal{T} + \mathcal{V}$.

N interacting particles in 3D space represent $3N$ degrees of freedom.

Phase-space coordinates: $\{x_i\} = \{(q_l, p_l)\}$, $i = 1, \dots, 6N$, $l = 1, \dots, 3N$.

Theorem in general form:

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle \doteq \frac{1}{Z} \int d^{6N} x x_i \frac{\partial \mathcal{H}}{\partial x_j} e^{-\mathcal{H}/k_B T} = -\frac{k_B T}{Z} \int d^{6N} x x_i \frac{\partial e^{-\mathcal{H}/k_B T}}{\partial x_j}.$$

Integrate by parts:

$$\Rightarrow \left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{k_B T}{Z} \int d^{6N} x e^{-\mathcal{H}/k_B T} \delta_{ij} = k_B T \delta_{ij}.$$

Equipartition: average kinetic energy per degree of freedom

$$\mathcal{T} = \sum_{l=1}^{3N} \frac{p_l^2}{2m} \Rightarrow \left\langle p_l \frac{\partial \mathcal{H}}{\partial p_l} \right\rangle = \langle m p_l^2 \rangle \Rightarrow \left\langle \frac{1}{2} m p_l^2 \right\rangle = \frac{1}{2} k_B T.$$

Virial: pair interactions

$$\mathcal{V} = \frac{1}{2} \sum_{l \neq l'} v(|q_l - q_{l'}|). \quad \text{Set } q_{ll'} \doteq q_l - q_{l'}.$$

$$\Rightarrow \frac{1}{6} \sum_{l \neq l'} \left\langle q_{ll'} \frac{\partial v}{\partial q_{ll'}} \right\rangle = N k_B T - pV.$$

Anharmonic crystal in 1D: average potential energy per bond

$$\mathcal{V} = \sum_{l=1}^{N-1} \frac{1}{2} u |q_l - q_{l+1}|^\nu \quad \text{with } \nu > 0. \quad \text{Set } p = 0.$$

$$\Rightarrow \left\langle \frac{1}{2} u |q_l - q_{l+1}|^\nu \right\rangle = \frac{k_B T}{\nu}.$$

[adapted from Schwabl 2006]

Systems of noninteracting particles [tln54]

Consider a classical systems of N noninteracting particles.

$$\text{Hamiltonian: } H = \sum_{l=1}^N h_l(\mathbf{q}_l, \mathbf{p}_l).$$

Canonical partition function of distinguishable particles:

$$Z_N = \frac{1}{C_N} \int_{\Gamma} d^{6N} X e^{-\beta H(\mathbf{X})} = \prod_{l=1}^N \tilde{Z}_l, \quad \tilde{Z}_l = \frac{1}{h^3} \int d^3 q_l d^3 p_l e^{-\beta h_l(\mathbf{q}_l, \mathbf{p}_l)}.$$

Factorizing phase-space probability density:

$$\rho(\mathbf{X}) = \frac{1}{Z_N C_N} e^{-\beta H(\mathbf{X})} = \prod_{l=1}^N \left[\frac{1}{h^3 \tilde{Z}_l} e^{-\beta h_l(\mathbf{q}_l, \mathbf{p}_l)} \right].$$

Identical one-particle Hamiltonians:

$$h_1 = \dots = h_n \equiv h(\mathbf{q}, \mathbf{p}) \quad \Rightarrow \quad \tilde{Z}_1 = \dots = \tilde{Z}_N = \tilde{Z} \equiv \frac{1}{h^3} \int d^3 q d^3 p e^{-\beta h(\mathbf{q}, \mathbf{p})}.$$

$$\Rightarrow Z_N = \tilde{Z}^N, \quad \rho(\mathbf{X}) = \prod_{l=1}^N \left[\frac{1}{h^3 \tilde{Z}} e^{-\beta h(\mathbf{q}_l, \mathbf{p}_l)} \right].$$

Indistinguishable particles:

$$Z_N = \frac{1}{N!} \tilde{Z}^N.$$

Note: It is important that we discriminate between noninteracting subsystems that are *identical but distinguishable* (e.g. atoms vibrating about rigid lattice sites) and noninteracting subsystems that are *identical and indistinguishable* (e.g. atoms of an ideal gas).

Further ensemble averages [tln55]

Probability density in one-particle phase space:

$$\rho_l(\mathbf{q}, \mathbf{p}) = \langle \delta(\mathbf{q}_l - \mathbf{q}) \delta(\mathbf{p}_l - \mathbf{p}) \rangle.$$

Position distribution and momentum distribution:

$$\rho_l(\mathbf{q}) = \langle \delta(\mathbf{q}_l - \mathbf{q}) \rangle, \quad \rho_l(\mathbf{p}) = \langle \delta(\mathbf{p}_l - \mathbf{p}) \rangle.$$

Distribution of distances and relative momenta between pairs of particles:

$$f_{lm}(r) = \langle \delta(r - |\mathbf{q}_l - \mathbf{q}_m|) \rangle, \quad F_{lm}(P) = \langle \delta(P - |\mathbf{p}_l - \mathbf{p}_m|) \rangle.$$

Average distance between pairs of particles:

$$\langle r_{lm} \rangle = \langle |\mathbf{q}_l - \mathbf{q}_m| \rangle = \int_0^\infty dr r f_{lm}(r).$$

Average magnitude of relative momentum between pairs of particles:

$$\langle P_{lm} \rangle = \langle |\mathbf{p}_l - \mathbf{p}_m| \rangle = \int_0^\infty dP P F_{lm}(P).$$

Applications to the classical ideal gas:

$$\text{Noninteracting particles: } h(\mathbf{q}, \mathbf{p}) = \frac{p^2}{2m} \Rightarrow \tilde{Z} = \frac{V}{\lambda_T^3}, \quad \lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}.$$

$$\Rightarrow \rho_l(\mathbf{q}, \mathbf{p}) = V^{-1} (2\pi m k_B T)^{-3/2} e^{-p^2/2m k_B T}.$$

$$\Rightarrow \rho_l(\mathbf{q}) = \int d^3p \rho_l(\mathbf{q}, \mathbf{p}) = \frac{1}{V}.$$

$$\Rightarrow \rho_l(\mathbf{p}) = \int d^3q \rho_l(\mathbf{q}, \mathbf{p}) = (2\pi m k_B T)^{-3/2} e^{-p^2/2m k_B T}.$$

$$\rho_l(\mathbf{p}) d^3p = f(\mathbf{v}) d^3v \Rightarrow f(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{-3/2} e^{-mv^2/2k_B T}.$$

The spatial distribution of ideal gas particles in a uniform gravitational field (law of atmospheres) is calculated in exercise [tex79].

The distribution of relative momenta between pairs of ideal gas particles is calculated in exercise [tex80].

[tex79] Classical ideal gas in uniform gravitational field

Consider a column with cross-sectional area A of a classical ideal gas (N atoms of mass m) in a uniform gravitational field of magnitude g . The gas is in thermal equilibrium at temperature T . The Hamiltonian reads:

$$H = \sum_{l=1}^N \left(\frac{p_l^2}{2m} + mgz_l \right),$$

where z_l is the height of particle l above sea level.

- (a) Find the probability density $\rho_1(z)$ for the vertical positions of individual gas atoms.
- (b) Find the pressure distribution $p(z)$.

Solution:

[tex135] Gas pressure and density inside centrifuge

Consider a hollow disk of width L and radius R filled with N particles of a dilute gas at temperature T . The disk is in a state of rotation with angular velocity ω about its axis.

(a) Find the probability density $\rho_1(r)$ for the radial position of a gas particle and find the particle density $n(r)$. Note that the unit of $\rho_1(r)$ is $[\text{m}^{-2}]$ and the unit of $n(r)$ is $[\text{m}^{-3}]$.

(b) Find the pressure $p(r)$.

(c) In an experiment that measures $p(0)$ and $p(R)$ at various values of ω and fixed T , which two quantities must be plotted against each other such that the data points are predicted to fall onto a straight line with slope equal to the mass of the gas particles?

Solution:

[tex80] Relative momentum of two ideal gas particles

Consider a classical ideal gas of N atoms with mass m confined to a box of volume V in thermal equilibrium with a heat reservoir at temperature T .

- (a) Find the distribution $F_{lm}(P) \equiv \langle \delta(P - |\mathbf{p}_l - \mathbf{p}_m|) \rangle$ of the magnitude of the relative momenta of two ideal gas particles.
- (b) Find the ratio of the average magnitudes $\langle P \rangle / \langle p \rangle$ of the relative momentum of two particles and the momentum of a single particle.

Solution:

Partition function and density of states [tln56]

Why do the microcanonical and canonical ensembles yield the same results?

(a) Derivation of Z_N from $\Omega(U, V, N)$.

Relation between the microcanonical phase-space volume $\Omega(U, V, N)$ and the number of microstates $\Sigma(U, V, N)$ up to the energy U :

$$\Omega(U, V, N) \equiv \int_{H(\mathbf{x}) < U} d^{6N} X = C_N \Sigma(U, V, N).$$

Density of microstates:

$$g(U) = \frac{\partial \Sigma}{\partial U}.$$

The canonical partition function is then obtained via Laplace transform:

$$\int_0^\infty dU g(U) e^{-\beta U} = \frac{1}{C_N} \int_{\Gamma} d^{6N} X e^{-\beta H(\mathbf{x})} = Z_N.$$

Here the energy scale has been shifted such that $U_0 = 0$.

(b) Derivation of $\Omega(U, V, N)$ from Z_N .

Complex continuation of the canonical partition function:

$$Z_N = Z(\beta) \text{ for } \beta = \beta' + i\beta'' \text{ with } \beta' > 0.$$

The microcanonical phase-space volume is then obtained via inverse Laplace transform:

$$g(U) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} d\beta e^{\beta U} Z(\beta), \quad \Omega(U, V, N) = C_N \int_0^U dU' g(U').$$

Both calculations are carried out in exercise [tex81] for the classical ideal gas.

[tex81] Ideal gas partition function and density of states

- (a) Starting from the result of [tex73] for the phase-space volume $\Omega(U, V, N)$ of a classical ideal gas (N particles with mass m) in the microcanonical ensemble, calculate the density of microstates, $g_N(u)$, and then, via Laplace transform, the result of [tex76] for the canonical partition function $Z_N(\beta)$, where $\beta = 1/k_B T$.
- (b) Starting from the canonical partition function $Z_N(\beta)$ analytically continued into the complex plane, calculate the density of state $g_N(U)$ via inverse Laplace transform.

Solution:

Vibrational heat capacities of solids [tln57]

The interaction between atoms is attractive at long distances and repulsive at short distances. The lowest-energy configuration of a macroscopic system of N atoms is a perfect lattice. This is the equilibrium state at $T = 0$. It has zero entropy. Heat input $\delta Q = CdT$ causes lattice vibrations. In the following we study vibrational heat capacities in successively improved approximations.

Atoms bound to rigid lattice by harmonic force (classical model):

The theory of Dulong and Petit considers an array of N classical 3D harmonic oscillators with identical angular frequencies. The resulting vibrational heat capacity, $C = 3Nk_B$, is T -independent and is calculated in exercise [tex74] for a microcanonical ensemble and in exercise [tex78] for a canonical ensemble.

The main insufficiency of the Dulong-Petit result is that C does not approach zero in the low-temperature limit, in violation of the third law.

Atoms bound to rigid lattice by harmonic force (quantum model):

The theory of Einstein considers an array of N quantum 3D harmonic oscillators with identical angular frequencies ω . The resulting vibrational heat capacity,

$$C = \left(\frac{\Theta_E}{k_B T} \right)^2 \frac{3Nk_B e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}, \quad k_B \Theta_E = \hbar\omega,$$

goes to zero exponentially in the low- T limit, $C \sim e^{-\Theta_E/T}$, and approaches the Dulong-Petit result, $C = 3Nk_B$, at high T . Einstein's result is derived in exercise [tex75] for the microcanonical ensemble and in exercise [tex82] for the canonical ensemble.

The main insufficiency of Einstein's result is that it contradicts experimental evidence, which suggests $C \sim T^3$ at low T .

Atoms interacting via harmonic force:

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{ij} A_{ij} q_i q_j = \sum_{i=1}^{3N} \left[\frac{p_i^2}{2m} + \frac{1}{2} m \omega_i^2 Q_i^2 \right].$$

Here $\{A_{ij}\}$ is the dynamical matrix. The second equation results from a transformation to normal-mode coordinates. In the present context the normal modes are sound waves (phonons).

Quantum mechanically, this system is an array of $3N$ independent harmonic oscillators with normal mode frequencies ω_i :

$$H = \sum_{i=1}^{3N} \hbar \omega_i \left(n_i + \frac{1}{2} \right), \quad n_i = 0, 1, 2, \dots$$

The resulting Helmholtz free energy (in generalization to the result derived in [tex82]) reads:

$$A = \frac{1}{2} \sum_{i=1}^{3N} \hbar \omega_i + k_B T \sum_{i=1}^{3N} \ln(1 - e^{-\beta \hbar \omega_i}).$$

In Debye's theory, the normal modes, which, in general, consist of multiple branches of acoustic and optical phonons, are replaced by a single branch of sound waves with linear dispersion $\omega = ck$ as is expected in a continuous isotropic elastic medium.

Total number of modes: $3N$ (same as in original lattice model).

Density of modes in k -space: $V/(2\pi)^3$.

Number of polarizations: 3 (2 transverse, 1 longitudinal).

Number of modes in $d\omega$: $n(\omega)d\omega = \frac{V}{8\pi^3} (3)(4\pi) \frac{\omega^2}{c^2} \frac{d\omega}{c} = \frac{3V}{2\pi^2 c^3} \omega^2 d\omega$.

Debye frequency: $\frac{3V}{2\pi^2 c^3} \int_0^{\omega_D} d\omega \omega^2 = 3N \Rightarrow \omega_D^3 = \frac{6N\pi^2 c^3}{V}$.

Density of modes: $n(\omega) = \frac{9N}{\omega_D^3} \omega^2$.

The resulting vibrational heat capacity is calculated in exercise [tex83] and does show the experimentally observed $\sim T^3$ behavior as $T \rightarrow 0$:

$$C = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}, \quad \Theta_D = \hbar \omega_D / k_B.$$

[tex82] **Array of quantum harmonic oscillators (canonical ensemble)**

Consider an array of N 3-dimensional quantum harmonic oscillators:

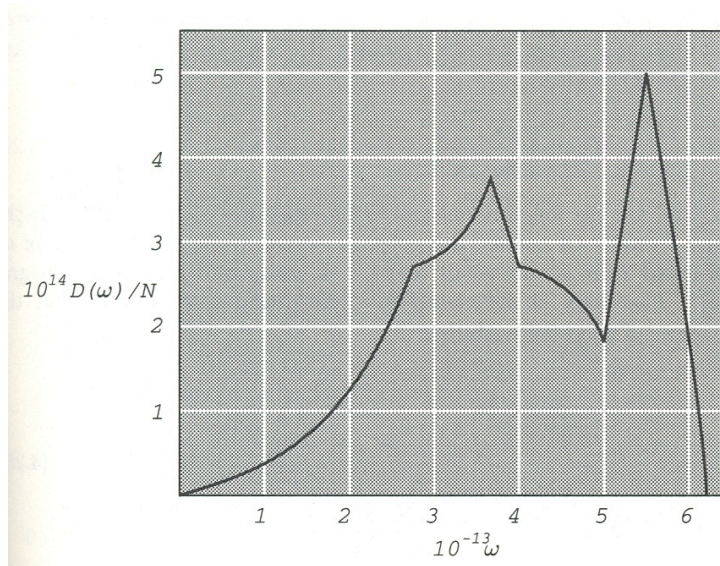
$$H = \sum_{i=1}^{3N} \left[\hbar\omega \left(n_i + \frac{1}{2} \right) \right], \quad n_i = 0, 1, 2, \dots$$

- (a) Calculate the canonical partition function Z_N for this model.
- (b) Derive from Z_N the Helmholtz free energy $A(T, N)$, the internal energy $U(T, N)$, and the heat capacity $C = (\partial U / \partial T)_N$.
- (c) Show that $U(T, N)$ approaches the result of [tex78] for the classical oscillators.
- (d) Calculate the quantity $\langle n_i \rangle$ for a single degree of freedom. It reflects the average number of elementary energy quanta that are excited in one oscillator when it is in thermal equilibrium at temperature T .

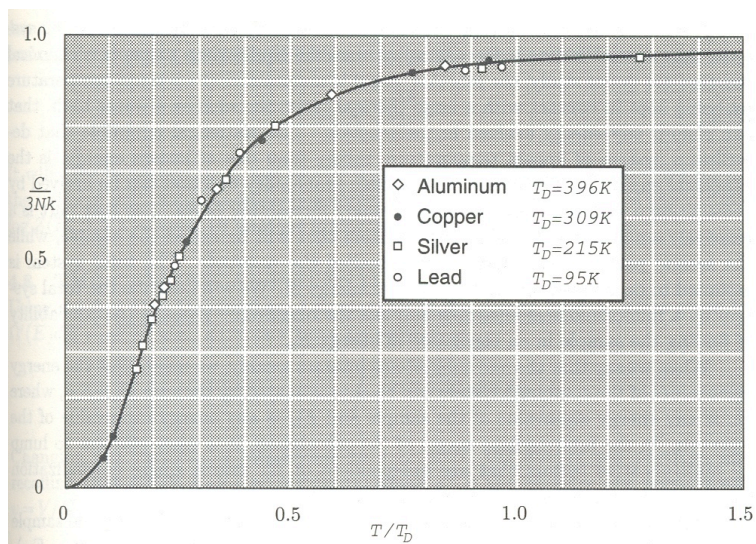
Solution:

Vibrational heat capacities of solids [tsl29]

Density of vibrational modes in aluminum



Debye prediction for heat capacity in comparison with experimental data



[from Garrod 1995]

Thermodynamic perturbation expansion [tln80]

Consider a classical dynamical system in the canonical ensemble.

$$\mathcal{H} = \mathcal{H}_0 + V.$$

The term \mathcal{H}_0 represents the dominant contribution to the energy of the system under the circumstances of interest. We assume that the Helmholtz free energy, $A_0(T, V, N)$, for that part alone can be calculated exactly:

$$e^{-\beta A_0} = \int d\Gamma e^{-\beta \mathcal{H}_0}, \quad d\Gamma \doteq d^{6N} X, \quad \beta \doteq \frac{1}{k_B T}.$$

We can then treat V perturbatively via the following expansion:

$$e^{-\beta A} = \int d\Gamma e^{-\beta(\mathcal{H}_0 + V)} \simeq \int d\Gamma e^{-\beta \mathcal{H}_0} \left(1 - \beta V + \frac{1}{2} \beta^2 V^2 \right).$$

This expression is then further expanded by using $\ln(1 - x) \simeq -x + x^2/2$:

$$\begin{aligned} -\beta A &\simeq \ln \left(e^{-\beta A_0} - \beta \int d\Gamma V e^{-\beta \mathcal{H}_0} + \frac{1}{2} \beta^2 \int d\Gamma V^2 e^{-\beta \mathcal{H}_0} \right) \\ &\simeq -\beta A_0 + \ln \left(1 - \beta \int d\Gamma V e^{\beta(A_0 - \mathcal{H}_0)} + \frac{1}{2} \beta^2 \int d\Gamma V^2 e^{\beta(A_0 - \mathcal{H}_0)} \right). \\ \Rightarrow A &= A_0 + \int d\Gamma \left(V - \frac{1}{2} \beta V^2 \right) e^{\beta(A_0 - \mathcal{H}_0)} + \frac{1}{2} \beta \left[\int d\Gamma V e^{\beta(A_0 - \mathcal{H}_0)} \right]^2. \end{aligned}$$

With ensemble averages,

$$\langle V \rangle \doteq \frac{\int d\Gamma V e^{-\beta \mathcal{H}_0}}{\int d\Gamma e^{-\beta \mathcal{H}_0}} = \int d\Gamma V e^{\beta(A_0 - \mathcal{H}_0)}, \quad \langle V^2 \rangle = \int d\Gamma V^2 e^{\beta(A_0 - \mathcal{H}_0)},$$

and the relation

$$\langle V^2 \rangle - \langle V \rangle^2 = \langle (V - \langle V \rangle)^2 \rangle,$$

we can write

$$A = A_0 + \langle V \rangle - \frac{1}{2} \beta \langle (V - \langle V \rangle)^2 \rangle.$$

The criterion of applicability for this expansion is $\langle V \rangle / N \ll k_B T$. Note that if $\langle V \rangle = 0$ then the leading-order perturbation always reduces the Helmholtz free energy.

[tex83] Vibrational heat capacity of a solid

The vibrational Helmholtz free energy of a harmonic crystal of N atoms in thermal equilibrium at temperature T is

$$A = \frac{1}{2} \sum_{i=1}^{3N} \hbar\omega_i + k_B T \sum_{i=1}^{3N} \ln(1 - e^{-\beta\hbar\omega_i}),$$

where the ω_i are the normal modes of transverse and longitudinal lattice vibrations (phonons). In Debye's theory, the density of modes is approximated by the functions $n(\omega) = 9N\omega^2/\omega_D^3$, where the Debye frequency ω_D is an undetermined parameter.

(a) Show that the internal energy $U = A + TS$ in the Debye approximation reads

$$U = \frac{9}{8} N \hbar \omega_D + 9 N k_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^3}{e^x - 1},$$

where $\Theta_D = \hbar\omega_D/k_B$ is called the Debye temperature.

(b) Derive an expression for the heat capacity $C = (\partial U / \partial T)_N$.

(c) At low temperatures the upper boundary Θ_D/T in the above integral may be replaced by infinity, $\int_0^\infty dx x^3 / (e^x - 1) = \pi^4/15$. Use this fact to determine the leading low-temperature term of the heat capacity C .

Solution:

[tex104] Anharmonic oscillator and thermodynamic perturbation

Consider an array of N one-dimensional anharmonic oscillators,

$$H = \sum_{l=1}^N \left[\frac{p_l^2}{2m} + V(q_l) \right], \quad V(q) = cq^2 - gq^3 + fq^4.$$

- (a) Evaluate the canonical partition function perturbatively by treating the quadratic term of V exactly and considering only the leading nonzero corrections of the cubic and the quartic terms.
- (b) Show that the heat capacity in this approximation is $C/Nk_B = 1 + [15g^2/16c^3 - 3f/4c^2]k_B T$.
- (c) Show that the mean displacement in this approximation is $\langle q \rangle = (3g/4c^2)k_B T$.

Solution: