

Lecture 19**Question 1.** Binomial distribution.

- (1) Please compute the number of ways to distribute 10 objects into two groups, with group 1 having $N_1 = 1$ object. Do the same computation for $N_1 = 2, 3, 4, 5, 6, 7, 8, 9$ objects, respectively. What is the value of $N_1 = N_1^*$ for the maximum number of ways of the distribution? Plot the number of ways vs. N_1 ; does this plot look like a normal distribution (i.e., Gaussian distribution)?
- (2) Compute $\ln N!$ accurately for $N = 10, 20, 30$, respectively, using your calculator or Excel. Compare these exact numerical results with the ones given by Stirling's formula (approximation); what are the percentage errors for $\ln N!$?
- (3) Let us denote the number of ways to distribute N objects (N is a huge number) into two groups, with group 1 having N_1 object, as $f(N_1)$. What is the value of $N_1 = N_1^*$ when the order of magnitude of the distribution $\ln f(N_1)$ reaches its maximum? Show the derivation.
- (4) Show that the second-order derivative of $\ln f(N_1)$ with respect to N_1 is proportional to N^{-1} at $N_1 = N_1^*$.
- (5) Show that the third-order derivative of $\ln f(N_1)$ with respect to N_1 is zero at $N_1 = N_1^*$.
- (6) Do Taylor expansion for $\ln f(N_1)$ around $N_1 = N_1^*$, and based on which, argue that we can ignore any terms higher than the second-order terms (i.e., the $(N - N_1^*)^n$ terms with $n \geq 3$).
- Hint:** Discuss the cases for which n is an odd number or an even number, respectively.
- (7) Show that $f(N_1)$ obeys a Gaussian distribution centered around $N_1 = N_1^*$. How does the width of this Gaussian distribution compare with the value of N_1^* ? Is this Gaussian distribution extremely sharp when N is a huge number so that we can ignore the values of $f(N_1)$ at all points other than $N_1 = N_1^*$?

Question 2. Microcanonical ensemble statistics.

- (1) Let us consider a mini microcanonical ensemble consisting of three ($N = 3$) two-dimensional rigid rotors. All these rigid rotors have the same moment of inertial and could be labeled, and thus, they are distinguishable. In addition, they do not interact with each other (i.e., independent). For each rigid rotor, the energy is given by $m^2 \varepsilon_0$, where the quantum number $m = 0, \pm 1, \pm 2, \pm 3$, etc., and ε_0 is the unit of energy that only depends on moment of inertial. The total energy of the system is $U = 9\varepsilon_0$.

Please write down all possible microstates and compute the total number of microstates Ω .

- (2) If the above rigid rotors are indistinguishable, what is the total number of microstates Ω ?
- (3) Entropy is an extensive thermodynamic property. Suppose we divide the whole macroscopic system (with number of particles $N \rightarrow 10^{23}$) into two macroscopic subsystems I and II. What is the relation between the total number of microstates for the whole system Ω and the number of microstates for the subsystems I and II, Ω_I and Ω_{II} ? Why?
- (4) For a microcanonical ensemble, prove that the entropy of the macroscopic system

$$S = -k_B \sum_{i=1}^{\Omega} p_i \ln p_i$$

where p_i is the probability of finding the system in the microstate i .

Hint: Principle of equal a prior probabilities for microcanonical ensemble.

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- Question 3.** Representing the macroscopic thermodynamic functions by the canonical partition function forms the foundations of applying canonical-ensemble statistical mechanics.

(1) Start from the concept of thermodynamic (internal) energy U as the ensemble average of energy,

$$U = \sum_i E_i P_i$$

where P_i is the probability of getting the state E_i in the canonical ensemble, please prove that

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

(2) By relating the macroscopic pressure p with the ensemble average of the microscopic

$$p_i = - \left(\frac{\partial E_i}{\partial V} \right)_{N,T}$$

prove

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T}$$

(3) From the macroscopic first law of thermodynamics, find the relation between U and entropy S , and then, prove that

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q$$

Hint: Integration of a derivative $df(x) = f'(x)$ is simply the original function $f(x)$ plus a constant (which could be set to zero here since the value of the constant does nothing but shift the absolute value of a thermodynamic function and has no effect on the relative change of the function in practice).

(4) The entropy in the canonical ensemble is given by (3). In addition, we know the probability distribution P_i in the canonical ensemble as well. Please prove that, for the canonical ensemble, the entropy could be represented by a function of the probability distribution P_i

$$S = -k_B \sum_{i=1}^{\text{All states}} P_i \ln P_i$$

Note: This expression has exactly the same mathematical form as the entropy in the microcanonical ensemble (See, **Question 2, (4)**). The difference is that the probability distribution in microcanonical ensemble obeys the principle of equal a priori probabilities. This result is more than just a happy coincidence. It reveals deep connections between different ensembles.

(5) The central characteristic function of the canonical ensemble is the Helmholtz free energy A , from which one could derive almost all thermodynamic functions (represented by the canonical partition function) easily. Prove that

$$A = -k_B T \ln Q$$

by using the definition of A and the results you have proved in (1) and (3).

Question 4. The canonical ensemble partition function is the summation of all quantum states

$$Q = \sum_{\text{all states } i} e^{-E_i/k_B T}$$

For a quantum system of which the energy levels may be degenerate, the canonical partition function can be written in the following equivalent form

$$Q = \sum_{\text{all energy levels } i} \Omega_i e^{-E_i/k_B T}$$

where Ω_i is the degeneracy of the N -particle quantum system at energy level E_i . Since, for the

same energy level, there are Ω_i quantum states with the same energy eigenvalue, the canonical partition function written in the form of a sum of energy levels has to include the degeneracy. For an N -particle system, Ω is a function of (N, V, E) . Therefore, one could view the microcanonical ensemble as part of the canonical ensemble in the following sense

$$Q = \sum_{\text{all energy levels } E} \Omega(N, V, E) e^{-E/k_B T}$$

Please prove that, at almost zero Kelvin (i.e., $T \sim 0$), the canonical ensemble entropy reduces to the Boltzmann entropy, namely,

$$\lim_{T \rightarrow 0} S = k_B \ln \Omega$$

Hint: At extremely low temperature, the canonical partition function is dominated by a single term.

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Question 5. Two-level system and the fancy concept of “negative” absolute temperature.

Consider N impurity atoms trapped in a solid. Each impurity can be in one of two energy levels, with energies 0 (i.e., the ground-state level) and ε (note that $\varepsilon > 0$, which is an excited-state level), respectively. The microstates of the two-level system are specified by the set of occupation numbers $\{n_i\}$, where $n_i = 0$ or 1 depending on whether the i -th impurity is in its ground state or excited. The overall energy of the N -impurity system is

$$U(\{n_i\}) = \varepsilon \sum_{i=1}^N n_i = \varepsilon N_1$$

where N_1 is the total number of excited impurities. The macroscopic system is specified by the overall energy U and the number of impurities N – we apply **microcanonical ensemble** to make predictions.

(1) As there are $N_1 = U/\varepsilon$ excited impurities, the number of microstates Ω is the number of ways of choosing N_1 excited levels among the available N . Please show that, when one has a huge number of impurities, the entropy is

$$S = -Nk_B \left[\left(\frac{U}{N\varepsilon} \right) \ln \left(\frac{U}{N\varepsilon} \right) + \left(1 - \frac{U}{N\varepsilon} \right) \ln \left(1 - \frac{U}{N\varepsilon} \right) \right]$$

(2) From the macroscopic first law of thermodynamics, find the relation between the inverse of temperature, i.e., $1/T$, and the entropy, and further prove that

$$\frac{1}{T} = -\frac{k_B}{\varepsilon} \ln \left(\frac{U}{N\varepsilon - U} \right)$$

(3) Rewrite (2) to obtain the expression of internal energy U as a function of T . Plot U vs. T , and label two critical U values εN and $\varepsilon N/2$ in this plot.

(4) It is perfectly possible to prepare the system with overall energy larger than $\varepsilon N/2$. For instance, one could excite all N impurities initially, and hence the initial overall energy is εN . The temperature for which the overall energy is between $\varepsilon N/2$ and εN can be considered as “negative”. There are physical examples of systems that are temporarily prepared at a *metastable* equilibrium of negative temperature, e.g., lasers and magnetic spins lattice.

(4a) Rationalize the existence of negative temperature for this two-level system.

(4b) Provide a physical interpretation of the negative temperature (e.g., when you have $T < 0$, what is the change of the order (or the degree of disorder) of the system when increasing overall energy? Why does a two-level system allow such a change?).

Note: Once a negative temperature system is brought into contact with the rest of the environment (or any portion of the surrounding without an upper bound in energy), it loses its

excess energy and comes to equilibrium at a positive temperature.

(5) Derive the expression for constant-volume heat capacity c_v . Plot c_v/Nk_B vs. T (for $T > 0$). Use Excel to help you by setting various values for $\varepsilon/k_B T$. Show that at high temperature, c_v is proportional to $(\varepsilon/2k_B T)^2$; and at low temperature ($T > 0$), c_v is proportional to $e^{-\varepsilon/k_B T}$. What are the zero-temperature limit ($T = 0$) and high-temperature limit of c_v ?

(6) Connection between the microcanonical and canonical ensembles.

(6a) Write down the expressions of the probability $P(n_i = 0)$ of having a particular impurity being at the ground-state level and the probability $P(n_i = 1)$ of having a single particular impurity at the excited-state level as a function of T by using the microcanonical ensemble statistics and the result in (3).

Hint: In a microcanonical ensemble, $P(n_1)$ is the unconditional probability for exciting n_1 particular impurities. That is, the total number of microstates $\Omega(E, N)$ multiplied by $P(n_1)$ gives the number of microstates in which all but n_1 selected impurities are at the ground-state level $\Omega(E - n_1 \varepsilon, N - 1)$.

(6b) Plot $P(0)$ and $P(1)$ vs. T . What is the high-temperature limit? Is the probability distribution at the high-temperature limit consistent with the maximum-entropy state in the microcanonical ensemble?

(6c) Is the probability distribution given by the canonical ensemble consistent with the one given by the microcanonical ensemble at any temperature?

Question 6. N indistinguishable and non-interacting 1D harmonic oscillators.

(1) Show that at the high-temperature limit, the molecular quantum mechanical vibrational partition function for a single 1D harmonic oscillator q^{vib} goes to the classical mechanical result, i.e., $k_B T / \omega$.

(2) Derive the vibrational internal energy U^{vib} from the quantum mechanical vibrational partition function. What is U^{vib} at $T = 0$?

(3) Derive the vibrational constant-volume heat capacity c_v from the quantum mechanical vibrational partition function.

(4) Show that at the high-temperature limit, the above c_v becomes Nk_B (classical energy equipartition principle).

Lecture 22

Question 7. Not-so-ideal gas: For N indistinguishable and non-interacting particles in the canonical ensemble, the canonical partition function is $Q = q^N / N!$. However, real-gas molecules do interact with each other. One way to think about the inclusion of the interaction in the canonical partition function is to modify the above Q to $Q = q^N f(V, T) / N!$, where $f(V, T)$ is a temperature- and volume-dependent function that characterizes intermolecular interactions. Suppose we have a not-so-ideal gas, whose macroscopic equation of state is

$$p = \frac{Nk_B T}{V} - \frac{a}{V^2}$$

where p is pressure and a is a positive constant. Please determine the function $f(V, T)$.

Question 8. Canonical ensemble statistics: Rotation of a rigid heteronuclear diatomic molecule.

(1) The quantum energy level of a rigid heteronuclear diatomic molecule is

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

where J is the rotational angular momentum quantum number ($J = 0, 1, 2, 3, \dots$), and I is the moment of inertial. For each energy level, the degeneracy is $2J + 1$ because with each J , the rotor has the projected quantum number $m_J = -J, -J+1, \dots, 0, \dots, J-1, J$.

At temperature that is not too low, it is safe to treat E_J as continuous (and so does J). Prove that the rotational partition function is

$$q_{\text{rot}} = \frac{2Ik_{\text{B}}T}{\hbar^2}$$

Hint: Replace dJ by $d[J(J+1)]$, and you will find a very easy integral to do.

(2) What is the corresponding rotational internal energy U^{rot} and the rotational constant-volume heat capacity c_v ?

(3) In a tank of N rigid diatomic molecules, N_J molecules are in the J -th rotational level. Plot the fraction N_J/N vs. temperature. (Do not forget about the energy-level degeneracy in the Boltzmann population.) What is the maximum quantum number J_{max} at which the fraction N_J/N reaches its maximum?

Question 9. Langmuir isotherms provide good descriptions of surface adsorption of ideal gases. The isotherms are very useful in heterogeneous catalysis, surface science, and materials chemistry.

Consider an ideal gas in equilibrium with the surface of a solid. Some of the molecules of the gas will be adsorbed onto the surface, and the number adsorbed will be a function of the pressure of the gas. A simple statistical mechanical model for this system is to picture the solid surface to be a two-dimensional lattice of M sites. Each of these sites can be either unoccupied or occupied by at most one of the molecules of the gas. Let the partition function of an unoccupied site be 1 and that of an occupied site be $q_{\text{site}}(T)$. We do not need to know the specific form of $q_{\text{site}}(T)$ here. Assuming that molecules adsorbed onto the lattice sites do not interact with each other, the partition function of N molecules adsorbed onto M sites is then

$$Q(N, M, T) = \frac{M!}{N!(M-N)!} [q_{\text{site}}(T)]^N$$

The binomial coefficient accounts for the number of ways of distributing the N molecules over the M sites. Let us use **canonical ensemble statistics** here – the total number of molecules (including the ones in the gas phase and the ones adsorbed on the surface), the total number of adsorption sites, system volume, and temperature are all fixed in the canonical ensemble. By using the fact that the adsorbed molecules are in equilibrium with the gas-phase molecules (considered to be an ideal gas), derive an expression for the fractional coverage, $\theta = N/M$, as a function of the pressure p of the gas, as the following:

$$\frac{1}{\theta} = 1 + \frac{1}{Kp}$$

where K is a constant at a given temperature. What is the expression (in terms of the partition function q_{site} of the adsorption sites and q of the gas-phase molecules) and the physical meaning of the constant K at a given temperature? Such an expression, that is, $\theta(p)$, is called an adsorption isotherm, and this model gives the so-called Langmuir adsorption isotherm.

Lecture 23

Question 10. Predict rate constant with transition-state theory in statistical mechanics.

The **bimolecular** gas-phase reaction $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ is of special interest because it is one of the simplest examples of an exothermic chemical reaction.

The relevant quantum mechanical properties for the reactants and the transition state structure are given in Table 1. The transition state structure F...H...H is bent with an angle of 119 degrees. The resulting three principal moments of inertia of this asymmetric rotor are given in the table. Note that the interatomic distances in the transition state structure are characteristic of an early barrier; H...H is close to its initial equilibrium bond length, and F...H is much longer than the final equilibrium bond length (which is 0.9168 Å). The vibrational frequencies (in wavenumbers) of the transition state structure are obtained from a normal-mode analysis at the saddle point on the potential energy surface. There are two real frequencies and one imaginary frequency. The imaginary frequency at $723i\text{ cm}^{-1}$ corresponds to the reaction coordinate and passage over the barrier. The frequency at 3772 cm^{-1} corresponds approximately to the H–H stretch in the complex, and the frequency at 296 cm^{-1} is the bending frequency of the non-linear complex.

In order to evaluate the electronic partition function of F ($1s^2 2s^2 2p^5$), we need to know that in its electronic ground state (with the term $^2P_{3/2}$ when the spin-orbit coupling is taken into account), the total angular momentum (orbital + spin) is $J = 3/2$, and the degeneracy is, therefore, $2J + 1 = 4$. Furthermore, **for the fluorine atom, it is necessary to include the doubly-degenerate first electronically excited state ($^2P_{1/2}$)** because its energy relative to the ground state is just $\Delta = 0.05\text{ eV}$. For H_2 ($1\sigma^2$), the total electronic angular momentum is 0, and the degeneracy is therefore 1. The electronic degeneracy of the activated complex (with an electronic state denoted by 2A , and in the special case of a linear configuration by $^2\Sigma$) is 2.

Table 1. Properties of the reactants and the transition-state structure for the F + H₂ reaction. Data are from a quantum mechanical potential energy surface.

Quantum properties	Transition state structure F...H...H	F	H ₂
$r(\text{F-H}), \text{Å}$	1.546		
$r(\text{H-H}), \text{Å}$	0.771		0.7417
$m, \text{g mol}^{-1}$	21.014	18.9984	2.016
$I_a, \text{g Å}^2 \text{mol}^{-1}$	0.173		
$I_b, \text{g Å}^2 \text{mol}^{-1}$	5.807		
$I_c, \text{g Å}^2 \text{mol}^{-1}$	5.981		
$\tilde{\nu}_1, \text{cm}^{-1}$	3772		4395.2
$\tilde{\nu}_2, \text{cm}^{-1}$	296		
$\tilde{\nu}_3, \text{cm}^{-1}$	723i (imaginary freq.)		
Electronic energy E^{elec} , hartree	-100.904859	-99.730524	-1.176817
Note: 1 hartree = 627.509 kcal mol ⁻¹			
Ground-state degeneracy (Electronic state)	2	4	1

Predict the reaction rate constant (in the unit of volume per molecule per second, which is commonly used in gas-phase kinetics, i.e., $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$) at $T = 300\text{ K}$ with the conventional transition state theory. Do not forget about the rotational symmetry number in the rotational partition function of H₂ molecule. Compare your prediction with the experimentally measured rate constant at 300 K: $2.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (reported in *J. Chem. Phys.*, 1980, 92, 4811). What is the percentage error of your prediction as compared to the measurement? Please note that the experiment has an error bar of about $\pm 0.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, which means the intrinsic uncertainty of the measurement is about 17%.