PHYS 301: Final Summary Problems

PHYS 301; Prof. Cyr-Racine

Problem 1: Surface Adsorption

Consider a solid surface with M distinct binding sites, placed inside a sealed container. The surface is in thermal and particle equilibrium with a classical ideal gas of identical atoms at temperature T and pressure P.

Each binding site on the surface can either be empty, or occupied by exactly one atom. When an atom binds to a site, its energy is lowered by an amount ϵ_0 (meaning the energy of a bound state is $-\epsilon_0$ relative to a free gas particle at rest).

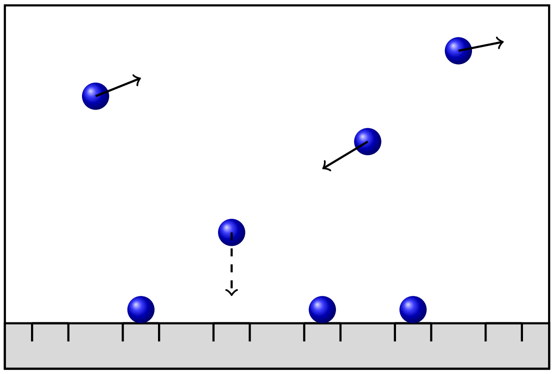
(a) **The Grand Partition Function:** Formulate the grand partition function $\mathcal{Z}$ for the surface.

(b) **Chemical Potential & Coverage:** Find the average number of adsorbed atoms $\langle N \rangle$ as a function of the gas pressure P and temperature T. (This is the Langmuir Isotherm).

(c) **Entropy:** Derive the exact entropy S of the adsorbed atoms on the surface. Show that your result matches the macroscopic thermodynamic expectation for the entropy of mixing.

(d) **Heat:** If an additional dN atoms adsorb onto the surface isothermally, calculate the heat δQ exchanged with the thermal bath. Express your answer in terms of ϵ_0 and the chemical potential μ.

Ideal Gas Reservoir (μ, T, P)



Solid Surface (M sites, Binding Energy $-\epsilon_0$)

Solution

(a) The Grand Partition Function

Because the surface can exchange particles with the gas, it is an open system. The natural ensemble to use is the Grand Canonical Ensemble, characterized by fixed temperature T and chemical potential μ.

Let us first consider a single binding site. It has exactly two microstates:

- State 0: Empty ($N_i = 0$, $E_i = 0$)
- State 1: Occupied ($N_i = 1$, $E_i = -\epsilon_0$)

The grand partition function for a single site is a sum over its microstates, weighted by the Gibbs factor $e^{-\beta(E-\mu N)}$:

$$\mathcal{Z}_1 = \sum_{N_i} e^{-\beta(E_i-\mu N_i)} = e^{-\beta(0-0)} + e^{-\beta(-\epsilon_0-\mu)} = 1 + e^{\beta(\epsilon_0+\mu)} \tag{1}$$

Since the M sites are distinguishable (fixed in space) and non-interacting, the total grand partition function for the entire surface is simply the product of the individual site partition functions:

$$\boxed{\mathcal{Z} = (\mathcal{Z}_1)^M = \left[1 + e^{\beta(\epsilon_0+\mu)}\right]^M} \tag{2}$$

(b) Chemical Potential & Coverage (Langmuir Isotherm)

In the Grand Canonical formalism, the average number of particles is found by taking the derivative of the grand potential with respect to the chemical potential:

$$\langle N \rangle = k_B T \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\left[M \ln\left(1 + e^{\beta(\epsilon_0+\mu)}\right)\right] \tag{3}$$

$$\langle N \rangle = M \frac{e^{\beta(\epsilon_0+\mu)}}{1 + e^{\beta(\epsilon_0+\mu)}} = \frac{M}{e^{-\beta(\epsilon_0+\mu)} + 1} \tag{4}$$

This looks exactly like the Fermi-Dirac distribution, which makes sense since each site can hold a maximum of 1 particle (a manifestation of the Pauli exclusion principle in a classical spatial context). Let us define the fractional coverage $\theta = \langle N \rangle / M$:

$$\theta = \frac{1}{e^{-\beta(\epsilon_0+\mu)} + 1} \tag{5}$$

Because the surface is in thermal and diffusive equilibrium with the surrounding gas, their chemical potentials must be equal: $\mu_{\text{surface}} = \mu_{\text{gas}}$. For a classical ideal monoatomic gas, the chemical potential is:

$$\mu = k_B T \ln\left(n \lambda_Q^3\right) = k_B T \ln\left(\frac{P \lambda_Q^3}{k_B T}\right) \tag{6}$$

where $n = P/k_B T$ is the number density and $\lambda_Q = h/\sqrt{2\pi m k_B T}$ is the thermal de Broglie wavelength.

Isolating $e^{\beta\mu}$ (the fugacity):

$$e^{\beta\mu} = \frac{P \lambda_Q^3}{k_B T} \tag{7}$$

Substitute this back into the coverage equation (5):

$$\theta = \frac{1}{e^{-\beta\epsilon_0}\left(\frac{k_BT}{P\lambda_Q^3}\right)+1} = \frac{P}{P+\frac{k_BT}{\lambda_Q^3}e^{-\beta\epsilon_0}} \tag{8}$$

Defining a temperature-dependent reference pressure $P_0(T) = \frac{k_BT}{\lambda_Q^3}e^{-\beta\epsilon_0}$, we recover the famous **Langmuir Isotherm**:

$$\boxed{\theta(P,T) = \frac{P}{P+P_0(T)}} \tag{9}$$

(c) Entropy

We can calculate the entropy of the adsorbed gas directly from our Grand Partition Function. The Grand Potential is $\Phi = -k_BT\ln\mathcal{Z}$. The thermodynamic identity for Φ is:

$$\Phi = E - TS - \mu\langle N\rangle \implies S = \frac{E-\mu\langle N\rangle-\Phi}{T} \tag{10}$$

Substitute $E = -\epsilon_0\langle N\rangle$ and $\Phi = -k_BTM\ln(1+e^{\beta(\epsilon_0+\mu)})$:

$$S = -\frac{\langle N\rangle}{T}(\epsilon_0+\mu) + k_BM\ln\left(1+e^{\beta(\epsilon_0+\mu)}\right) \tag{11}$$

We can express this purely in terms of the coverage fraction θ. From Eq. (5), we can write:

$$1+e^{\beta(\epsilon_0+\mu)} = \frac{1}{1-\theta} \tag{12}$$

$$\beta(\epsilon_0+\mu) = \ln\left(\frac{\theta}{1-\theta}\right) \implies \frac{\epsilon_0+\mu}{T} = k_B\ln\left(\frac{\theta}{1-\theta}\right) \tag{13}$$

Substitute these into the entropy equation, noting that $\langle N\rangle = M\theta$:

$$\begin{aligned} S &= -M\theta k_B\ln\left(\frac{\theta}{1-\theta}\right) + k_BM\ln\left(\frac{1}{1-\theta}\right) \\ &= -Mk_B\left[\theta\ln\theta - \theta\ln(1-\theta) + \ln(1-\theta)\right] \\ &= -Mk_B\left[\theta\ln\theta + (1-\theta)\ln(1-\theta)\right] \end{aligned} \tag{14}$$

$$\boxed{S = -k_BM\left[\theta\ln\theta + (1-\theta)\ln(1-\theta)\right]} \tag{15}$$

Physical Interpretation: This perfectly matches the microcanonical combinatorics for the entropy of mixing! If you have M total sites and N identical particles, the number of ways to arrange them is $\Omega = \frac{M!}{N!(M-N)!}$. Using Stirling's approximation on $S = k_B\ln\Omega$ yields exactly the formula derived above from the Grand Canonical ensemble.

(d) Heat

We are asked to find the heat exchanged δQ when an additional dN particles adsorb onto the surface at a constant temperature T.

We apply the First Law of Thermodynamics to the open system of the surface. The fundamental thermodynamic identity is:

$$dE = TdS + \mu dN \tag{16}$$

For a reversible, isothermal process, the heat added to the system is exactly TdS:

$$\delta Q_{\text{in}} = TdS = dE - \mu dN \tag{17}$$

We know that every time a particle adsorbs, the energy of the surface changes by $-\epsilon_0$. Therefore, $dE = -\epsilon_0 dN$. Substituting this into our heat equation:

$$\delta Q_{\text{in}} = (-\epsilon_0 - \mu)dN \tag{18}$$

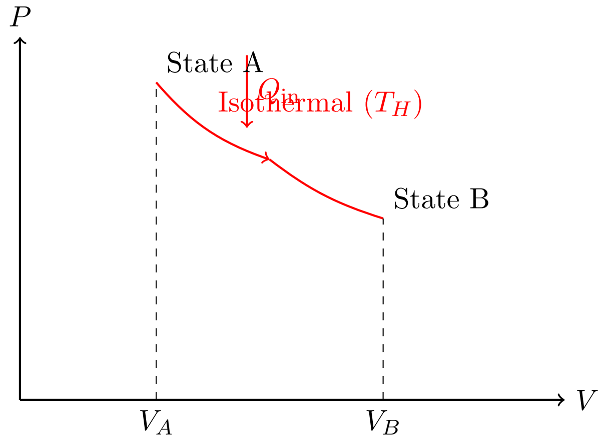
If dN is positive (particles are adsorbing), this value is typically negative, meaning heat is released. The heat released to the thermal bath per particle adsorbed (the isosteric heat of adsorption, q) is:

$$\boxed{q = \frac{-\delta Q_{\text{in}}}{dN} = \epsilon_0 + \mu} \tag{19}$$

Physical Interpretation: When a particle adsorbs, it drops into a potential well of depth ϵ_0, releasing energy. However, it also brings its chemical potential μ from the gas reservoir. The net heat released to the environment is the binding energy minus the energetic "cost" of extracting a particle from the surrounding gas bath.

Problem 2: The Microscopic Engine

Consider a classical ideal gas of N indistinguishable monoatomic particles that serves as the working fluid for a Carnot heat engine. We will analyze the first stroke of this engine: a reversible isothermal expansion at the hot reservoir temperature T_H from an initial volume V_A to a final volume V_B.



(a) **Macroscopic Thermodynamics:** Using the First Law of Thermodynamics and the ideal gas law, calculate the work done W by the gas and the heat Q_{in} absorbed from the reservoir during this stroke. From this, use the classical Clausius definition to calculate the macroscopic entropy change, ΔS_{macro}.

(b) **Microscopic Statistical Mechanics:** Now, forget about heat entirely. In statistical mechanics, the number of accessible microstates Ω for an ideal gas can be separated into a spatial part (depending on volume) and a momentum part (depending on energy/temperature). Since the expansion is isothermal, the momentum part remains strictly constant. Write down the ratio of the final to initial number of accessible microstates, Ω_B/Ω_A.

(c) **The Bridge:** Use Boltzmann's entropy formula to calculate the microscopic entropy change, ΔS_{micro}. Show that it exactly matches your result from part (a).

(d) **The Full Cycle:** The engine completes the Carnot cycle by expanding adiabatically to V_C, compressing isothermally at T_C to V_D, and compressing adiabatically back to V_A. For a reversible cycle, we know macroscopically that $\oint dS = 0$. Microscopically, this implies the number of accessible states at the end of the cycle must be exactly equal to the states at the beginning. Use the adiabatic relation $TV^{\gamma-1} = \text{const}$ to prove that the ratio of volumes in the hot expansion exactly matches the ratio of volumes in the cold compression, thereby ensuring the accessible spatial microstates perfectly "reset."

Solution

(a) Macroscopic Thermodynamics

For an ideal gas, the internal energy depends only on temperature ($E = \frac{3}{2}Nk_BT$). Since the process is isothermal, $\Delta E = 0$.

By the First Law of Thermodynamics, $\Delta E = Q_{\text{in}} - W_{\text{by}} = 0$, which means the heat absorbed exactly equals the work done by the gas:

$$Q_{\text{in}} = W_{\text{by}} = \int_{V_A}^{V_B} P dV \tag{20}$$

Using the ideal gas law $P = \frac{Nk_BT_H}{V}$:

$$Q_{\text{in}} = \int_{V_A}^{V_B} \frac{Nk_BT_H}{V} dV = Nk_BT_H \ln\left(\frac{V_B}{V_A}\right) \tag{21}$$

The macroscopic entropy change is defined by the reversible heat transfer:

$$\Delta S_{\text{macro}} = \int \frac{\delta Q_{\text{rev}}}{T} = \frac{Q_{\text{in}}}{T_H} \tag{22}$$

$$\boxed{\Delta S_{\text{macro}} = Nk_B \ln\left(\frac{V_B}{V_A}\right)} \tag{23}$$

(b) Microscopic Statistical Mechanics

The total number of microstates $\Omega(E, V, N)$ for a monoatomic ideal gas is proportional to the accessible phase space volume. For N indistinguishable particles, the spatial volume contribution is simply $V^N/N!$.

Because the temperature is constant, the kinetic energy E is constant, meaning the momentum surface area (the $\int d^{3N}p$ part of the phase space) does not change. Therefore, the ratio of final microstates to initial microstates depends *only* on the spatial volume:

$$\frac{\Omega_B}{\Omega_A} = \frac{V_B^N/N!}{V_A^N/N!} = \left(\frac{V_B}{V_A}\right)^N \tag{24}$$

(c) The Bridge

Boltzmann's fundamental postulate of statistical mechanics is $S = k_B \ln \Omega$. The change in microscopic entropy is:

$$\begin{aligned}\Delta S_{\text{micro}} &= S_B - S_A \\ &= k_B \ln \Omega_B - k_B \ln \Omega_A \\ &= k_B \ln \left(\frac{\Omega_B}{\Omega_A} \right) \end{aligned} \tag{25}$$

Substitute the microstate ratio from part (b):

$$\Delta S_{\text{micro}} = k_B \ln \left[\left(\frac{V_B}{V_A} \right)^N \right] \tag{26}$$

Using the logarithm power rule ($\ln(x^N) = N \ln x$):

$$\boxed{\Delta S_{\text{micro}} = N k_B \ln \left(\frac{V_B}{V_A} \right)} \tag{27}$$

This perfectly matches the macroscopic derivation! We see that absorbing heat to do work essentially expands the physical "room" the particles have to move in, thereby exponentially increasing the number of ways the system can be arranged.

(d) The Full Cycle

For a closed thermodynamic cycle, the net change in entropy is zero ($\Delta S_{\text{total}} = 0$).

$$\Delta S_{\text{total}} = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA} = 0 \tag{28}$$

Since paths BC and DA are reversible adiabats, there is no heat exchange, and they are isentropic ($\Delta S_{BC} = \Delta S_{DA} = 0$). Therefore, the entropy gained during the hot expansion must perfectly cancel the entropy lost during the cold compression:

$$\Delta S_{AB} + \Delta S_{CD} = 0 \tag{29}$$

Using our formula from part (c), we get:

$$N k_B \ln \left(\frac{V_B}{V_A} \right) + N k_B \ln \left(\frac{V_D}{V_C} \right) = 0 \implies \ln \left(\frac{V_B}{V_A} \right) = - \ln \left(\frac{V_D}{V_C} \right) = \ln \left(\frac{V_C}{V_D} \right) \tag{30}$$

Thus, we must have:

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} \tag{31}$$

To prove this holds, we use the adiabatic relation $TV^{\gamma-1} = \text{const}$ for the two adiabatic strokes (B → C and D → A):

$$\text{Path B} \to \text{C:} \quad T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1} \tag{32}$$

$$\text{Path D} \to \text{A:} \quad T_C V_D^{\gamma-1} = T_H V_A^{\gamma-1} \tag{33}$$

Divide equation (32) by equation (33):

$$\frac{T_H V_B^{\gamma-1}}{T_H V_A^{\gamma-1}} = \frac{T_C V_C^{\gamma-1}}{T_C V_D^{\gamma-1}} \tag{34}$$

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \tag{35}$$

Taking the $1/(\gamma - 1)$ root of both sides perfectly recovers $\frac{V_B}{V_A} = \frac{V_C}{V_D}$.

Conclusion: The adiabatic mechanics of the gas force the volume ratios of the two isotherms to be equal. Because the volume ratios dictate the ratio of accessible microstates ($\Omega \propto V^N$), this mathematical reality guarantees that the number of spatial microstates stripped away from the gas during the cold compression exactly equals the number of microstates granted to the gas during the hot expansion, resetting the system for the next cycle.