

From Partition Functions to Thermodynamic Observables

PHAS0076:

TYC Materials Modelling

Academic Year 2018-2019

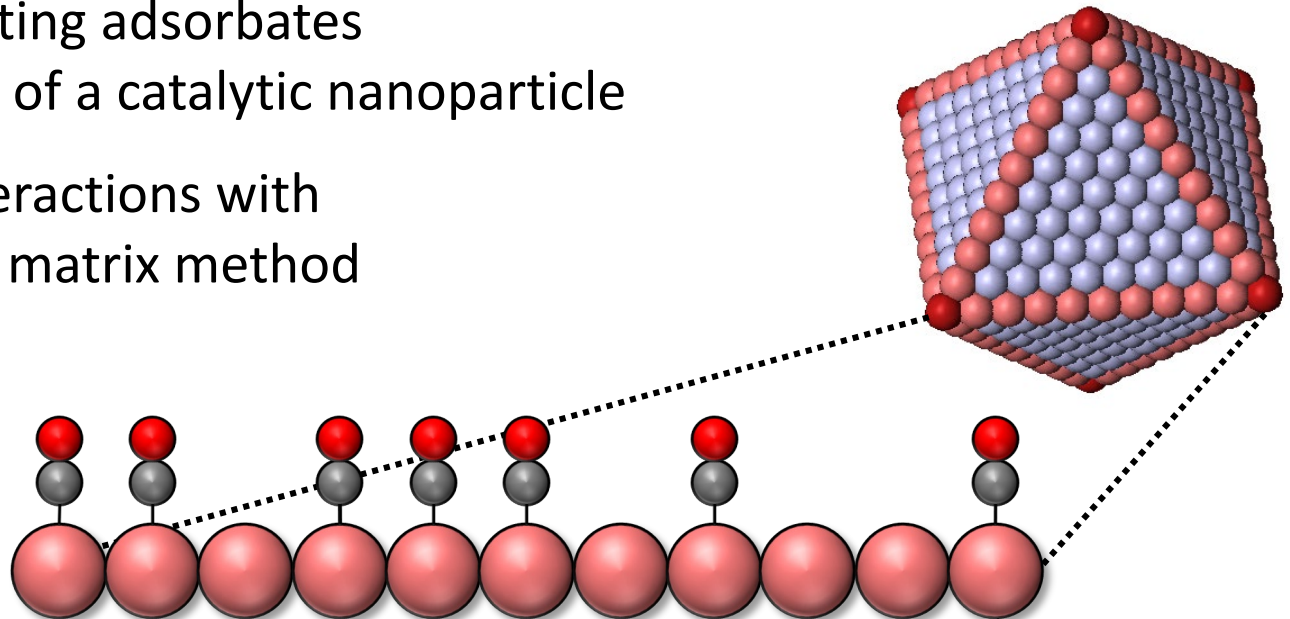
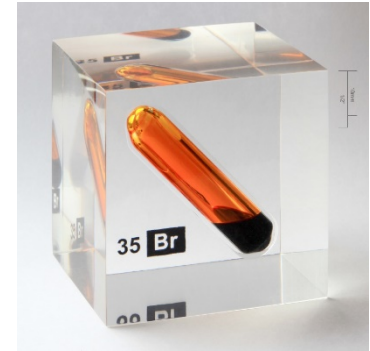
Dr Michail Stamatakis

- We would like to employ statistical-mechanical arguments to obtain thermodynamic expressions for systems such as:
 - Monoatomic ideal gas
 - Diatomic ideal gas
 - Adsorbates on the edge of a catalytic nanoparticle
(in the absence versus in the presence of lateral interactions)
- We will employ a common methodology:
 - Start from a Hamiltonian, giving energies of microstates
 - Choose an ensemble
 - Perform appropriate averaging operations

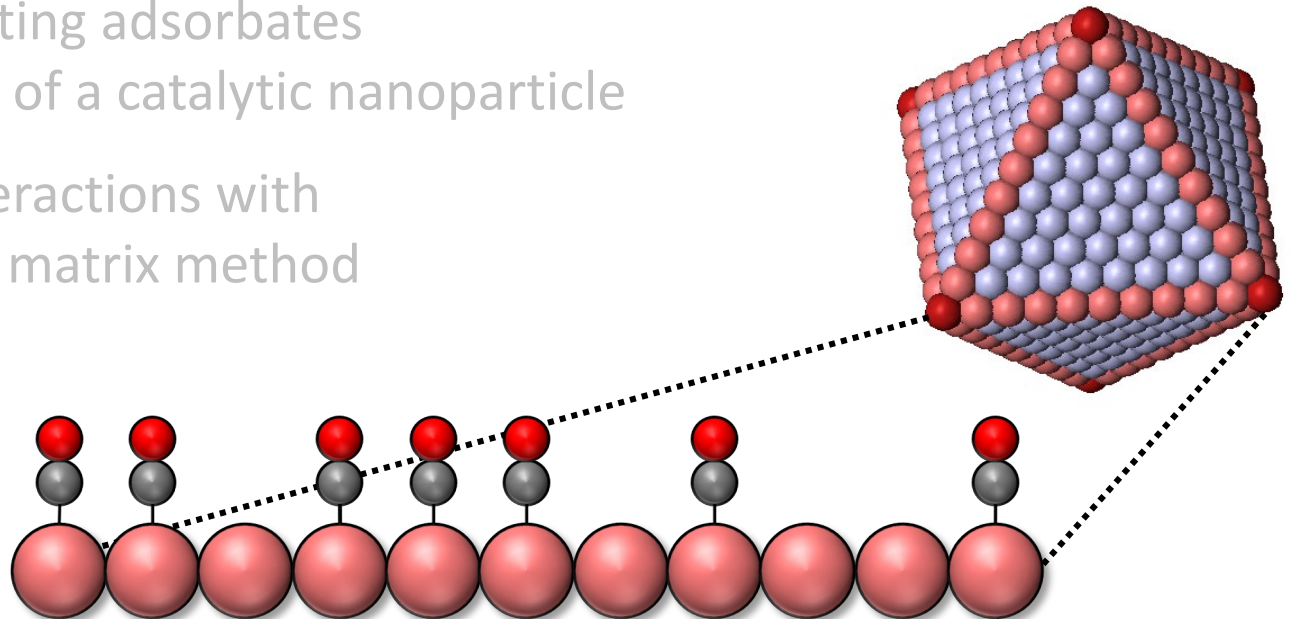
Outline

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- Statistical Mechanics of Ideal Gases
 - Monoatomic
 - Polyatomic (with focus on diatomic)
- Statistical Mechanics of Condensed Matter
 - Non-interacting adsorbates on the edge of a catalytic nanoparticle
 - Treating interactions with the transfer matrix method

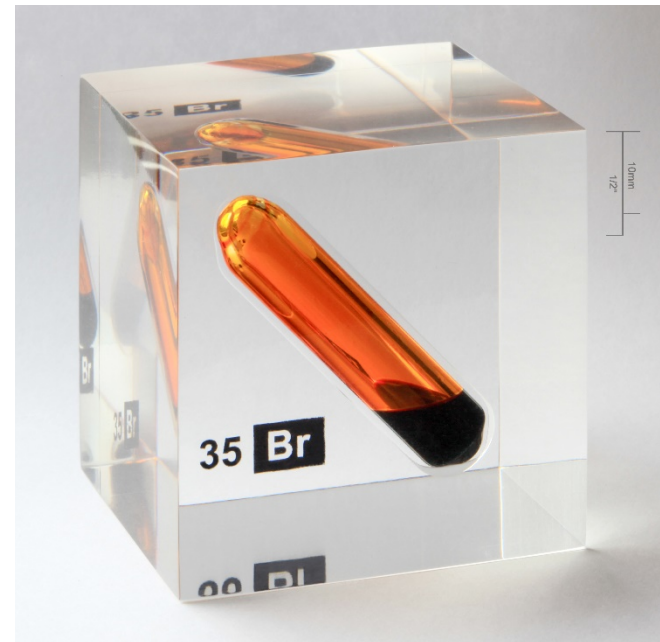


- **Statistical Mechanics of Ideal Gases**
 - **Monoatomic**
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Thermodynamics of Ideal Gases

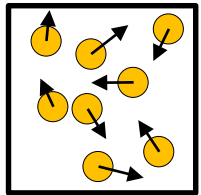
- We will consider the two cases of **monoatomic** and **diatomic** gases. We would like to derive:
 - the **ideal gas law** from statistical mechanics principles
 - equations for the **heat capacities** of such gases...



Monoatomic Gas

- The Hamiltonian for a classical gas with N molecules is:

$$\mathcal{H}(\mathbf{s}) = \underbrace{\sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m_i}}_{\text{kinetic energy}} + \underbrace{\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}_{\text{potential energy}}$$



- We choose to work in the Canonical Ensemble (N, V, T) for which the *classical partition function* is:

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int \dots \int \dots \int \dots \int \exp\left(-\frac{\mathcal{H}(\mathbf{s})}{k_B T}\right) d^3\mathbf{p}_1 \dots d^3\mathbf{p}_N \dots d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N$$

- The $N!$ factor arises because the particles are indistinguishable.
- The h^{3N} factor gives an approximate count of quantum states and makes the integral dimensionless.

Partition Function for Monoatomic Gas

- How can we evaluate this integral? Break it into 2 terms:

$$Q = \underbrace{\frac{1}{N! h^{3N}} \int \dots \int \exp \left(-\frac{1}{k_B T} \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m_i} \right) d^3 \mathbf{p}_1 \dots d^3 \mathbf{p}_N}_{\text{kinetic energy term}} \underbrace{\int \dots \int \exp \left(-\frac{\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{k_B T} \right) d^3 \mathbf{r}_1 \dots d^3 \mathbf{r}_N}_{\text{configuration integral}}$$

- For ideal gases $\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0 \Rightarrow$ config. integral \propto volume^N
 - For non-ideal gases, liquids, or solids evaluating the configuration integral requires simulation.
- Thus, assuming ideal gas, the partition function becomes:

$$Q_{\text{ideal gas}} = \frac{V^N}{N! h^{3N}} \int \dots \int \prod_{i=1}^N \exp \left(-\frac{|\mathbf{p}_i|^2}{2m_i k_B T} \right) d^3 \mathbf{p}_1 \dots d^3 \mathbf{p}_N$$

Partition Function for Monoatomic Ideal Gas

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- All particles are the same ($m_i = m \forall i = 1, \dots, N$):

$$Q_{\text{ideal gas}} = \frac{V^N}{N! h^{3N}} \left[\int \exp\left(-\frac{|\mathbf{p}_1|^2}{2mk_B T}\right) d^3 \mathbf{p}_1 \right]^N \Rightarrow$$

$$Q_{\text{ideal gas}} = \frac{V^N}{N! h^{3N}} \left[\iiint \exp\left(-\frac{p_{1,x}^2 + p_{1,y}^2 + p_{1,z}^2}{2mk_B T}\right) dp_{1,x} dp_{1,y} dp_{1,z} \right]^N$$

- The space is isotropic, therefore integrals in the x, y, z directions are the same:

$$Q_{\text{ideal gas}} = \frac{V^N}{N! h^{3N}} \left[\int \exp\left(-\frac{p_{1,x}^2}{2mk_B T}\right) dp_{1,x} \right]^{3N}$$

Partition Function for Monoatomic Ideal Gas

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- Need to evaluate the integral in the final expression...

$$Q_{\text{ideal gas}} = \frac{V^N}{N! h^{3N}} \left[\int_{-\infty}^{\infty} \exp\left(-\frac{p_{1,x}^2}{2mk_B T}\right) dp_{1,x} \right]^{3N}$$

– but from mathematics: $\int_{-\infty}^{\infty} \exp(-\xi^2) d\xi = \sqrt{\pi} \quad \Rightarrow$

$$\int_{-\infty}^{\infty} \exp\left(-\frac{\zeta^2}{c}\right) d\zeta \stackrel[\substack{\frac{\zeta}{\sqrt{c}} = \xi \\ d\zeta = \sqrt{c} \cdot d\xi}]{=} \sqrt{c} \int_{-\infty}^{\infty} \exp(-\xi^2) d\xi = \sqrt{c} \pi \quad \Rightarrow$$

$$Q_{\text{ideal gas}} = \frac{V^N}{N! h^{3N}} (2\pi m k_B T)^{\frac{3N}{2}} = \frac{V^N}{N! h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

Thermal Energy & Pressure of Monoatomic Ideal Gas⁹

- Thermal energy from the canonical ensemble formula:

$$\langle E \rangle = - \frac{\partial \log Q}{\partial \beta} \bigg|_{N,V} = - \frac{\partial}{\partial \beta} \log \left(\frac{V^N}{N! h^{3N}} \left(\frac{2 \pi m}{\beta} \right)^{\frac{3N}{2}} \right) \Rightarrow$$

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \log \left(\text{const.} \beta^{-\frac{3N}{2}} \right) = \frac{3N}{2\beta} = \frac{3}{2} N k_B T$$

Recall: heat capacity of ideal monoatomic gas: $C_v = \frac{3}{2} R = \frac{3}{2} k_B N_A$

- Pressure from the canonical ensemble formula:

$$p = k_B T \frac{\partial \log Q}{\partial V} \bigg|_{N,T} = k_B T \frac{N}{V} \Rightarrow pV = \frac{N}{N_A} R T \quad \text{We recovered the ideal gas law!}$$

Entropy of Ideal Monoatomic Gas

- Recall from thermodynamics that: $S = -\left.\frac{\partial A}{\partial T}\right|_{N,V}$
- Therefore:
$$S = \frac{\partial}{\partial T} \left[k_B T \log \left(\frac{V^N}{N! h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \right) \right]$$
- The differentiation will yield two terms; we focus on the “difficult one” first:

$$k_B T \frac{\partial}{\partial T} \left[\log \left(\frac{V^N}{N!} \left(\frac{2\pi m k_B}{h^2} \right)^{\frac{3N}{2}} \right) + \frac{3N}{2} \log(T) \right] = \frac{3}{2} N k_B$$

Entropy of Ideal Monoatomic Gas

- Therefore, going back to the entropy formula:

$$S = k_B \log \left(\frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \right) + \frac{3}{2} N k_B$$

- Invoking Stirling's approximation: $\log(N!) \approx N \log(N) - N$

$$\frac{S}{k_B} = -N \log(N) + N + N \log \left(V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \right) + \frac{3}{2} N \Rightarrow$$

$$\frac{S}{N k_B} = \log \left(\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2}$$

Sackur–Tetrode equation
for the entropy of ideal
monoatomic gas

Chemical Potential of Monoatomic Ideal Gas

- Recall from thermodynamics that: $\mu = \left. \frac{\partial A}{\partial N} \right|_{V,T}$

- Therefore: $\mu = -k_B T \frac{\partial}{\partial N} \log \left[\frac{V^N}{N! h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \right] \Rightarrow$

$$\mu = -k_B T \frac{\partial}{\partial N} \left[-\log(N!) + N \log(V) + \frac{3N}{2} \log \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

- Invoking Stirling's approximation: $\log(N!) \approx N \log(N) - N$

$$\mu = -k_B T \frac{\partial}{\partial N} \left[-N \log(N) + N + N \log(V) + \frac{3N}{2} \log \left(\frac{2\pi m k_B T}{h^2} \right) \right] \Rightarrow$$

$$\mu = -k_B T \left[-\log(N) + \log(V) + \frac{3}{2} \log \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

Chemical Potential of Monoatomic Ideal Gas

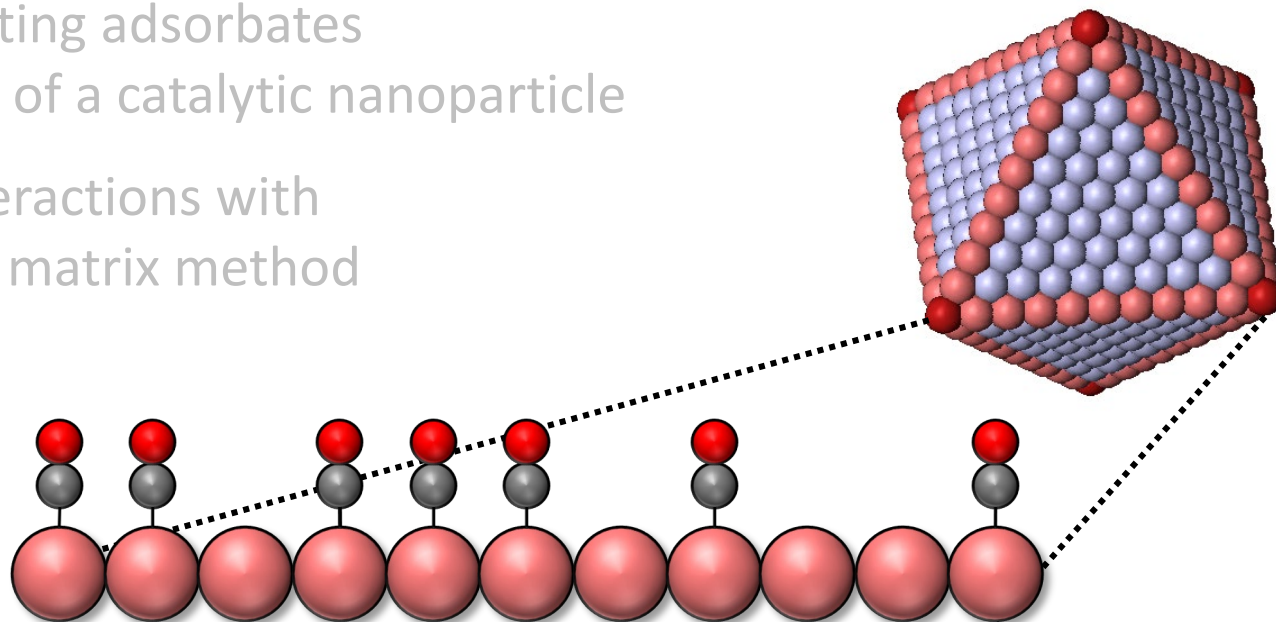
- We have thus found:
$$\mu = k_B T \log \left[\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} \right]$$
- By making use of the ideal gas law, we see that for constant temperature, the chemical potential scales with $\log(p)$

$$\mu = k_B T \log \left[\frac{p}{k_B T} \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} \right]$$

We will come back to this scaling later (on slide 31), when we talk about adsorbates on the edge of a catalytic nanoparticle...

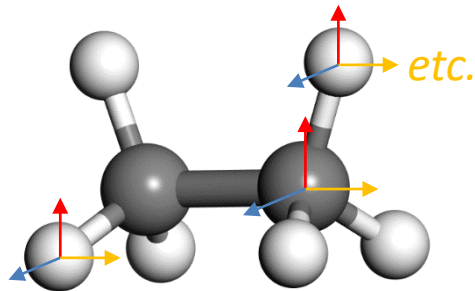
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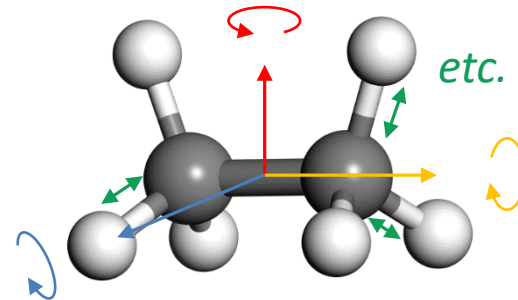


Polyatomic Gas

- Turning our attention to **polyatomic** molecules, note that
 - the configurational part of this molecule's microstate contains information about the position of all its atoms



$3 \cdot m$ positions of atoms ($m=6$)



3 translational DoF

3 rotational DoF

$3 \cdot m - 3$ vibrational DoF

- equally well we can represent the configuration using other degrees of freedom (DoF):
 - ✓ position of the centre of mass (translational DoF)
 - ✓ angles of rotation with respect to x, y, z axes (rotational DoF)
 - ✓ internal coordinates (vibrational DoF)

Polyatomic Ideal Gas

- To a very good approximation these DoF are decoupled, thus, the partition function for a single molecule can be written as:


$$Q_{\text{polyatomic ideal gas}}^{1 \text{ molecule}} = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}}$$

and for a population of N molecules:

$$Q_{\text{polyatomic ideal gas}} = \frac{1}{N!} \left(Q_{\text{polyatomic ideal gas}}^{1 \text{ molecule}} \right)^N$$

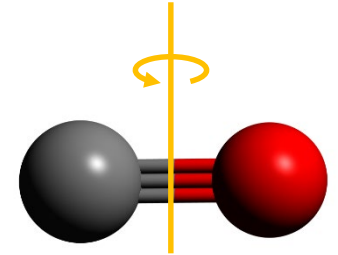
- No interactions
- Indistinguishable molecules

- We've already learned the translational partition function!
- We will now look into the rotational and vibrational parts focusing on a diatomic molecule (3 trans., 2 rot., 1 vib.)

 Homework: would the ideal gas equation (which we recovered on slide 7 for monoatomic gas) still hold? Prove your assertion...

Rotational Partition Function of Diatomic Gas ¹⁷

- We will treat this as a quantum rigid rotor...
- The energy levels and degeneracies are:



$$E_{\ell} = \frac{\hbar^2}{2I} \ell(\ell + 1) \quad g_{\ell} = 2\ell + 1$$

- The rotational *quasi-partition function* is therefore:

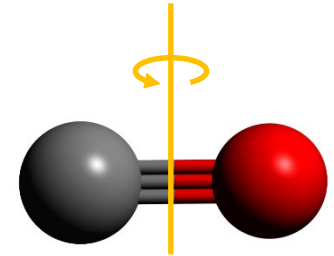
$$q_{\text{rot}} = \sum_{\ell \geq 0} g_{\ell} \exp(-\beta E_{\ell})$$

- Treating this sum is not easy. We can convert it to an integral by making the assumption that the spacing between energy levels are small compared to $k_B T$.
 - Usually a good approximation, except for hydrogen...

Rotational Partition Function of Diatomic Gas

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- The rotational quasi-partition function is then approximated as:



$$q_{\text{rot}} \approx \int_0^{\infty} (2\ell + 1) \exp\left(-\frac{\beta \hbar^2}{2I} \ell(\ell + 1)\right) d\ell$$

$$\stackrel{\substack{\xi = \ell(\ell+1) \\ d\xi = (2\ell+1)d\ell}}{=} \int_0^{\infty} \exp\left(-\frac{\beta \hbar^2}{2I} \xi\right) d\xi = \frac{2I}{\beta \hbar^2} = \frac{2Ik_B T}{\hbar^2}$$

- One can define a rotational temperature θ_{rot} :

$$\theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B} \Rightarrow q_{\text{rot}} = \frac{T}{\theta_{\text{rot}}}$$

- Note: for homonuclear diatomics $q_{\text{rot}} = \frac{T}{2\theta_{\text{rot}}} \text{ (symmetry number)}$

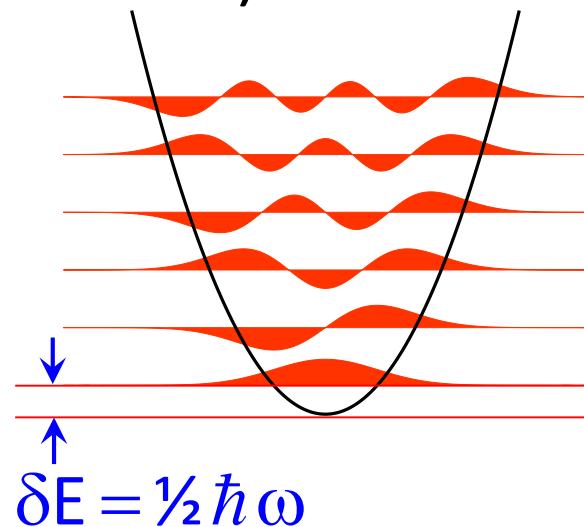
Vibrational Partition Function of Diatomic Gas

- We will treat this as a quantum harmonic oscillator...
- The energy levels (which are non-degenerate) are:

$$E_v = \hbar \omega \left(v + \frac{1}{2} \right)$$

– Note that we have used the bottom of the “well” as the reference energy

– The difference between the energy at the bottom of the well and the first (vibrationally) excited state is termed the **zero-point energy correction**



- The vibrational quasi-partition function is therefore:

$$q_{\text{vib}} = \sum_{v \geq 0} \exp(-\beta E_v)$$

Vibrational Partition Function of Diatomic Gas²⁰

- After substituting the energy levels:

$$q_{\text{vib}} = \sum_{v \geq 0} \exp\left(-\beta \hbar \omega \left(v + \frac{1}{2}\right)\right)$$

- Easy to treat, after noting that it's an infinite sum of terms of a geometric progression!

Recall:

$$\alpha \sum_{v \geq 0} r^v = \frac{\alpha}{1-r}$$

- Therefore:

$$q_{\text{vib}} = \exp\left(-\frac{1}{2}\beta \hbar \omega\right) \sum_{v \geq 0} \left[\exp\left(-\beta \hbar \omega\right)\right]^v = \frac{\exp\left(-\frac{1}{2}\beta \hbar \omega\right)}{1 - \exp\left(-\beta \hbar \omega\right)}$$

Vibrational Partition Function of Diatomic Gas

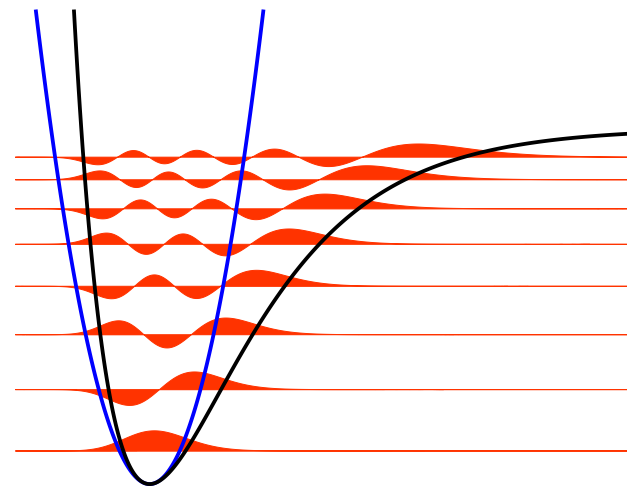
- At high temperatures $\beta \rightarrow 0$, therefore we can introduce Taylor expansions of the exponentials:

$$\exp(-\tfrac{1}{2}\beta\hbar\omega) = 1 - \frac{1}{2}\beta\hbar\omega + \frac{1}{2!2^2}(\beta\hbar\omega)^2 - \frac{1}{3!2^3}(\beta\hbar\omega)^3 + \dots$$

$$\exp(-\beta\hbar\omega) = 1 - \beta\hbar\omega + \frac{1}{2!}(\beta\hbar\omega)^2 - \frac{1}{3!}(\beta\hbar\omega)^3 + \dots$$

- Retaining the leading terms up in the partition function:

$$q_{\text{vib}} = \frac{\exp(-\tfrac{1}{2}\beta\hbar\omega)}{1 - \exp(-\beta\hbar\omega)} \approx \frac{1}{\beta\hbar\omega} = \frac{k_B T}{\hbar\omega}$$



- Caution:** the harmonic potential approximation is *invalid* for “very” high temperatures (**anharmonic** region or **dissociated** state)

Heat Capacity of Ideal Diatomic Gas

- We now have all the components necessary to find an expression for the thermal energy of the diatomic gas:
 - Focus on a single molecule:

$$-\frac{\partial \log q_{\text{trans}}}{\partial \beta} = \frac{3}{2} k_B T \quad \text{as we have seen already}$$

$$-\frac{\partial \log q_{\text{rot}}}{\partial \beta} = -\frac{\partial}{\partial \beta} \log \left(\frac{2I}{\beta \hbar^2} \right) = \frac{1}{\beta} = k_B T$$

- The above two contributions give the well known result:

$$C_v^{\text{ideal diatomic}} = \frac{5}{2} R$$

which is valid at *intermediate temperatures*!

Heat Capacity of Ideal Diatomic Gas

- At high temperatures additional contributions arise from the kinetic and potential energy of vibrations:

$$-\frac{\partial \log q_{\text{vib}}}{\partial \beta} = -\frac{\partial}{\partial \beta} \log \left(\frac{\exp(-\frac{1}{2}\beta \hbar \omega)}{1 - \exp(-\beta \hbar \omega)} \right)$$

(provided T is not too large so as to sample the anharmonic region or completely dissociate the molecule)

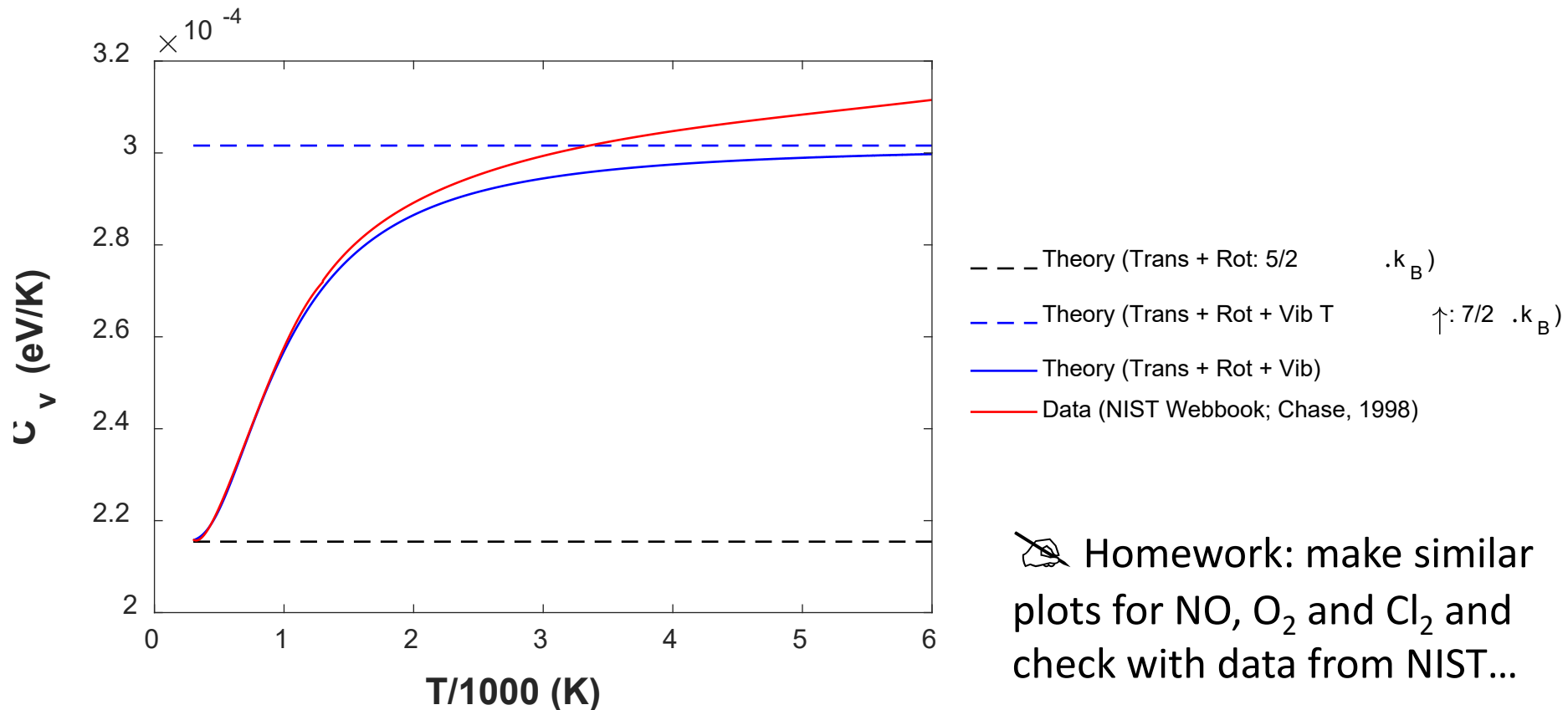
- In the limit of high temperatures:

$$-\frac{\partial \log q_{\text{vib}}}{\partial \beta} = -\frac{\partial}{\partial \beta} \log \left(\frac{1}{\beta \hbar \omega} \right) = \frac{1}{\beta} = k_B T$$

- In this temperature regime: $C_v^{\text{ideal diatomic}} = \frac{7}{2}R$

Case Study: Heat Capacity of CO Molecule

- Let's see how these approximations of perform...
 - Constant volume heat capacity (C_v) of CO



- Moments of Inertia from "Chemical thermodynamics: advanced applications" by J. Bevan Ott, Juliana Boerio-Goates, Academic Press, 2000
- Vibrational frequencies from "Modern Physics from a to Z⁰" by James William Rohlif, Wiley, 1994

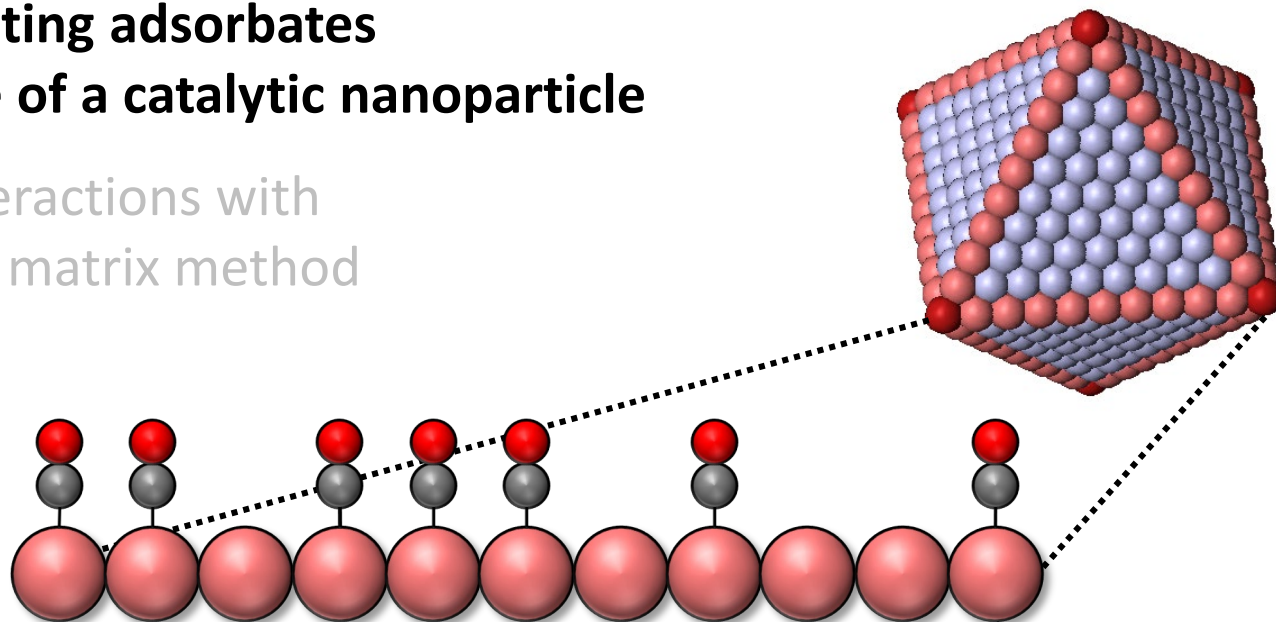
A Quick Note on the Equipartition Theorem

- The conceptual generalisation of the formulas discussed is given by the “**equipartition theorem**” (also known as “**law of equipartition**” or “**equipartition of energy**”)

*In **thermal equilibrium**, any **degree of freedom** (such as a component of the position or velocity of a particle) which appears only quadratically in the energy has an average energy of $\frac{1}{2}k_B T$ and therefore **contributes** $\frac{1}{2}k_B$ to the system's heat capacity.*

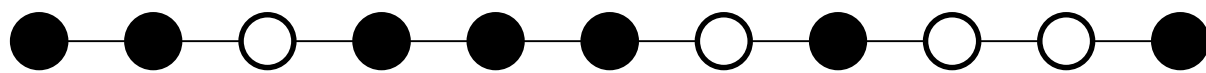
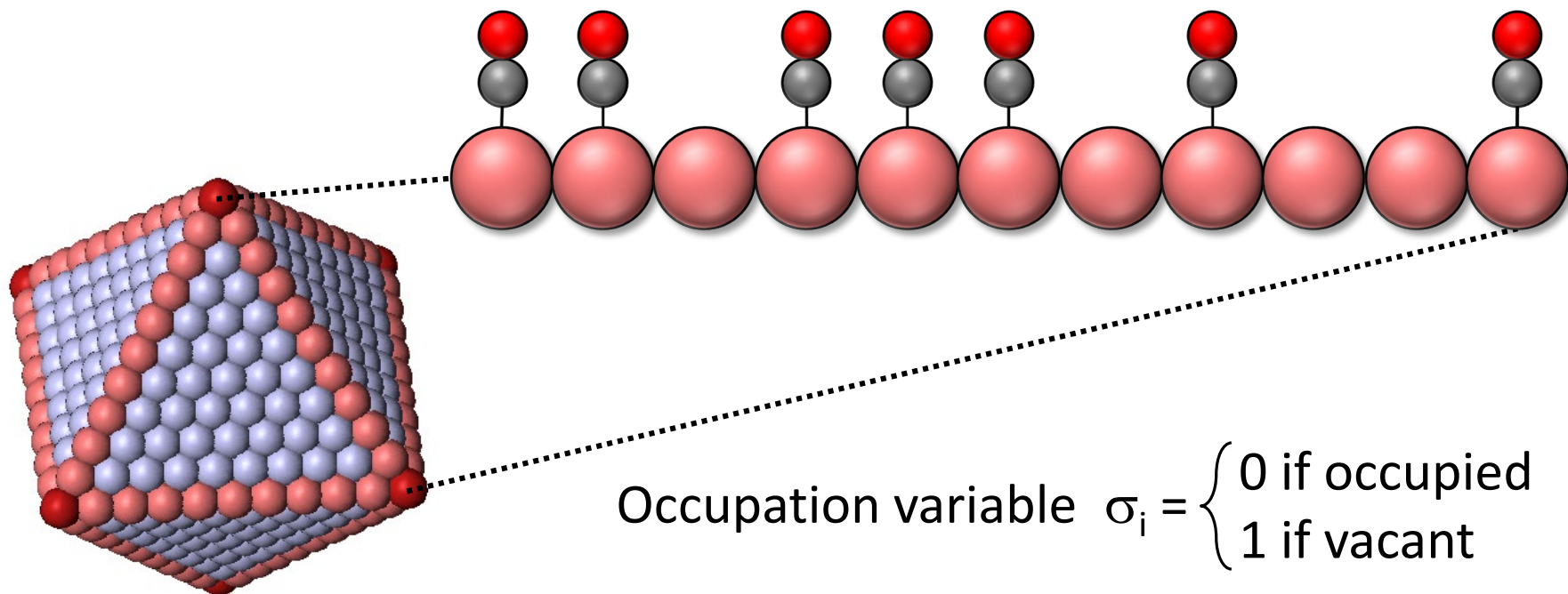
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Adsorbates on the Edge of a Catalyst

- Consider the sites on the edge of a catalytic nanoparticle
 - We would like to derive equations for the occupation statistics of adsorbates on these sites...



Microstate: $\sigma = \{\sigma_i\}_{i=1}^{N_L}$

Non-Interacting Adsorbates

- In the case of non-interacting adsorbates, each site (out of the N_L lattice sites) can have two energy states:
 - $E = 0$ if vacant
 - $E = \mathcal{E}$ if occupied $\Rightarrow \mathcal{H}(\boldsymbol{\sigma}) = \mathcal{E} \sum_{i=1}^{N_L} \sigma_i$

Note that the sites are **distinguishable**!
- We choose to work in the Grand Canonical Ensemble (μ, V, T) for which the partition function is:

$$\Xi(\mu, V, T) = \sum_{\sigma_1=0}^1 \sum_{\sigma_2=0}^1 \cdots \sum_{\sigma_{N_L}=0}^1 \exp\left(-\beta \mathcal{E} \sum_{i=1}^{N_L} \sigma_i + \beta \mu N\right) \Rightarrow$$

$$\Xi(\mu, V, T) = \sum_{\sigma_1=0}^1 \sum_{\sigma_2=0}^1 \cdots \sum_{\sigma_{N_L}=0}^1 \exp\left(-\beta (\mathcal{E} - \mu) \sum_{i=1}^{N_L} \sigma_i\right)$$

since $N = \sum_{i=1}^{N_L} \sigma_i$

Partition Function for Non-Interacting Adsorbates

- The partition function can thus be expressed as:

$$\Xi(\mu, V, T) = \sum_{\sigma_1=0}^1 \sum_{\sigma_2=0}^1 \cdots \sum_{\sigma_{N_L}=0}^1 \prod_{i=1}^{N_L} \exp(-\beta (\mathcal{E} - \mu) \sigma_i)$$

- One can show that the above can be rewritten as

$$\Xi(\mu, V, T) = \prod_{i=1}^{N_L} \sum_{\sigma_i=0}^1 \exp(-\beta (\mathcal{E} - \mu) \sigma_i)$$

 Homework: convince yourselves that the above equation is correct...

- Further, notice that the product involves identical terms, therefore:

$$\Xi(\mu, V, T) = \left[1 + \exp(-\beta (\mathcal{E} - \mu)) \right]^{N_L}$$

Average Occupation for Non-Interacting Adsorbates

- Recall the average number of particles in the grand canonical ensemble:

$$\langle N \rangle = \left. \frac{\partial \log(\Xi)}{\partial(\beta\mu)} \right|_{V,T} \Rightarrow \langle N \rangle = N_L \frac{\exp(-\beta(\mathcal{E} - \mu))}{1 + \exp(-\beta(\mathcal{E} - \mu))}$$

from which the average occupation of a site is:

$$\langle \sigma \rangle = \frac{\langle N \rangle}{N_L} = \frac{1}{\exp\left(\frac{\mathcal{E} - \mu}{k_B T}\right) + 1}$$

- Fermi-Dirac statistics**, since particles obey an exclusion principle (maximum one adsorbate per site)

Recall that...

- In our discussion of the chemical potential of ideal monoatomic gas, we had found (slide 13):

$$\mu = k_B T \log \left[\frac{p}{k_B T} \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} \right]$$

- Define the chemical potential at a reference pressure p_0 :

$$p_0 = 1 \text{ bar}$$

$$\mu_0 = k_B T \log \left[\frac{p_0}{k_B T} \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} \right] \quad \Rightarrow \quad \mu = \mu_0 + k_B T \log \left(\frac{p}{p_0} \right)$$

- Familiar expression of μ with respect to **activity** p/p_0 (ideal gas)
- For polyatomic gases, μ_0 will contain additional contributions...

Langmuir Isotherm

- Substituting the chemical potential of the ideal gas into the site occupancy equation:

$$\langle \sigma \rangle = \frac{1}{\exp\left(\frac{\mathcal{E} - \mu_0}{k_B T}\right) \frac{p_0}{p} + 1}$$

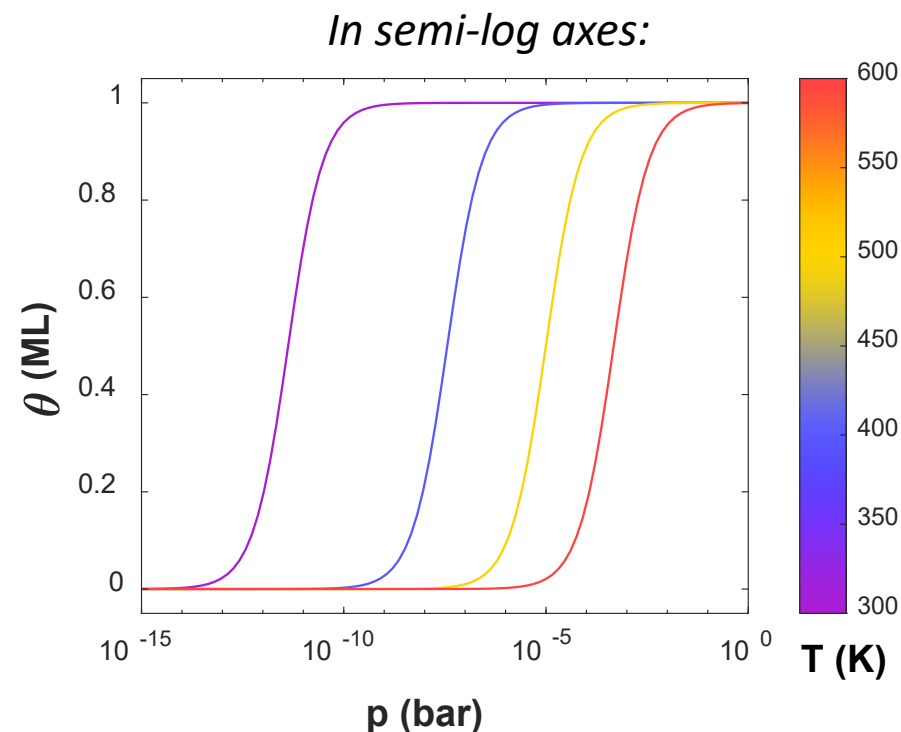
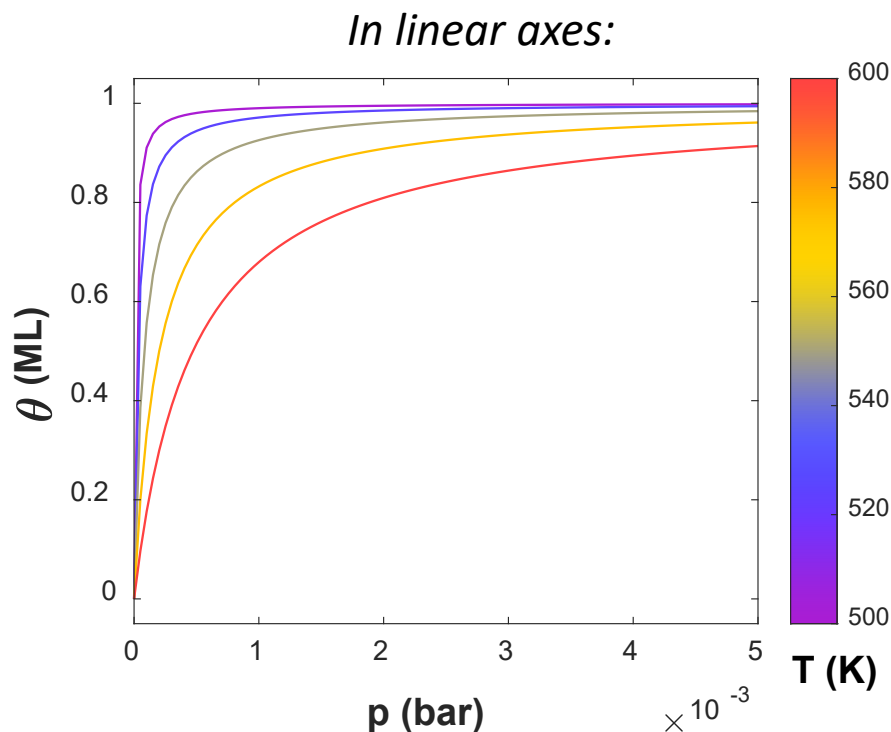
- Defining the adsorption thermodynamic constant K and noting that the site occupancy is the coverage θ :

$$K = \frac{1}{p_0} \exp\left(-\frac{\mathcal{E} - \mu_0}{k_B T}\right) \quad \Rightarrow \quad \theta = \frac{K p}{1 + K p}$$

- Langmuir isotherm**, valid for ideal adlayers in the case of non-competitive, non-dissociative adsorption

Case Study: CO on Cu(211)

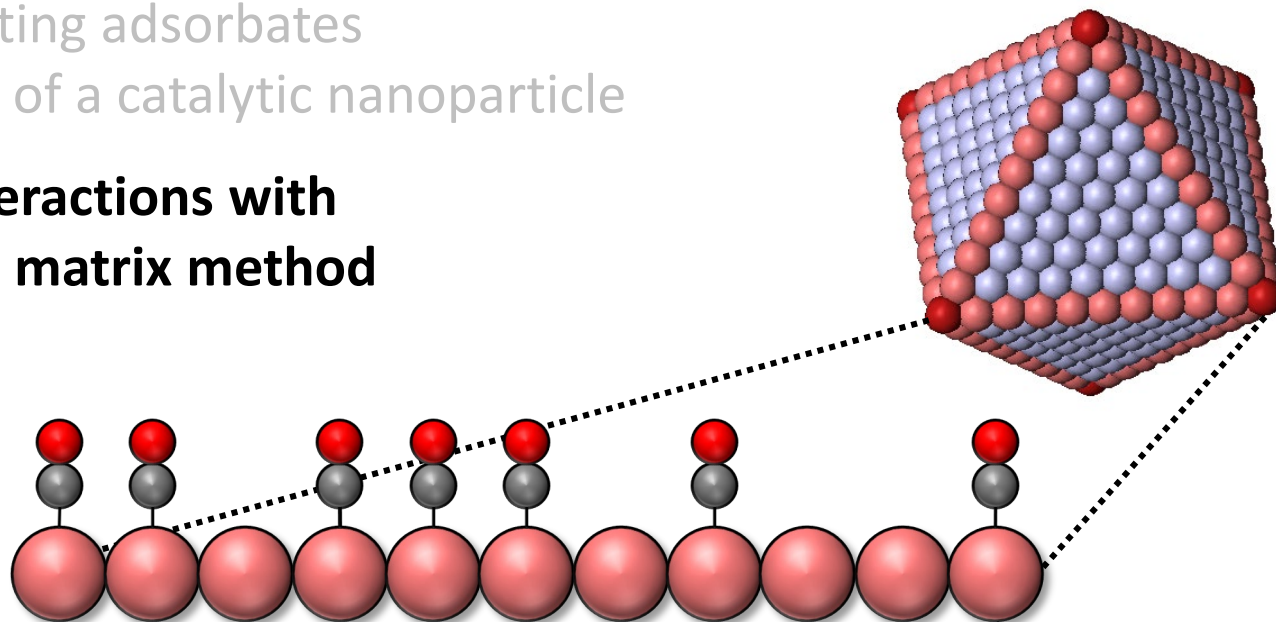
- Let's see how the Langmuir isotherm looks like for...
 - CO adsorbing on Cu(211) step edge sites



- Moments of Inertia from "Chemical thermodynamics: advanced applications" by J. Bevan Ott, Juliana Boerio-Goates, Academic Press, 2000
- Vibrational frequencies from "Modern Physics from a to Z" by James William Rohlif, Wiley, 1994
- $E_{\text{ads,CO}} = -0.7$ calculated from DFT by Konstantinos Papanikolaou (RPBE functional, 3×1 slab, 4 layers, $6 \times 5 \times 1$ k-point mesh)

Outline

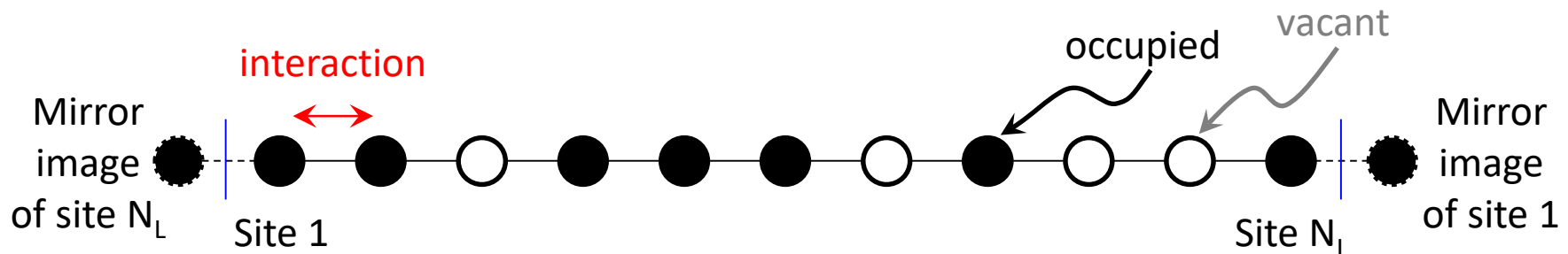
- Statistical Mechanics of Ideal Gases
 - Monoatomic
 - Polyatomic (with focus on diatomic)
- **Statistical Mechanics of Condensed Matter**
 - Non-interacting adsorbates on the edge of a catalytic nanoparticle
 - **Treating interactions with the transfer matrix method**



Interacting Adsorbates

- In the case of interacting adsorbates, we have:
 - the adsorption energy per site, \mathcal{E} , as before, but also
 - an interaction energy term \mathcal{J} for adsorbate pairs.

$$\mathcal{H}(\boldsymbol{\sigma}) = \mathcal{E} \sum_{i=1}^{N_L} \sigma_i + \mathcal{J} \sum_{i=1}^{N_L} \sigma_i \sigma_{i+1} \quad \text{with } \sigma_{N_L+1} \equiv \sigma_1$$



- The Grand Canonical partition function is:

$$\Xi(\mu, V, T) = \sum_{\sigma_1=0}^1 \sum_{\sigma_2=0}^1 \cdots \sum_{\sigma_{N_L}=0}^1 \exp \left(-\beta (\mathcal{E} - \mu) \sum_{i=1}^{N_L} \sigma_i - \beta \mathcal{J} \sum_{i=1}^{N_L} \sigma_i \sigma_{i+1} \right)$$

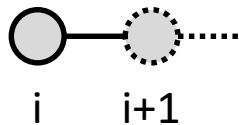
Transfer Matrix Method

- This partition function is much harder to calculate! Fortunately, there is a technique for this:

transfer matrix method

- To understand how the method works, focus on a pair of sites:

Now consider the factor:



$$\Lambda_{\sigma_i, \sigma_{i+1}} = \exp(-\beta(\mathcal{E} - \mu)\sigma_i - \beta\mathcal{J}\sigma_i\sigma_{i+1})$$

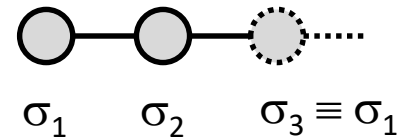
- If our periodic lattice consists of only one site, then:

$$\Xi(\mu, V, T) = \Lambda_{0,0} + \Lambda_{1,1} = 1 + \exp(-\beta(\mathcal{E} - \mu) - \beta\mathcal{J})$$

since site $i+1$ is the mirror image of site i , and the latter can exist in either of two states: 0, 1.

Transfer Matrix Method

- Continue with a periodic lattice of two sites:



$$\begin{aligned}
 \Xi(\mu, V, T) &= \sum_{\sigma_1=0}^1 \sum_{\sigma_2=0}^1 \exp \left(-\beta (\mathcal{E} - \mu) \sum_{i=1}^2 \sigma_i - \beta \mathcal{J} \sum_{i=1}^2 \sigma_i \sigma_{i+1} \right) \\
 &= \sum_{\sigma_1=0}^1 \sum_{\sigma_2=0}^1 \prod_{i=1}^2 \exp \left(-\beta (\mathcal{E} - \mu) \sigma_i - \beta \mathcal{J} \sigma_i \sigma_{i+1} \right) \\
 &= \sum_{\sigma_1=0}^1 \sum_{\sigma_2=0}^1 \prod_{i=1}^2 \Lambda_{\sigma_i, \sigma_{i+1}} = \sum_{\sigma_1=0}^1 \sum_{\sigma_2=0}^1 \Lambda_{\sigma_1, \sigma_2} \Lambda_{\sigma_2, \sigma_1} \\
 &= \Lambda_{0,0} \Lambda_{0,0} + \Lambda_{0,1} \Lambda_{1,0} + \Lambda_{1,0} \Lambda_{0,1} + \Lambda_{1,1} \Lambda_{1,1}
 \end{aligned}$$

where with **red** we have highlighted the state of the second site...

Transfer Matrix Method

- The expression we just found:

$$\Xi(\mu, V, T) = \Lambda_{0,0} \Lambda_{0,0} + \Lambda_{0,1} \Lambda_{1,0} + \Lambda_{1,0} \Lambda_{0,1} + \Lambda_{1,1} \Lambda_{1,1}$$

can be written as:

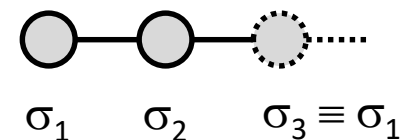
$$\Xi(\mu, V, T) = \text{tr} \left[\begin{pmatrix} \Lambda_{0,0} & \Lambda_{0,1} \\ \Lambda_{1,0} & \Lambda_{1,1} \end{pmatrix}^2 \right]$$

Matrix trace (sum of diagonal elements)

- Quick validation:

$$\begin{pmatrix} \Lambda_{0,0} & \Lambda_{0,1} \\ \Lambda_{1,0} & \Lambda_{1,1} \end{pmatrix} \begin{pmatrix} \Lambda_{0,0} & \Lambda_{0,1} \\ \Lambda_{1,0} & \Lambda_{1,1} \end{pmatrix} = \begin{pmatrix} \Lambda_{0,0} \Lambda_{0,0} + \Lambda_{0,1} \Lambda_{1,0} & \Lambda_{0,0} \Lambda_{0,1} + \Lambda_{0,1} \Lambda_{1,1} \\ \Lambda_{1,0} \Lambda_{0,0} + \Lambda_{1,1} \Lambda_{1,0} & \Lambda_{1,0} \Lambda_{0,1} + \Lambda_{1,1} \Lambda_{1,1} \end{pmatrix}$$

- This matrix is called “transfer” matrix and has an interesting structure...



Transfer Matrix Method

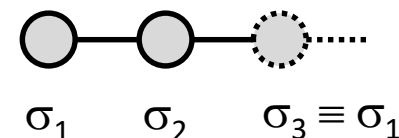
$$\Xi(\mu, V, T) = \Lambda_{0,0}\Lambda_{0,0} + \Lambda_{0,1}\Lambda_{1,0} + \Lambda_{1,0}\Lambda_{0,1} + \Lambda_{1,1}\Lambda_{1,1} = \text{tr} \left[\begin{pmatrix} \Lambda_{0,0} & \Lambda_{0,1} \\ \Lambda_{1,0} & \Lambda_{1,1} \end{pmatrix}^2 \right]$$

- Quick validation:

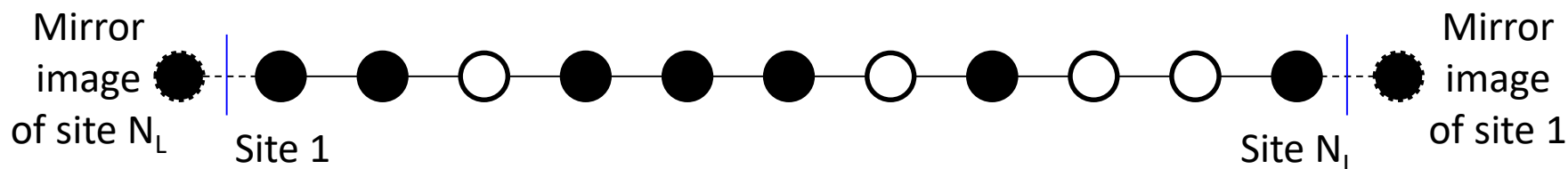
$$\begin{pmatrix} \Lambda_{0,0} & \Lambda_{0,1} \\ \Lambda_{1,0} & \Lambda_{1,1} \end{pmatrix} \begin{pmatrix} \Lambda_{0,0} & \Lambda_{0,1} \\ \Lambda_{1,0} & \Lambda_{1,1} \end{pmatrix} = \begin{pmatrix} \Lambda_{0,0}\Lambda_{0,0} + \Lambda_{0,1}\Lambda_{1,0} & \Lambda_{0,0}\Lambda_{0,1} + \Lambda_{0,1}\Lambda_{1,1} \\ \Lambda_{1,0}\Lambda_{0,0} + \Lambda_{1,1}\Lambda_{1,0} & \Lambda_{1,0}\Lambda_{0,1} + \Lambda_{1,1}\Lambda_{1,1} \end{pmatrix}$$

- Observe that:

- The sequences of states in each product in the main diagonal, start and end with the same state (marked in black bold).
- These are the terms that we “want” because of periodicity!
- The red states range over all possible values of the “other/intermediate” site...



Partition Function from Transfer Matrix



- The observations we just made can be generalised and thus, the partition function for N_L sites can be written as:

$$\Xi(\mu, V, T) = \text{tr}(\Lambda^{N_L})$$

States of a site
0
1
States of the next site

 $\begin{pmatrix} \Lambda_{0,0} & \Lambda_{0,1} \\ \Lambda_{1,0} & \Lambda_{1,1} \end{pmatrix} = \Lambda$
Transfer matrix

- Every additional factor Λ adds one more site to the lattice so we get “probabilities” of every possible sequence of “site states”
- The trace operation, closes the “ring”, imposing periodicity

Partition Function from Transfer Matrix

- To simplify the calculations one can invoke the following fact:

$$\text{tr}(\Lambda^{N_L}) = \sum_i \lambda_i^{N_L} \quad \text{eigenvalues of } \Lambda$$

- Typically, one eigenvalue is larger than the rest, so, to a very good approximation (which gets better as $N_L \rightarrow \infty$):

$$\Xi(\mu, V, T) = \text{tr}(\Lambda^{N_L}) = \lambda_{\max}^{N_L}$$

- Then, the average occupation can be computed as usual:

$$\langle N \rangle = \left. \frac{\partial \log(\Xi)}{\partial(\beta\mu)} \right|_{V, T}$$

Partition Function from Transfer Matrix

- Going back to our system:

$$\Lambda = \begin{pmatrix} 1 & 1 \\ \exp(-\beta(\mathcal{E} - \mu)) & \exp(-\beta(\mathcal{E} - \mu) - \beta\mathcal{J}) \end{pmatrix}$$

- The eigenvalues can be expressed as:

$$\lambda_{\pm} = \frac{1}{2} e^{-\beta(\mathcal{E} + \mathcal{J} - \mu)} \left(1 + e^{\beta(\mathcal{E} + \mathcal{J} - \mu)} \pm \sqrt{1 - 2e^{\beta(\mathcal{E} + \mathcal{J} - \mu)} + e^{2\beta(\mathcal{E} + \mathcal{J} - \mu)} + 4e^{\beta(\mathcal{E} + 2\mathcal{J} - \mu)}} \right)$$

- The eigenvalue with the plus sign is the largest, and thus the average occupancy can be expressed as:

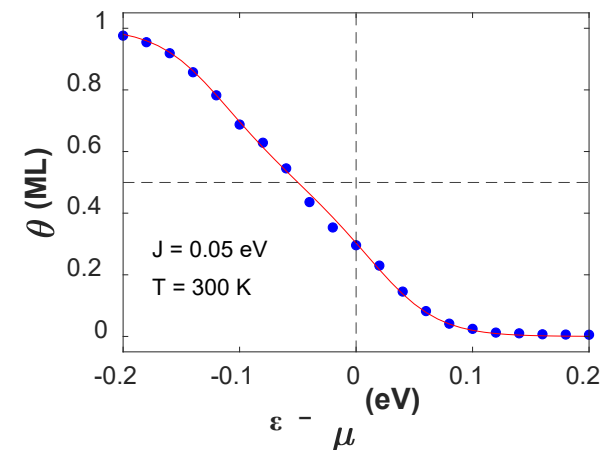
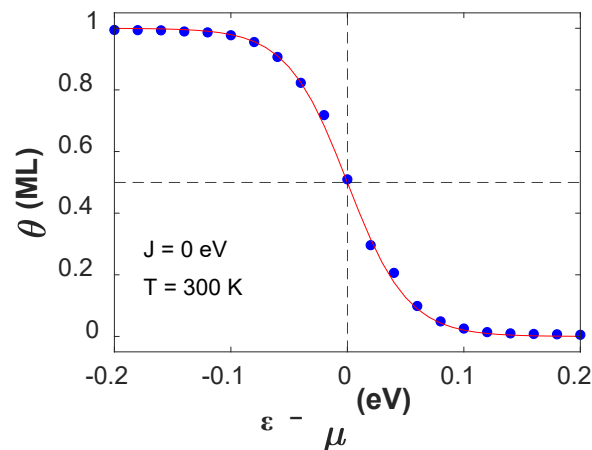
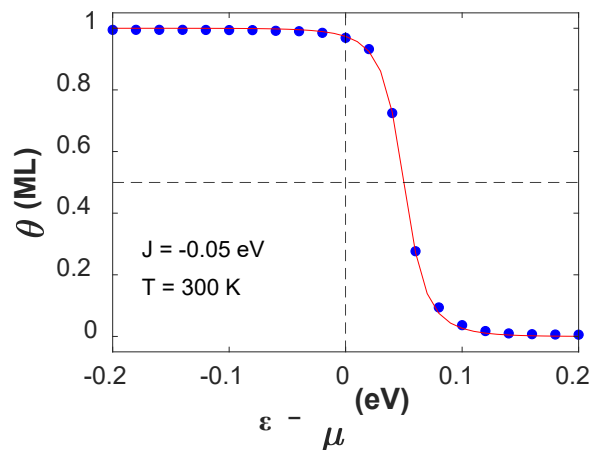
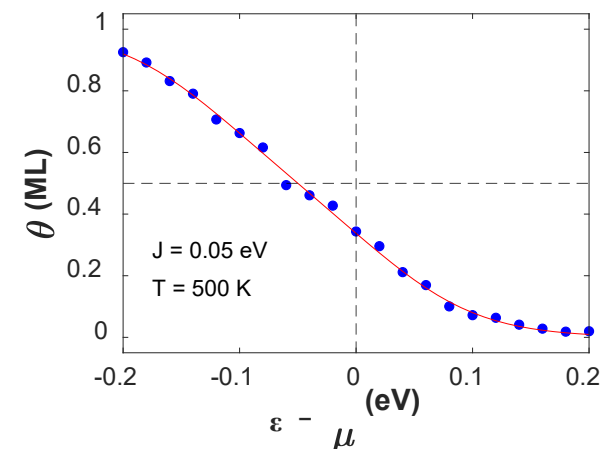
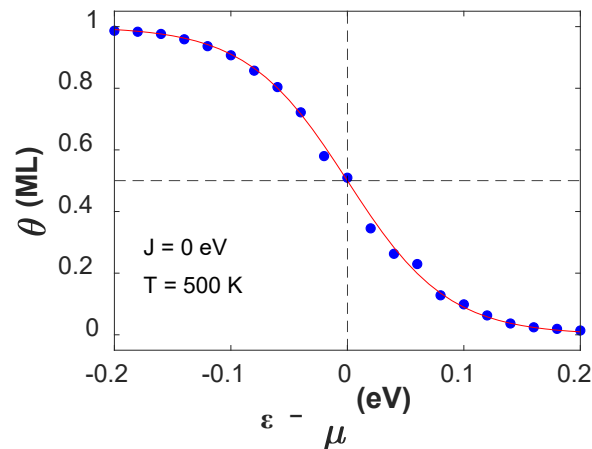
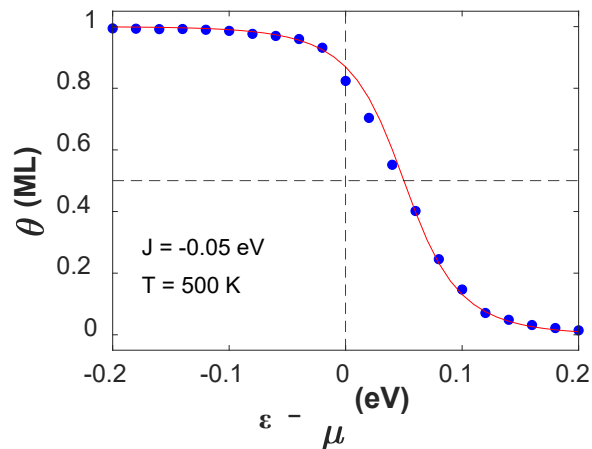
$$\langle \sigma \rangle = -k_B T \left. \frac{\partial \log(\lambda_+)}{\partial (\mathcal{E} - \mu)} \right|_{V, T}$$

which can be evaluated computationally or can be treated symbolically with Mathematica or similar...

Results of Transfer Matrix Method

- To showcase the method, we consider the cases:
 - $\mathcal{J} = -0.05, 0.00, 0.05$ eV
 - Two temperatures: 300 K and 500 K

• Monte Carlo simulation
 — Transfer matrix result



Take Home Messages

- Statistical mechanics provides a **general** and **powerful methodology** for calculating thermodynamic quantities:
 - Start from a Hamiltonian, giving energies of microstates
 - Choose an ensemble
 - Perform appropriate averaging operations
- Using this methodology we were able to prove from first principles the validity of:
 - the ideal gas law
 - the Langmuir isotherm
- By analyzing the thermal energy of an ideal gas, we were able to understand the **equipartition theorem**.

Appendix: Chemical Potential of Polyatomic Ideal Gas

- From slides 8 and 16:

$$Q_{\text{polyatomic ideal gas}} = \frac{1}{N!} \left(\frac{V}{h^3} (2\pi m k_B T)^{\frac{3}{2}} q_{\text{rot}} q_{\text{vib}} \right)^N = \frac{1}{N!} \left(q_{\text{polyatomic ideal gas}}^{\text{1 molec}} \right)^N$$

- Chemical potential calculated as (using Stirling's formula for the factorial and the ideal gas law):

$$\mu \approx -k_B T \frac{\partial}{\partial N} \left[-N \log(N) + N + N \log \left(q_{\text{polyatomic ideal gas}}^{\text{1 molec}} \right) \right]$$

$$= -k_B T \log \left(\frac{1}{N} q_{\text{polyatomic ideal gas}}^{\text{1 molec}} \right)$$

$$= -k_B T \log \left(\frac{k_B T (2\pi m k_B T)^{\frac{3}{2}}}{p h^3} q_{\text{rot}} q_{\text{vib}} \right)$$