10.1 Adsorption kinetics. Let us consider the Langmuir isotherm within reaction kinetics. The reaction is

\[
\text{[empty site]} + \text{[molecule in vapor phase]} \xleftrightarrow[k_a, k_d]{\frac{k_a}{k_d}} \text{[occupied site]}
\]

Let \( k_a \) and \( k_d \) be the rate constants of the forward and reverse reactions. The surface has \( N \) sites, and we define \( \theta \) as we did in Eq. (10.6).

(1) We denote the concentration of molecules in the vapor phase by \([M]\). The “concentrations” of the empty sites and occupied sites can be expressed as \( N(1-\theta) \) and \( N\theta \), respectively. Balance the forward and reverse rates.

(2) Express \( \theta \) with \( k_a \) and \( k_d \).

(3) Assume an ideal gas law for the vapor phase to express \( \theta \) as a function the pressure \( p \).

(4) How is \( k_d/k_a \) related to \( q \) defined by Eq. (10.9)?

\[
\begin{align*}
(1) & \quad k_a N \left(1 - \theta\right)[M] = k_d N\theta \\
(2) & \quad \theta = \frac{k_a [M]}{k_d + k_a [M]} = \frac{1}{1 + \frac{k_d}{k_a} \left(\frac{1}{M}\right)} \\
(3) & \quad p = [M]RT. \text{ Therefore,} \\
& \quad \theta = \frac{1}{1 + \frac{k_d RT}{k_a p}} = \frac{k_a p}{k_d RT + k_a p} \\
(4) & \quad \frac{k_d}{k_a} = \frac{q e^{-\beta e}}{RT} \\
& \quad \text{which is further rewritten to} \\
& \quad \frac{k_d}{k_a} = \frac{e^{-\beta e}}{N_A A_T^3}
\end{align*}
\]
10.2 Microcalorimetry. Section 10.2 considered a surface with $N$ adsorption sites in contact with vapor-phase molecules of chemical potential $\mu$. The surface lowers the energy per site by $\varepsilon$ when it captures a molecule.

(1) Calculate the mean of the energy of the surface, $\langle E \rangle$.

(2) The chemical potential of a molecule in the vapor of pressure $p$ is given by Eq. (6.40). Express $\langle E \rangle$ as a function of $p$ and $T$.

(3) What is the high-temperature asymptote of $\langle E \rangle$?

(4) Draw a sketch for a plot of $\langle E \rangle/(N\varepsilon)$ as a function of $T$.

(5) Calculate the heat capacity $C$ of the surface. Draw a sketch for a plot of $C$ as a function of $T$.

\[
\langle E \rangle = -\varepsilon \langle n \rangle = -\frac{N\varepsilon}{1 + e^{-\beta(\mu + \varepsilon)}}
\]

\[
\langle E \rangle = \frac{-N\varepsilon}{1 + \frac{k_B T}{p} \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} e^{-\beta \varepsilon}}
\]

(3) At high temperatures, $e^{-\beta \varepsilon} \approx 1$. Therefore,

\[
\langle E \rangle \approx \frac{-N\varepsilon}{1 + \frac{k_B T}{p} \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \approx -\frac{N\varepsilon p}{k_B T} \left( \frac{h^2}{2\pi mk_B T} \right)^{3/2}}
\]

(4)
10.3 Maximizing fluctuation. Show that the fluctuations in the surface coverage in the Langmuir isotherm maximizes when \( \theta = \frac{1}{2} \).

The variance of \( n \) is calculated according to

\[
\langle \Delta n^2 \rangle = \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial \mu^2} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \langle n \rangle
\]

With Eq. (10.5), the variance is calculated as

\[
\langle \Delta n^2 \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \frac{N}{1 + e^{-\beta(\mu + \varepsilon)}} = \frac{Ne^{-\beta(\mu + \varepsilon)}}{[1 + e^{-\beta(\mu + \varepsilon)}]^2}
\]

Since

\[ e^{-\beta(\mu + \varepsilon)} = \frac{N}{\langle n \rangle} - 1 \]

we obtain

\[
\langle \Delta n^2 \rangle = \frac{\langle n \rangle (N - \langle n \rangle)}{N}
\]

which maximizes when \( \langle n \rangle = \frac{1}{2} N \).
10.4 Maximizing entropy. This problem continues on what we learned in the Langmuir isotherm.

(1) Find the entropy $S$ of the surface in the Langmuir adsorption model. Express $S/(Nk_B)$ as a function of $x = e^{\beta(\mu+\varepsilon)}$.

(2) Draw a sketch for a plot of $S/(Nk_B)$ as a function of $x$. Find when $S$ maximizes.

(1) Since

$$\langle E \rangle = -e \langle n \rangle$$

the entropy is expressed as

$$S = k_B \left[ \ln Z + \beta \left( \langle E \rangle - \mu \langle n \rangle \right) \right] = k_B \left[ \ln Z - \beta \left( \varepsilon + \mu \right) \langle n \rangle \right]$$

With Eqs. (10.2) and (10.5), it is rewritten to

$$\frac{S}{Nk_B} = \ln \left( 1 + e^{\beta(\mu+\varepsilon)} \right) - \frac{\beta(\mu+\varepsilon)}{1 + e^{-\beta(\mu+\varepsilon)}}$$

Therefore

$$\frac{S}{Nk_B} = f(x) = \ln (1 + x) - \frac{x \ln x}{1 + x}$$

(2)

$$f'(x) = -\frac{\ln x}{(1 + x)^2}$$

$f(x)$ increases with $x$ when $x < 1$ and decreases with $x$ when $x > 1$. $f(x)$ maximizes to $\ln 2$ when $x = 1$. 

![Graph of S/(Nk_B) vs x = e^{\beta(\mu+\varepsilon)}]
**10.5 BET adsorption.** Section 10.3 used the result of the Langmuir isotherm in layer-by-layer adsorption to derive the BET isotherm. Here, we treat it directly in the grand canonical ensemble. Each of the \( N \) sites of the surface adsorbs molecules independently. We denote by \( i_j \) the number of molecules on the \( j \)th site (\( j = 1, \ldots, N \)). The energy \( \varepsilon(i_j) \) of the site follows the following table.

<table>
<thead>
<tr>
<th>( i_j )</th>
<th>Energy, ( \varepsilon(i_j) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>(-\varepsilon_1)</td>
</tr>
<tr>
<td>2</td>
<td>(-\varepsilon_1-\varepsilon_L)</td>
</tr>
<tr>
<td>3</td>
<td>(-\varepsilon_1-2\varepsilon_L)</td>
</tr>
<tr>
<td>4</td>
<td>(-\varepsilon_1-3\varepsilon_L)</td>
</tr>
<tr>
<td>( \vdots )</td>
<td>( \vdots )</td>
</tr>
</tbody>
</table>

The surface is in contact with a reservoir of molecules of chemical potential \( \mu \) at temperature \( T \).

1. The state of the \( n \) sites on the surface is specified by \( i_1, i_2, \ldots, i_N \). Write the grand partition function \( Z \) for the system and calculate \( Z \).

2. Derive a formula to calculate the mean number of molecules adsorbed per site, \( \langle i \rangle \), and calculate it. Confirm that it is identical to the result we obtained in Section 10.3.

3. Derive a formula to calculate the mean number of liquefied molecules per site, \( \langle i_{L} \rangle \), and calculate it. Liquefied molecules are those in the second, third, \( \ldots \), layers.

4. What is the fraction of empty sites, \( \theta_{\text{empty}} \)?

5. Use \( e^{-\beta \mu} = q/p \) to rewrite your answer in (4). What is the low-pressure asymptote of \( \theta_{\text{empty}} \)?

\[
Z = \sum_{i_1} \sum_{i_2} \cdots \sum_{i_N} \exp \left( \beta \mu \sum_{j=1}^{N} i_j - \beta \sum_{j=1}^{N} \varepsilon(i_j) \right)
\]
Since each site is independent, it is rewritten to

\[
Z = \left[ \sum_i e^{\beta(\mu - \varepsilon(i))} \right]^N
\]

where

\[
\sum_i e^{\beta(\mu - \varepsilon(i))} = 1 + \exp(\beta(\mu + \varepsilon_1)) + \exp(\beta(2\mu + \varepsilon_1 + \varepsilon_L)) + \exp(\beta(3\mu + \varepsilon_1 + 2\varepsilon_L)) \\
+ \exp(\beta(4\mu + \varepsilon_1 + 3\varepsilon_L)) + \cdots = 1 + \frac{\exp(\beta(\mu + \varepsilon_1))}{1 - \exp(\beta(\mu + \varepsilon_L))} = 1 + \frac{\exp(\beta\varepsilon_1)}{e^{-\beta\mu} - \exp(\beta\varepsilon_L)}
\]

Therefore,

\[
\mathcal{Z} = \left[ 1 + \frac{\exp(\beta\varepsilon_1)}{e^{-\beta\mu} - \exp(\beta\varepsilon_L)} \right]^N
\]

(2)

\[
\ln Z = N \ln \left( 1 + \frac{\exp(\beta\varepsilon_1)}{e^{-\beta\mu} - \exp(\beta\varepsilon_L)} \right)
\]

\[
\langle i \rangle = \frac{1}{N} \left\langle \sum_{j=1}^N i_j \right\rangle = \frac{1}{N} \frac{\partial \ln Z}{\partial \mu} = \frac{1}{N} \frac{\beta \exp(\beta\varepsilon_1) e^{-\beta\mu}}{\left[ e^{-\beta\mu} - \exp(\beta\varepsilon_L) \right]^2} \\
\frac{1}{1 + \frac{\exp(\beta\varepsilon_1)}{e^{-\beta\mu} - \exp(\beta\varepsilon_L)}} \\
= \frac{1}{e^{-\beta\mu} - \exp(\beta\varepsilon_L)} \times \frac{\exp(\beta\varepsilon_1) e^{-\beta\mu}}{e^{-\beta\mu} - \exp(\beta\varepsilon_L) + \exp(\beta\varepsilon_1)}
\]

Since \(e^{\beta\mu} = q/p\), we find that this equation is identical to Eq. (10.24).

(3)
The number of molecules in the first layer is

\[
\langle i \rangle_L = \frac{1}{N} \left( \sum_{j=1, j \neq 2}^{N} (i_j - 1) \right) = \frac{1}{N \beta} \frac{\partial \ln Z}{\partial \varepsilon_L} = \frac{1}{N \beta} \frac{\beta \exp(\beta \varepsilon_i) \exp(\beta \varepsilon_L)}{\left[ e^{-\beta \mu} - \exp(\beta \varepsilon_L) \right]^2 + \frac{\exp(\beta \varepsilon_i)}{e^{-\beta \mu} - \exp(\beta \varepsilon_L) + \exp(\beta \varepsilon_i)}}
\]

\[
= \frac{1}{e^{-\beta \mu} - \exp(\beta \varepsilon_L)} \times \frac{\exp(\beta \varepsilon_i) \exp(\beta \varepsilon_L)}{e^{-\beta \mu} - \exp(\beta \varepsilon_L) + \exp(\beta \varepsilon_i)}
\]

(4) The number of molecules in the first layer is

\[
\langle i \rangle - \langle i \rangle_L = \frac{\exp(\beta \varepsilon_i)}{e^{-\beta \mu} - \exp(\beta \varepsilon_L) + \exp(\beta \varepsilon_i)}
\]

Then,

\[
\theta_{\text{empty}} = 1 - \left( \langle i \rangle - \langle i \rangle_L \right) = \frac{e^{-\beta \mu} - \exp(\beta \varepsilon_L)}{e^{-\beta \mu} - \exp(\beta \varepsilon_L) + \exp(\beta \varepsilon_i)}
\]

(5)

\[
\theta_{\text{empty}} = \frac{q / p - \exp(\beta \varepsilon_L)}{q / p - \exp(\beta \varepsilon_L) + \exp(\beta \varepsilon_i)} = \frac{q - p \exp(\beta \varepsilon_i)}{q + p \left[ \exp(\beta \varepsilon_i) - \exp(\beta \varepsilon_L) \right]}
\]

At low pressures,

\[
\theta_{\text{empty}} \approx 1 - \frac{p}{q} \exp(\beta \varepsilon_i)
\]

which is equivalent to the low-pressure asymptote of the Langmuir isotherm.

---

10.6 Pressure dependence in the BET isotherm. Show that \( \langle n_{\text{ads}} \rangle \) increases when \( p \) increases (\( p < p^* \)) in Eq. (10.27).

\[
\frac{N_c}{\langle n_{\text{ads}} \rangle} = \frac{p^* - p}{p} + (c - 1) \frac{p^* - p}{p} = c - 2 + \frac{p^*}{p} - (c - 1) \frac{p}{p^*}
\]

\[
\frac{\partial}{\partial p} \frac{N_c}{\langle n_{\text{ads}} \rangle} = -\frac{p^*}{p^2} - (c - 1) \frac{1}{p^*} = -\frac{p^{*2} - p^2 + cp^2}{p^2 p^*}
\]
Since $c > 0$, the derivative is negative for $p < p^*$. $\langle n_{\text{ads}} \rangle$ increases with an increasing $p$.

10.7 Competitive adsorption. A surface of $n$ sites is in contact with a mixture of gas A and B. Each site can adsorb up to one molecule, either A or B. When the site adsorbs molecule $i$ ($i = A, B$), its energy is lowered by $\varepsilon_i$ ($\varepsilon_i > 0$). The chemical potential of molecule $i$ is $\mu_i$. Let $n_A$ and $n_B$ be the numbers of sites that have A molecules and B molecules, respectively.

(1) What is the grand partition function?

(2) Find $\langle n_A \rangle$ and $\langle n_B \rangle$.

(3) As we did for the Langmuir isotherm of pure monatomic gas, we introduce $q_i$ by $p_i/q_i = \exp(\beta \mu_i)$.

where $p_i$ is the partial pressure of component $i$. Rewrite your answers in (2) using $y_A \equiv (p_A/q_A)\exp(\beta \varepsilon_A)$ and $y_B \equiv (p_B/q_B)\exp(\beta \varepsilon_B)$.

(1) The number $W$ of ways to arrange $n_A$ molecules of A and $n_B$ molecules of B on the surface of $n$ sites is given as

$$W = \frac{n!}{n_A!n_B!(n-n_A-n_B)!}$$

The grand partition function is

$$Z = \sum_{n_A=0}^{n} \sum_{n_B}^{n-n_A} \exp(\beta \mu_A n_A + \beta \mu_B n_B) \frac{n!}{n_A!n_B!(n-n_A-n_B)!} \exp(\beta n_A \varepsilon_A + \beta n_B \varepsilon_B)$$

With a multinomial theorem,

$$Z = \left[1 + \exp(\beta (\mu_A + \varepsilon_A)) + \exp(\beta (\mu_B + \varepsilon_B))\right]^n$$

(2)

$$\ln Z = n \ln \left(1 + \exp(\beta (\mu_A + \varepsilon_A)) + \exp(\beta (\mu_B + \varepsilon_B))\right)$$
10.8 Diatomic molecules. This problem considers adsorption of diatomic molecules of mass $m$ onto a surface that consists of $N$ adsorption sites. The molecules in the reservoir (single-molecule partition function is $Z_{1F}$) are in contact with the surface. The molecule occupies one of the sites when adsorbed, and the single-molecule partition function changes to $Z_{1A}$.

(1) First, we consider $M$ molecules in the reservoir of volume $V$. The $Z_{1F}$ is given as

$$Z_{1F} = V \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} Z_{1Frv}$$

where $Z_{1Frv}$ is the roto-vibrational part of $Z_{1F}$. What is the chemical potential $\mu$?

(2) Now, we consider the system of adsorbed molecules. Express the grand partition function $Z$ of the system using $\mu$. What is the surface coverage $\theta$?

(3) We can express $Z_{1Frv}$ as $Z_{1Frv} = (T/\Theta)Z_{1Fv}$, where $Z_{1Fv}$ is the vibrational part of $Z_{1F}$. Likewise, we can write $Z_{1A}$ as $Z_{1A} = Z_{1Av}e^{\epsilon}$, where $Z_{1Av}$ is the vibrational part of $Z_{1A}$, and adsorption lowers the energy by $\epsilon$. We assume, for simplicity, that the adsorbed molecule retains the same vibrational degree of freedom as the molecule in free space. Use these relationships to express $\theta$.

(1) The partition function of the system is
Let \( n \) be the number of adsorbed molecules.

\[
Z = \frac{Z_{1F}^M}{M!} = \frac{V^M}{M!} \left( \frac{2\pi m}{\beta h^2} \right)^{3M/2} Z_{1Fr}^M
\]

\[
F = -Mk_B T \left( -\ln M + 1 + \ln V + \frac{3}{2} \ln \frac{2\pi m}{\beta h^2} + \ln Z_{1Fr} \right)
\]

\[
\mu = -k_B T \left( -\ln M + \ln V + \frac{3}{2} \ln \frac{2\pi m}{\beta h^2} + \ln Z_{1Fr} \right)
\]

\[
e^{-\beta\mu} = \frac{V}{M} \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} Z_{1Fr} = \frac{k_B T}{p} \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} Z_{1Fr}
\]

(2) Let \( n \) be the number of adsorbed molecules.

\[
Z = \sum_{n=0}^{N} e^{\beta\mu n} \left( \frac{N}{n} \right) Z_{1A}^n = \left( 1 + e^{\beta\mu} Z_{1A} \right)^N
\]

\[
\ln Z = N \ln \left( 1 + e^{\beta\mu} Z_{1A} \right)
\]

\[
\theta = \frac{\langle n \rangle}{N} = \frac{1}{N} \frac{\partial \ln Z}{\partial \mu} = \frac{e^{\beta\mu} Z_{1A}}{1 + e^{\beta\mu} Z_{1A}} = \frac{1}{1 + e^{-\beta\mu} / Z_{1A}}
\]

(3)

\[
\theta = \frac{1}{1 + \frac{1}{\beta p} \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \frac{T}{\Theta_r} e^{-\beta\epsilon}}
\]

10.9 Adsorption of two particles. Consider a system that has \( N \) adsorption sites. Each site can adsorb one particle or more. The site acquires energy \( \epsilon \) each time it adsorbs a particle. The particles are indistinguishable.

(1) Two particles are on the \( N \) sites. If they do not interact, what is the partition function of the system?

(2) If the two particles interact and the interaction \( \Phi \) exists for the two particles sharing a site, what is the partition function of the system? Also calculate the mean energy.
The two particles are either on the same site or on different sites. If they share a site, there are $N$ possibilities. If they do not, and the number of ways to arrange two indistinguishable particles in $N$ sites is $\frac{1}{2}N(N-1)$. Their sum is $\frac{1}{2}N(N+1)$. The energy of the system is $2\beta\epsilon$, regardless of whether they share a site or not. Therefore,

$$Z = \frac{N(N+1)}{2}e^{-2\beta\epsilon}$$

(2)

$$Z = Ne^{-\beta(2\epsilon+\Phi)} + \frac{N(N-1)}{2}e^{-2\beta\epsilon}$$

$$\ln Z = \ln N - 2\beta\epsilon + \ln\left(\frac{N-1}{2} + e^{-\beta\Phi}\right)$$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = 2\epsilon + \frac{\Phi e^{-\beta\Phi}}{N-1} + e^{-\beta\Phi} = 2\epsilon + \frac{\Phi}{1 + \frac{N-1}{2}e^{\beta\Phi}}$$