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12. Grandcanonical Ensemble

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Abstract
Part twelve of course materials for Statistical Physics I: PHY525, taught by Gerhard Müller at the University of Rhode Island. Documents will be updated periodically as more entries become presentable.

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12. Grandcanonical Ensemble

Grandcanonical ensemble [tln60]

Consider an open classical system (volume V, temperature T, chemical potential μ). The goal is to determine the thermodynamic potential $\Omega(T, V, \mu)$ pertaining to that situation, from which all other thermodynamic properties can be derived.

A quantitative description of the grandcanonical ensemble requires a set of phase spaces Γ_N, $N = 0, 1, 2, \ldots$ with probability densities $\rho_N(\mathbf{X})$. The interaction Hamiltonian for a system of N particles is $H_N(\mathbf{X})$.

Maximize Gibbs entropy $S = -k_B \sum_{N=0}^{\infty} \int_{\Gamma} d^{6N}X \, \rho_N(\mathbf{X}) \ln[C_N \rho_N(\mathbf{X})]$

subject to the three constraints

- $\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) = 1 \quad \text{(normalization)},$
- $\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) H_N(\mathbf{X}) = \langle H \rangle = U \quad \text{(average energy)},$
- $\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) N = \langle N \rangle = \mathcal{N} \quad \text{(average number of particles)}.$

Apply calculus of variation with three Lagrange multipliers:

$$\delta \left[\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \left\{ -k_B \rho_N \ln[C_N \rho_N] + \alpha_0 \rho_N + \alpha_U H_N \rho_N + \alpha_N N \rho_N \right\} \right] = 0$$

$$\Rightarrow \sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \delta\rho_N \left\{ -k_B \ln[C_N \rho_N] - k_B + \alpha_0 + \alpha_U H_N + \alpha_N N \right\} = 0$$

$$\Rightarrow \{\cdots\} = 0 \;\Rightarrow\; \rho_N(\mathbf{X}) = \frac{1}{C_N} \exp\left(\frac{\alpha_0}{k_B} - 1 + \frac{\alpha_U}{k_B} H_N(\mathbf{X}) + \frac{\alpha_N}{k_B} N \right).$$

Determine the Lagrange multipliers $\alpha_0, \alpha_U, \alpha_N$:

$$\exp\left(1 - \frac{\alpha_0}{k_B}\right) = \sum_{N=0}^{\infty} \frac{1}{C_N} \int_{\Gamma_N} d^{6N}X \exp\left(\frac{\alpha_U}{k_B} H_N(\mathbf{X}) + \frac{\alpha_N}{k_B} N \right) \equiv Z,$$

$$\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) \{\cdots\} = 0 \;\Rightarrow\; S - k_B + \alpha_0 + \alpha_U U + \alpha_N \mathcal{N} = 0$$

$$\Rightarrow\; U + \frac{1}{\alpha_U} S + \frac{\alpha_N}{\alpha_U} \mathcal{N} = \frac{k_B}{\alpha_U} \ln Z.$$

Compare with $U - TS - \mu\mathcal{N} = -pV = \Omega \;\Rightarrow\; \alpha_U = -\frac{1}{T},\; \alpha_N = \frac{\mu}{T}$.

Grand potential: $\Omega(T, V, \mu) = -k_B T \ln Z = -pV$.

Grand partition function: $Z = \sum_{N=0}^{\infty} \frac{1}{C_N} \int_{\Gamma_N} d^{6N}X\, e^{-\beta H_N(\mathbf{X}) + \beta\mu N},\; \beta = \frac{1}{k_B T}$.

Probability densities: $\rho_N(\mathbf{X}) = \frac{1}{ZC_N}\, e^{-\beta H_N(\mathbf{X}) + \beta\mu N}$.

Grandcanonical ensemble in quantum mechanics:

$$Z = \mathrm{Tr}\, e^{-\beta(H - \mu N)}, \quad \rho = \frac{1}{Z}\, e^{-\beta(H - \mu N)}, \quad \Omega = -k_B T \ln Z.$$

Derivation of thermodynamic properties from grand potential:

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \quad p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}, \quad \mathcal{N} = \langle N \rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}.$$

Relation between canonical and grandcanonical partition functions:

$$Z = \sum_{N=0}^{\infty} e^{\mu N/k_B T} Z_N = \sum_{N=0}^{\infty} z^N Z_N, \quad z \equiv e^{\mu/k_B T} \text{ (fugacity)}.$$

Open system of indistinguishable noninteracting particles:

$$Z_N = \frac{1}{N!}\tilde{Z}^N, \quad Z = \sum_{N=0}^{\infty} \frac{1}{N!} z^N \tilde{Z}^N = e^{z\tilde{Z}}$$

$$\Rightarrow\; \Omega = -k_B T \ln Z = -k_B T z\tilde{Z}.$$

Thermodynamic properties of the classical ideal gas in the grandcanonical ensemble are calculated in exercise [tex94].

[tex94] Classical ideal gas (grandcanonical ensemble)

Consider a classical ideal gas $[H_N = \sum_{l=1}^{N}(p_l^2/2m)]$ in a box of volume V in equilibrium with heat and particle reservoirs at temperature T and chemical potential μ, respectively.
(a) Show that the grand partition function is $Z = \exp(zV/\lambda_T^3)$, where $z = \exp(\mu/k_BT)$ is the fugacity, and $\lambda_T = \sqrt{h^2/2\pi m k_B T}$ is the thermal wavelength.
(b) Derive from Z the grand potential $\Omega(T,V,\mu)$, the entropy $S(T,V,\mu)$. the pressure $p(T,V,\mu)$, and the average particle number $\langle N\rangle = \mathcal{N}(T,V,\mu)$.
(c) Derive from these expressions the familiar results for the internal energy $U = \frac{3}{2}\mathcal{N}k_BT$, and the ideal gas equation of state $pV = \mathcal{N}k_BT$.

Solution:

Density fluctuations and compressibility [tln61]

Average number of particles in volume V:

$$\mathcal{N} = \langle N \rangle = \sum_{N=0}^{\infty} \frac{1}{ZC_N} \int_{\Gamma_N} d^{6N}X \, N e^{-\beta H_N(\mathbf{X}) + \beta\mu N} = \frac{1}{Z\beta}\frac{\partial Z}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln Z.$$

Fluctuations in particle number (in volume V):

$$\langle N^2\rangle - \langle N\rangle^2 = \frac{1}{Z\beta^2}\frac{\partial^2 Z}{\partial\mu^2} - \left[\frac{1}{Z\beta}\frac{\partial Z}{\partial\mu}\right]^2 = \frac{1}{\beta^2}\frac{\partial^2 \ln Z}{\partial\mu^2} = \frac{1}{\beta^2}\frac{\partial(\beta\langle N\rangle)}{\partial\mu} = k_B T\left(\frac{\partial\mathcal{N}}{\partial\mu}\right)_{TV}.$$

Here we use $Z = Z(\beta, V, \mu)$.

Gibbs-Duhem: $d\mu = \frac{V}{\mathcal{N}}\,dp - \frac{S}{\mathcal{N}}\,dT \;\Rightarrow\; \left(\frac{\partial\mu}{\partial(V/\mathcal{N})}\right)_T = \frac{V}{\mathcal{N}}\left(\frac{\partial p}{\partial(V/\mathcal{N})}\right)_T.$

For $V =$ const: $\frac{\partial}{\partial(V/\mathcal{N})} = \frac{\partial\mathcal{N}}{\partial(V/\mathcal{N})}\frac{\partial}{\partial\mathcal{N}} = -\frac{\mathcal{N}^2}{V}\frac{\partial}{\partial\mathcal{N}}.$

For $\mathcal{N} =$ const: $\frac{\partial}{\partial(V/\mathcal{N})} = \frac{\partial V}{\partial(V/\mathcal{N})}\frac{\partial}{\partial V} = \mathcal{N}\frac{\partial}{\partial V}.$

$$\Rightarrow\; -\frac{\mathcal{N}^2}{V}\left(\frac{\partial\mu}{\partial\mathcal{N}}\right)_{TV} = V\left(\frac{\partial p}{\partial V}\right)_{T\mathcal{N}} \quad\Rightarrow\; \left(\frac{\partial\mu}{\partial\mathcal{N}}\right)_{TV} = \frac{V}{\mathcal{N}^2}\,\kappa_T^{-1}.$$

Compressibility: $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T\mathcal{N}}.$

Fluctuations in particle number: $\langle N^2\rangle - \langle N\rangle^2 = \frac{\mathcal{N}^2}{V}\,k_B T\kappa_T.$

An alternative expression for $\langle N^2\rangle - \langle N\rangle^2$ is calculated in exercise [tex95].

The density fluctuations for a classical ideal gas are calculated in exercise [tex96].

At the critical point of a liquid-gas transition, the isotherm has an inflection point with zero slope ($\partial p/\partial V = 0$), implying $\kappa_T \to \infty$. The strongly enhanced density fluctuations are responsible for critical opalescence.

[tex95] Density fluctuations in the grandcanonical ensemble

Consider a system of indistinguishable particles in the grandcanonical ensemble. Derive the following two expressions for the fluctuations in the number of particles N for an open system of volume V in equilibrium with heat and particle reservoirs at temperature T and chemical potential μ, respectively:

$$\langle N^2\rangle - \langle N\rangle^2 = z\frac{\partial}{\partial z}z\frac{\partial}{\partial z}\ln Z = k_BTV\frac{\partial^2 p}{\partial\mu^2},$$

where $z = \exp(\mu/k_BT)$ is the fugacity, $p(T,V,\mu) = -(\partial\Omega/\partial V)_{T\mu} = -\Omega/V$ is the pressure, and $\Omega(T,V,\mu) = -k_BT\ln Z$ is the grand potential.

Solution:

[tex96] Density fluctuations and compressibility of the classical ideal gas

(a) Use the results of [tex94] and [tex95] to show that the variance of the number of particles in a classical ideal gas (open system) is equal to the average number of particles:

$$\langle N^2\rangle - \langle N\rangle^2 = \langle N\rangle = \mathcal{N}.$$

(b) Use this result to show that the isothermal compressibility of the classical ideal gas is $\kappa_T = 1/p$.

Solution:

[tex103] Energy fluctuations and thermal response functions

(a) Show that the following relation holds between the energy fluctuations in the microscopic ensemble and the heat capacity of a system described by a microscopic Hamiltonian H:

$$\langle (H - \langle H \rangle)^2 \rangle = k_B T^2 C_V.$$

(b) Prove the following relation in a similar manner:

$$\langle (H - \langle H \rangle)^3 \rangle = k_B^2 \left[T^4 \left(\frac{\partial C_V}{\partial T} \right)_V + 2T^3 C_V \right].$$

(c) Determine the relative fluctuations as measured by the quantities $\langle (H - \langle H \rangle)^2 \rangle / \langle H \rangle^2$ and $\langle (H - \langle H \rangle)^3 \rangle / \langle H \rangle^3$ for the classical ideal gas with N atoms.

Solution:

Microscopic states of ideal quantum gases [tln62]

Hamiltonian: $\hat{H}_N = \sum_{\ell=1}^{N} \hat{h}_\ell$.

1-particle eigenvalue equation: $\hat{h}_\ell|\mathbf{k}_\ell\rangle = \epsilon_\ell|\mathbf{k}_\ell\rangle$.

N-particle eigenvalue equation: $\hat{H}_N|\mathbf{k}_1,\ldots,\mathbf{k}_N\rangle = E_N|\mathbf{k}_1,\ldots,\mathbf{k}_N\rangle$.

Energy: $E_N = \sum_{\ell=1}^{N} \epsilon_\ell, \quad \epsilon_\ell = \frac{\hbar^2\mathbf{k}_\ell^2}{2m}$.

N-particle product eigenstates: $|\mathbf{k}_1,\ldots,\mathbf{k}_N\rangle = |\mathbf{k}_1\rangle\ldots|\mathbf{k}_N\rangle$.

Symmetrized states for bosons: $|\mathbf{k}_1,\ldots,\mathbf{k}_N\rangle^{(S)}$.

- $N=2$: $|\mathbf{k}_1,\mathbf{k}_2\rangle^{(S)} = \frac{1}{\sqrt{2}}\left(|\mathbf{k}_1\rangle|\mathbf{k}_2\rangle + |\mathbf{k}_2\rangle|\mathbf{k}_1\rangle\right)$.

Antisymmetrized states for fermions: $|\mathbf{k}_1,\ldots,\mathbf{k}_N\rangle^{(A)}$.

- $N=2$: $|\mathbf{k}_1,\mathbf{k}_2\rangle^{(A)} = \frac{1}{\sqrt{2}}\left(|\mathbf{k}_1\rangle|\mathbf{k}_2\rangle - |\mathbf{k}_2\rangle|\mathbf{k}_1\rangle\right)$.

Occupation number representation: $|\mathbf{k}_1,\ldots,\mathbf{k}_N\rangle \equiv |n_1,n_2,\ldots\rangle$.

Here $\mathbf{k}_1$ represents the wave vector of the first particle, whereas n_1 refers to the number of particles in the first 1-particle state.

- energy: $\hat{H}|n_1,n_2,\ldots\rangle = E|n_1,n_2,\ldots\rangle, \quad E = \sum_{k=1}^{\infty} n_k\epsilon_k$.
- number of particles: $\hat{N}|n_1,n_2,\ldots\rangle = N|n_1,n_2,\ldots\rangle, \quad N = \sum_{k=1}^{\infty} n_k$.

ϵ_ℓ: energy of particle ℓ. $\quad$ ϵ_k: energy of 1-particle state k.

Allowed occupation numbers:

- bosons: $n_k = 0,1,2,\ldots$
- fermions: $n_k = 0,1$.

Partition function of ideal quantum gases [tln63]

Canonical partition function: $Z_N = \sum_{\{n_k\}}' \sigma(n_1, n_2, \ldots) \exp\left(-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right)$.

$\sum_{\{n_k\}}'$: sum over all occupation numbers compatible with $\sum_{k=1}^{\infty} n_k = N$.

The statistical weight factor $\sigma(n_1, n_2, \ldots)$ is different for fermions and bosons:

- Bose-Einstein statistics: $\sigma_{BE}(n_1, n_2, \ldots) = 1$ for arbitrary values of n_k.
- Fermi-Dirac statistics: $\sigma_{FD}(n_1, n_2, \ldots) = \begin{cases} 1 & \text{if all } n_k = 0, 1 \\ 0 & \text{otherwise} \end{cases}$.

What is the statistical weight factor for the Maxwell-Boltzmann gas?

$$Z_N = \frac{1}{N!}\tilde{Z}^N = \frac{1}{N!}\left(\sum_{k=1}^{\infty} e^{-\beta\epsilon_k}\right)^N = \frac{1}{N!}\sum_{\{n_k\}}' \frac{N!}{n_1!n_2!\ldots}\left(e^{-\beta\epsilon_1}\right)^{n_1}\left(e^{-\beta\epsilon_2}\right)^{n_2}\cdots$$

$$= \sum_{\{n_k\}}' \frac{1}{n_1!n_2!\ldots} \exp\left(-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right).$$

- Maxwell-Boltzmann statistics: $\sigma_{MB}(n_1, n_2, \ldots) = \dfrac{1}{n_1!n_2!\ldots}$.

Grandcanonical partition function:

$$\Rightarrow \; \mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N = \sum_{\{n_k\}} \sigma(n_1, n_2, \ldots) \exp\left(-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right),$$

where we have used $z^N = (e^{\beta\mu})^N = \exp\left(\beta\mu \sum_{k=1}^{\infty} n_k\right)$.

- $\mathcal{Z}_{BE} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots \exp\left(-\beta\sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right) = \prod_{k=1}^{\infty}\left(1 - ze^{-\beta\epsilon_k}\right)^{-1}$.
- $\mathcal{Z}_{FD} = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots \exp\left(-\beta\sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right) = \prod_{k=1}^{\infty}\left(1 + ze^{-\beta\epsilon_k}\right)$.
- $\mathcal{Z}_{MB} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots \frac{1}{n_1!n_2!\ldots} \exp\left(-\beta\sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right) = \prod_{k=1}^{\infty} \exp\left(ze^{-\beta\epsilon_k}\right)$.

Ideal quantum gases: grand potential and thermal averages [tln64]

Grand potential: $\Omega(T,V,\mu) = -k_BT\ln Z = U - TS - \mu\mathcal{N} = -pV$.

- $\Omega_{MB} = -k_BT\sum_{k=1}^{\infty} ze^{-\beta\epsilon_k} = -k_BT\sum_{k=1}^{\infty} e^{-\beta(\epsilon_k-\mu)}$,
- $\Omega_{BE} = k_BT\sum_{k=1}^{\infty}\ln\left(1-ze^{-\beta\epsilon_k}\right) = k_BT\sum_{k=1}^{\infty}\ln\left(1-e^{-\beta(\epsilon_k-\mu)}\right)$,
- $\Omega_{FD} = -k_BT\sum_{k=1}^{\infty}\ln\left(1+ze^{-\beta\epsilon_k}\right) = -k_BT\sum_{k=1}^{\infty}\ln\left(1+e^{-\beta(\epsilon_k-\mu)}\right)$.

Parametric representation [$a=1$ (FD), $a=0$ (MB), $a=-1$ (BE)]:

$$\ln Z = \frac{pV}{k_BT} = \frac{1}{a}\sum_{k=1}^{\infty}\ln\left(1+aze^{-\beta\epsilon_k}\right).$$

Average number of particles:

$$\mathcal{N} = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \frac{1}{\beta}\left(\frac{\partial\ln Z}{\partial\mu}\right)_{T,V} = \sum_{k=1}^{\infty}\frac{1}{z^{-1}e^{\beta\epsilon_k}+a} = \sum_{k=1}^{\infty}\langle n_k\rangle.$$

Average energy (internal energy):

$$U = -\left(\frac{\partial\ln Z}{\partial\beta}\right)_{z,V} = \sum_{k=1}^{\infty}\frac{\epsilon_k}{z^{-1}e^{\beta\epsilon_k}+a} = \sum_{k=1}^{\infty}\epsilon_k\langle n_k\rangle.$$

Average occupation number of energy level ϵ_k:

$$\langle n_k\rangle = -\beta^{-1}\frac{\partial\ln Z}{\partial\epsilon_k} = \frac{1}{e^{\beta(\epsilon_k-\mu)}+a}.$$

Fluctuations in occupation number [tex110]:

$$\langle n_k^2\rangle - \langle n_k\rangle^2 = \beta^{-2}\frac{\partial^2\ln Z}{\partial\epsilon_k^2}.$$

Average occupation numbers for MB, FD, and BE gases [tsl35]

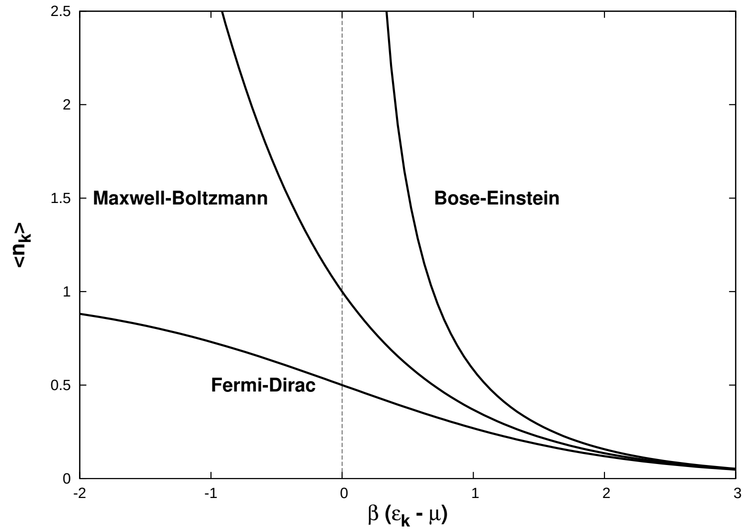
Average occupation number of energy level ϵ_k:

$$\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} + a}$$

- $a = 1$: Fermi-Dirac gas,
- $a = 0$: Maxwell-Boltzmann gas,
- $a = -1$: Bose-Einstein gas.

Range of 1-particle energies: $\epsilon_k \geq 0$.

BE gas restriction: $\mu \leq 0 \quad \Rightarrow \; 0 \leq z \leq 1$.



The BE and FD gases are well approximated by the MB gas provided the thermal wavelength $\lambda_T = \sqrt{h^2/2\pi m k_B T}$ is small compared to the average interparticle distance:

$$\beta(\epsilon_k - \mu) \gg 1 \quad \Rightarrow \; -\beta\mu \gg 1 \quad \Rightarrow \; z \ll 1.$$

$$\text{[tex94] for } \mathcal{D} = 3: \quad \Rightarrow \; \lambda_T \ll (V/\mathcal{N})^{1/3}.$$

[tex110] Occupation number fluctuations

Consider an ideal quantum gas specified by the grand partition function Z. Start from the expressions

$$\langle n_k^2\rangle - \langle n_k\rangle^2 = \frac{1}{Z}\beta^{-2}\frac{\partial^2 Z}{\partial\epsilon_k^2} - \left[\frac{1}{Z}\beta^{-1}\frac{\partial Z}{\partial\epsilon_k}\right]^2, \quad \ln Z = \frac{1}{a}\sum_{k=1}^{\infty}\ln(1+aze^{-\beta\epsilon_k}),$$

where $a = +1, 0, -1$ represent the FD, MB, and BE cases, respectively, to derive the following result for the relative fluctuations in the occupation numbers:

$$\frac{\langle n_k^2\rangle - \langle n_k\rangle^2}{\langle n_k\rangle^2} = \frac{1}{\langle n_k\rangle} - a.$$

Note that in the BE (FD) statistics, these fluctuations are enhanced (suppressed) relative to those in the MB statistics.

Solution:

[tex111] Density of energy levels for ideal quantum gas

Consider a nonrelativistic ideal quantum gas in $\mathcal{D}$ dimensions and confined to a box of volume $V = L^{\mathcal{D}}$ with rigid walls. Show that the density of energy levels is

$$D(\epsilon) = \frac{L^{\mathcal{D}}}{\Gamma(\mathcal{D}/2)} \left(\frac{m}{2\pi\hbar^2}\right)^{\mathcal{D}/2} \epsilon^{\mathcal{D}/2-1}.$$

Solution:

[tex112] Maxwell-Boltzmann gas in $\mathcal{D}$ dimensions

From the expressions for the grand potential and the density of energy levels of an ideal Maxwell-Boltzmann gas in $\mathcal{D}$ dimensions and confined to a box of volume $V = L^{\mathcal{D}}$ with rigid walls,

$$\Omega(T, V, \mu) = -k_B T \sum_k e^{-\beta(\epsilon_k - \mu)}, \qquad D(\epsilon) = \frac{L^{\mathcal{D}}}{\Gamma(\mathcal{D}/2)} \left(\frac{m}{2\pi\hbar^2}\right)^{\mathcal{D}/2} \epsilon^{\mathcal{D}/2-1},$$

derive the familiar results $pV = \mathcal{N} k_B T$ for the equation of state, $C_{V\mathcal{N}} = (\mathcal{D}/2)\mathcal{N} k_B$ for the heat capacity, and $pV^{(\mathcal{D}+2)/\mathcal{D}} = \text{const}$ for the adiabate at fixed $\mathcal{N}$.

Solution: