

Chemical Thermodynamics and Statistical Mechanics

Presented By
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Why Thermodynamics?

- The macroscopic description of a system of $\sim 10^{23}$ particles may involve only a few variables!

“Simple systems”: Macroscopically homogeneous, isotropic, uncharged, large enough that surface effects can be neglected, not acted upon by electric, magnetic, or gravitational fields.

- Only those few particular combinations of atomic coordinates that are essentially time-independent are macroscopically observable. Such quantities are the energy, momentum, angular momentum, etc.
- There are “thermodynamic” variables in addition to the standard “mechanical” variables.

Thermodynamic Equilibrium

In all systems there is a tendency to evolve toward states whose properties are determined by intrinsic factors and not by previously applied external influences. Such simple states are, by definition, time-independent. They are called equilibrium states.

Thermodynamics describes these simple static equilibrium states.

Postulate:

There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U , the volume V , and the mole numbers N_1, \dots, N_r of the chemical components.

The central problem of thermodynamics is the determination of the equilibrium state that is eventually attained after the removal of internal constraints in a closed, composite system.

➤ Laws of Thermodynamics

What is Statistical Mechanics?

- ❑ Link macroscopic behavior to atomic/molecular properties
- ❑ Calculate thermodynamic properties from “first principles”

(Uses results for energy levels etc. obtained from quantum mechanical calculations.)

The Course

- ❖ Discovery of fundamental physical laws and concepts
- ❖ An exercise in logic (description of intricate phenomena from first principles)
- ❖ An explanation of macroscopic concepts from our everyday experience as they arise from the simple quantum mechanics of atoms and molecules.

...not collection of facts and equations!!!

The Course

Prerequisites

- Tools from elementary calculus
- Basic quantum mechanical results

Resources

- “Physical Chemistry: A Molecular Approach”, by D. A. McQuarrie and J. D. Simon, University Science Books 1997
- **Lectures**
(principles, procedures, interpretation, tricks, insight)
- Homework problems and solutions
- Course web site (links to notes, course planner)

Course Planner

- o Organized in units.
- o Material covered in lectures. What to focus on or review.
- o What to study from the book.
- o Homework assignments.
- o Questions for further thinking.

<http://www.scs.uiuc.edu/~makri/444-web-page/chem-444.html/444-course-planner.html>

Grading Policy

Homework	30%	(Generally, weekly assignment)
Hour Exam #1	15%	(September 29 th)
Hour Exam #2	15%	(November 3 rd)
Final Exam	40%	(December 14 th)

Please turn in homework on time! May discuss, but do not copy solutions from any source!

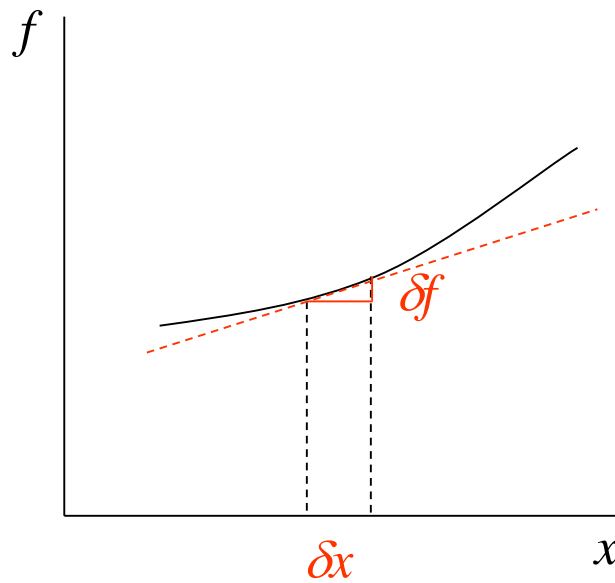
10% penalty for late homework.

No credit after solutions have been posted, except in serious situations.

Math Review

- Partial derivatives
- Ordinary integrals
- Taylor series
- Differential forms

Differential of a Function of One Variable



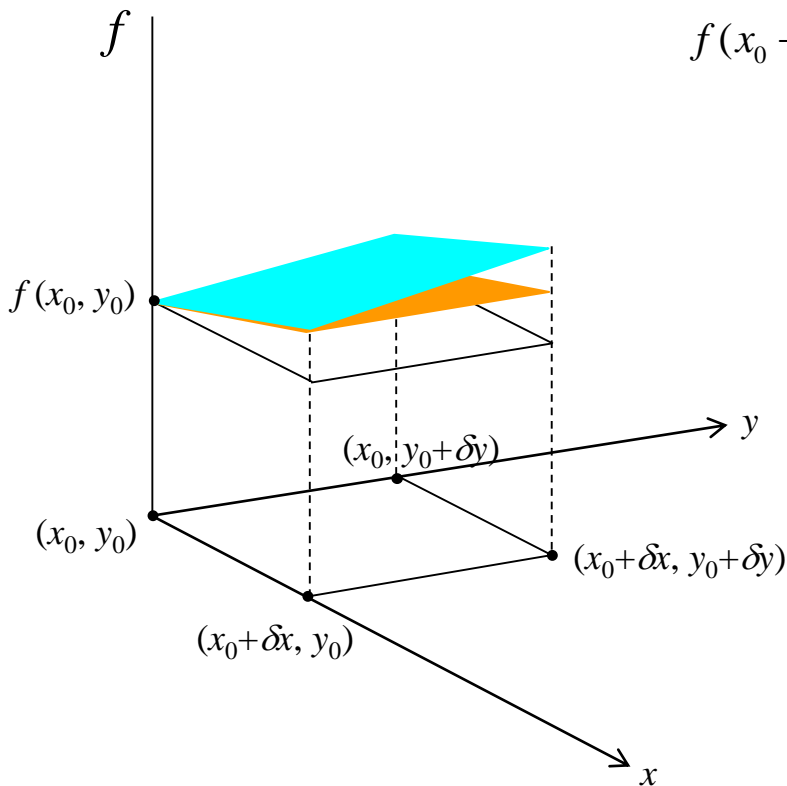
$$\delta f \approx \frac{df}{dx} \delta x$$

Differential of a Function of Two Variables

$$f(x_0 + \delta x, y_0) \approx f(x_0, y_0) + \left(\frac{\partial f}{\partial x} \right)_y \delta x$$

$$f(x_0 + \delta x, y_0 + \delta y) \approx f(x_0 + \delta x, y_0) + \left(\frac{\partial f}{\partial y} \right)_x \delta y$$

$$\approx f(x_0, y_0) + \left(\frac{\partial f}{\partial x} \right)_y \delta x + \left(\frac{\partial f}{\partial y} \right)_x \delta y$$



$$df = f(x_0 + \delta x, y_0 + \delta y) - f(x_0, y_0)$$

$$\approx \left(\frac{\partial f}{\partial x} \right)_y \delta x + \left(\frac{\partial f}{\partial y} \right)_x \delta y$$

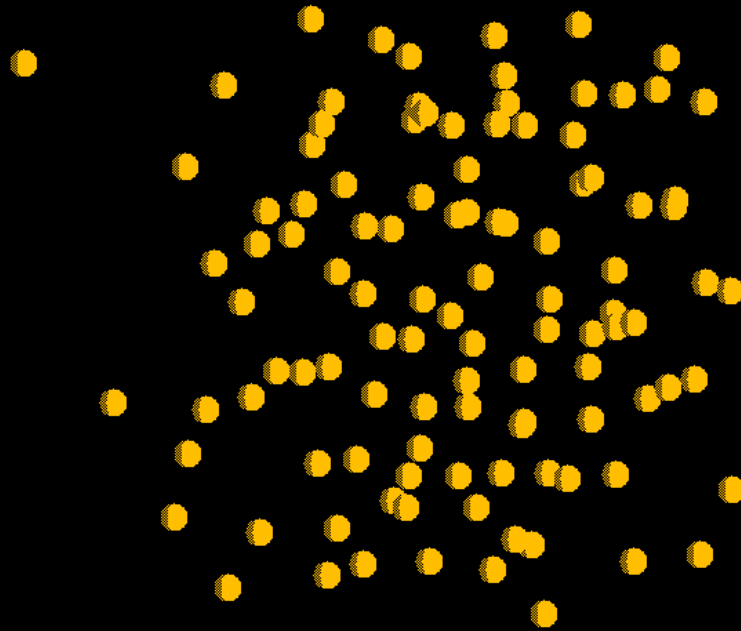
Special Math Tool

If $z = z(x, y)$, then

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

PROPERTIES OF GASES

MOLDEN



The Ideal Gas Law

$$PV = nRT \text{ or } P\bar{V} = RT, \quad \bar{V} = V/n$$

Extensive vs. intensive properties

Units of pressure

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$1 \text{ torr} = \frac{1}{760} \text{ atm}$$

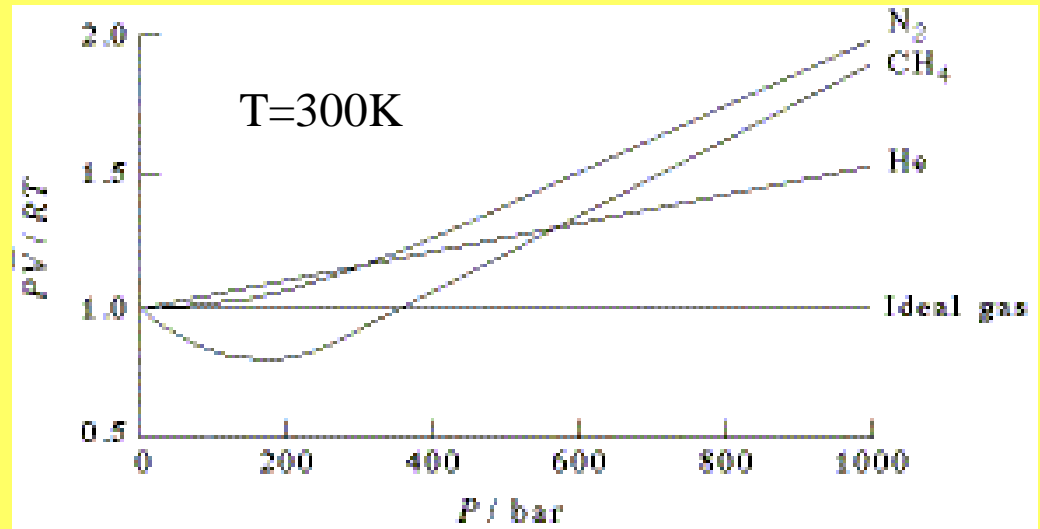
Units of temperature

Triple point of water occurs
at 273.16 K (0.01°C)

Deviations from Ideal Gas Behavior

$$z = \frac{P\bar{V}}{RT}$$

“compressibility factor”



Ideal gas: $z = 1$

$z < 1$: attractive intermolecular forces dominate

$z > 1$: repulsive intermolecular forces dominate

Van der Waals equation

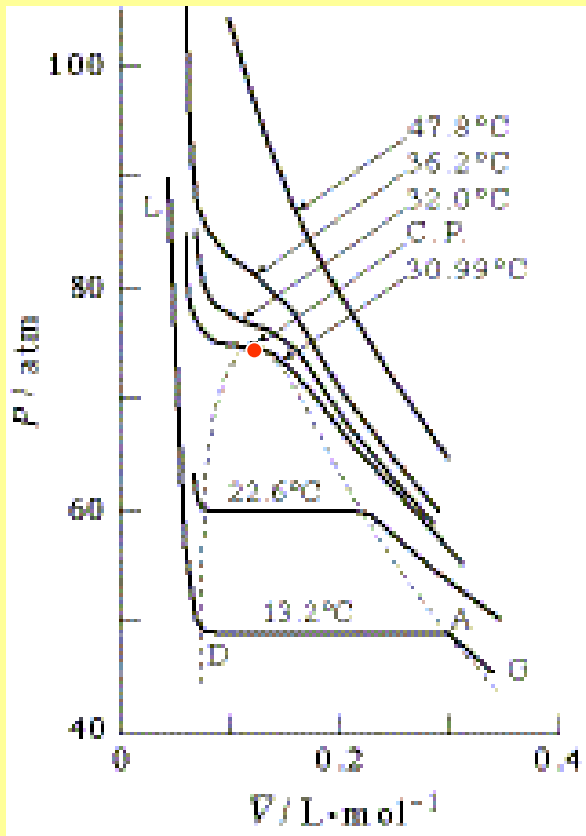
$$\left(P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT$$

At fixed P and T , V is the solution of a cubic equation. There may be one or three real-valued solutions.

The set of parameters P_c , V_c , T_c for which the number of solutions changes from one to three, is called the **critical point**. The van der Waals equation has an inflection point at T_c .

Isotherms

(P vs. V at constant T)



$$T > T_c : \left(\frac{\partial P}{\partial \bar{V}} \right)_T < 0$$

$$\left(\frac{\partial P}{\partial \bar{V}} \right)_T > 0 : \text{unstable region}$$

- Large V : ideal gas behavior.
- Only one phase above T_c .
- Unstable region: liquid+gas coexistence.

Critical Point of van der Waals Equation

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = -\frac{RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3}$$
$$= 0 \text{ for } \bar{V}^3 = \frac{2a(\bar{V}-b)^2}{RT} \quad (3 \text{ or } 1 \text{ real roots})$$

$$\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = \frac{2RT}{(\bar{V}-b)^3} - \frac{6a}{\bar{V}^4}$$
$$= 0 \text{ for } \bar{V}^4 = \frac{3a(\bar{V}-b)^3}{RT}$$

Both are satisfied at the critical (inflection) point, so...

$$\bar{V}_c = 3b$$
$$T_c = \frac{8a}{27Rb}$$
$$P_c = \frac{a}{27b^2}$$

The law of corresponding states

Eliminate a and b from the van der Waals equation:

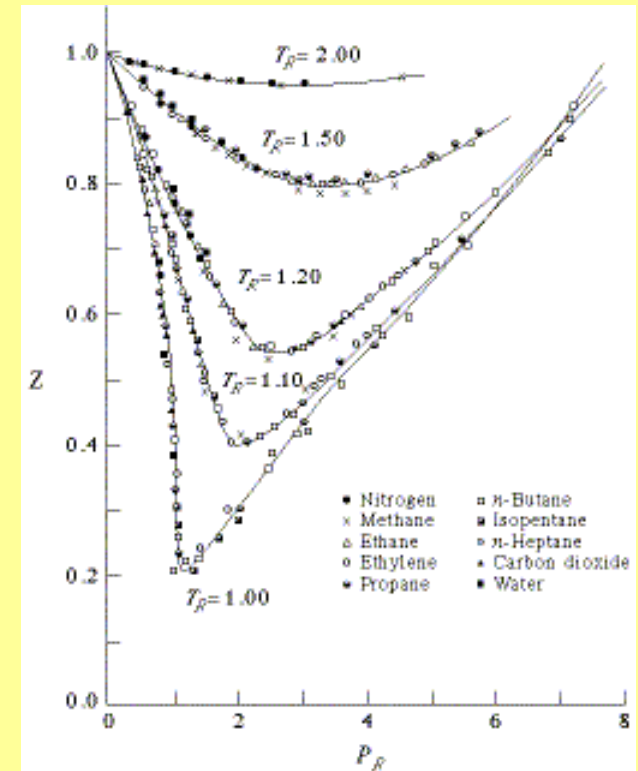
$$b = \frac{1}{3}\bar{V}_c, \quad a = 27b^2P_c = 3P_c\bar{V}_c^2, \quad \dots \Rightarrow$$

$$\left(P_R + \frac{3}{\bar{V}_R^2}\right)\left(\bar{V}_R - \frac{1}{3}\right) = \frac{8}{3}T_R$$

$$P_R \equiv \frac{P}{P_c}, \quad V_R \equiv \frac{V}{V_c}, \quad T_R \equiv \frac{T}{T_c} \quad \text{"reduced" variables}$$

All gases behave the same way under similar conditions relative to their critical point.

(This is approximately true.)



Virial Coefficients

$$Z \equiv \frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}}{\bar{V}} + \frac{B_{3V}}{\bar{V}^2} + \dots \quad \text{Virial expansion}$$

B_{2V} : second virial coefficient,

B_{3V} : third virial coefficient, etc.

Using partition functions, one can show that

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1 \right) r^2 dr$$

$u(r)$: rotationally averaged intermolecular potential

Simple Models for Intermolecular Interactions

(a) Hard Sphere Model

$$u(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma \end{cases} \quad \dots \Rightarrow B_{2V}(T) = \frac{2}{3} \pi N_A \sigma^3$$

(b) Square Well Potential

$$u(r) = \begin{cases} \infty, & r < \sigma \\ -\varepsilon, & \sigma < r < \lambda\sigma \\ 0, & r > \lambda\sigma \end{cases} \quad \dots \Rightarrow B_{2V}(T) = \frac{2}{3} \pi N_A \sigma^3 \left[1 - (\lambda^3 - 1) \left(e^{\varepsilon/k_B T} - 1 \right) \right]$$

(c) Hard Sphere Potential with r^{-6} Attraction

$$u(r) = \begin{cases} \infty, & r < \sigma \\ -\frac{c_6}{r^6}, & r > \sigma \end{cases} \quad \dots \Rightarrow B_{2V}(T) \approx \frac{2}{3} \pi N_A \left(\sigma^3 - \frac{c_6}{k_B T \sigma^3} \right) \quad (\text{high } T)$$

Interpretation of van der Waals Parameters

From the van der Waals equation, ... $B_{2V}(T) \approx b - \frac{a}{RT}$

Comparing to the result of the square well model,

$$b = \frac{2}{3} \pi N_A \sigma^3, \quad a = \frac{2}{3} \pi N_A^2 \sigma^3 (\lambda^3 - 1) \varepsilon$$

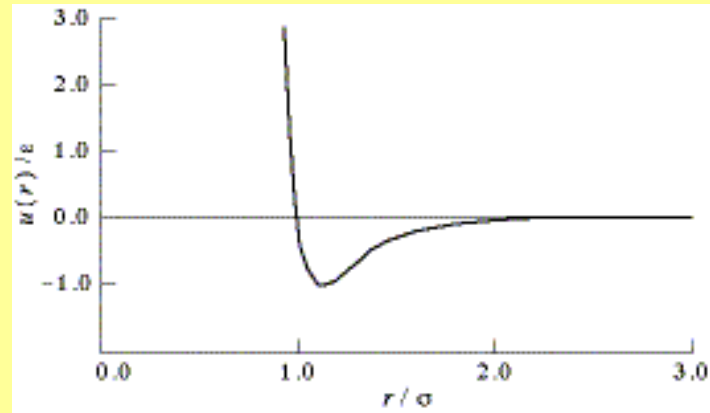
Comparing to the result of the hard sphere model with r^{-6} attraction,

$$b = \frac{2}{3} \pi N_A \sigma^3, \quad a = \frac{2}{3} \pi N_A^2 \frac{c_6}{\sigma^3}$$

- σ \square molecular diameter
- b \square molecular volume (repulsive interaction)
- a \square related to strength/range of attractive interaction

The Lennard-Jones Model

$$u(r) = 4\epsilon \left(\frac{c_{12}}{r^{12}} - \frac{c_6}{r^6} \right)$$



Attractive term: dipole-dipole, or dipole-induced dipole, or induced dipole-induced dipole (London dispersion) interactions.

Origin of Intermolecular Forces


$$\hat{H} = \hat{T}_{\text{nucl}}(\{\mathbf{R}_i\}) + \hat{H}_{\text{el}}(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \quad \text{Only Coulomb-type terms!}$$

\mathbf{r}_i : electronic coordinates

\mathbf{R}_i : nuclear coordinates

The Born-Oppenheimer Approximation:

Electrons move much faster than nuclei. Fixing the nuclear positions,

$$\hat{H}_{\text{el}}(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \Phi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_i\}) = E_n(\{\mathbf{R}_i\}) \Phi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_i\})$$


Adiabatic or electronic or
Born-Oppenheimer states

Electronic energies; form potential energy surface.
Responsible for intra/intermolecular forces.

INTRODUCTION TO STATISTICAL MECHANICS

The concept of statistical ensembles

An ensemble is a collection of a very large number of systems, each of which is a replica of the thermodynamic system of interest.

The Canonical Ensemble

A collection of a very large number A of systems (of volume V , containing N molecules) in contact with a heat reservoir at temperature T . Each system has an energy that is one of the eigenvalues E_j of the Schrodinger equation.

A state of the entire ensemble is specified by specifying the “occupation number” a_j of each quantum state. The energy E of the ensemble is

$$E = \sum_j a_j E_j$$

The principle of equal a priori probabilities:

Every possible state of the canonical ensemble, i.e., every distribution of occupation numbers (consistent with the constraint on the total energy) is equally probable.

How many ways are there of assigning energy eigenvalues to the members of the ensemble? In other words, how many ways are there to place a_1 systems in a state with energy E_1 , a_2 systems in a state with energy E_2 , etc.?

Recall binomial distribution:

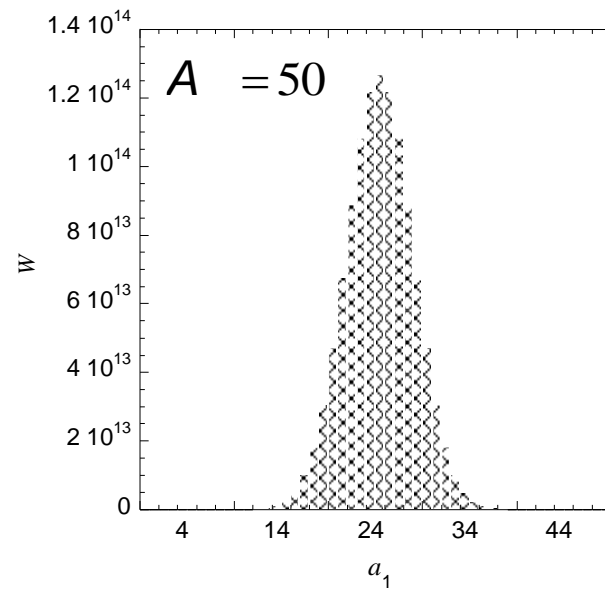
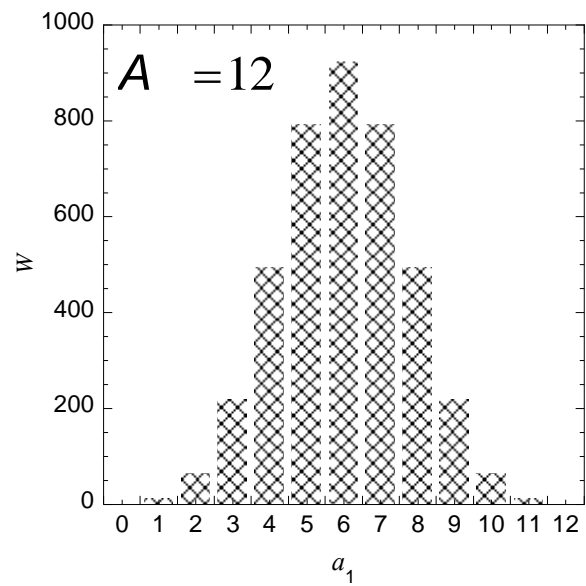
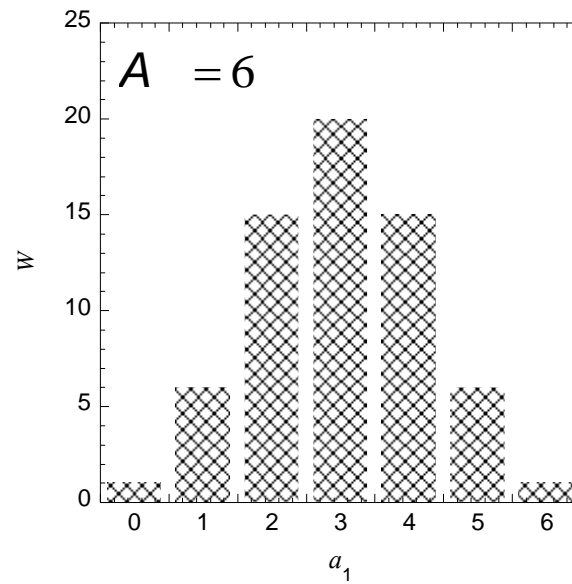
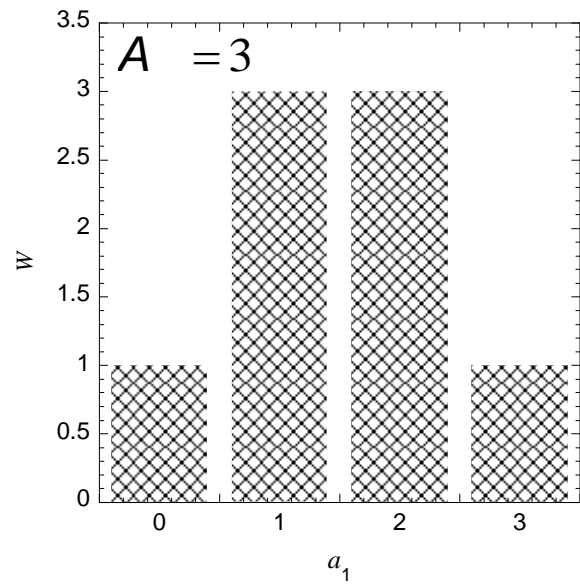
The number of ways A distinguishable objects can be divided into 2 groups containing a_1 and $a_2 = A - a_1$ objects is

$$W(a_1, a_2) = \frac{A!}{a_1! a_2!}$$

Multinomial distribution:

The number of ways A distinguishable objects can be divided into groups containing a_1, a_2, \dots objects is

$$W(a_1, a_2, \dots) = \frac{A!}{a_1! a_2! \dots} = \frac{\left(\sum_k a_k \right)!}{\prod_k a_k!}$$



The Method of the Most Probable Distribution

The distribution peaks sharply about its maximum as A increases.

To obtain ensemble properties, we replace the weighted average by the most probable distribution.

To find the most probable distribution we need to find the maximum of W subject to the constraints of the ensemble.

This requires two mathematical tools, Stirling's approximation and Lagrange's method of undetermined multipliers.

Stirling's Approximation

This is an approximation for the logarithm of the factorial of large numbers. The result is easily derived by approximating the sum by an integral.

$$\ln N! \approx N \ln N - N$$

Lagrange's Method of Undetermined Multipliers

Extremize the function $f(x_1, \dots, x_n)$ subject to the constraint $g(x_1, \dots, x_n) = 0$.

The function has an extremum if $\delta f = \sum_{j=1}^n \frac{\partial f}{\partial x_j} \delta x_j = 0$.

The constraint condition is satisfied at all points, so $\delta g = \sum_{j=1}^n \frac{\partial g}{\partial x_j} \delta x_j = 0$.

This relation connects the variations of the variables, so only $n-1$ of them are independent. We introduce a parameter λ and combine the two relations into

$$\sum_{j=1}^n \left(\frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} \right) \delta x_j = 0.$$

Let's pick variable x_μ as the dependent one. We choose λ such that

$$\frac{\partial f}{\partial x_\mu} - \lambda \frac{\partial g}{\partial x_\mu} = 0$$

This allows us to rewrite the previous equation in the form

$$\sum_{j \neq \mu}^n \left(\frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} \right) \delta x_j = 0.$$

Because all the variables in this equation are independent, we can vary them arbitrarily, so we conclude

$$\frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} = 0 \quad \text{for all } j \neq \mu$$

Combined with the equation specifying λ , we have

$$\frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} = 0 \quad \text{for all } j$$

Notice that Lagrange's method doesn't tell us *how* to determine λ .

The Boltzmann Factor

Maximize $W(a_1, a_2, \dots)$ subject to the constraints $\sum_j a_j = A$, $\sum_j a_j E_j = E$

$$\frac{\partial}{\partial a_j} \left(\ln W - \alpha \sum_k a_k - \beta \sum_k a_k E_k \right) = 0, \quad j = 1, 2, \dots$$

where α and β are Lagrange multipliers. Using the expression for W , applying Stirling's approximation and evaluating the derivative we find

$$a_j \propto e^{-\beta E_j}$$

It can be shown that

$$\beta = 1/k_B T$$

At a temperature T the probability that a system is in a state with quantum mechanical energy E_j is

$$P_j = \frac{e^{-\beta E_j}}{Q}$$

$$Q = \sum_j e^{-\beta E_j} \quad (\beta = 1/k_B T) \quad \text{canonical partition function}$$

Thermodynamic Properties of the Canonical Ensemble

Postulate:

The ensemble average

$$\sum_j P_j E_j = Q^{-1} \sum_j e^{-\beta E_j} E_j = Q^{-1} \mathbf{E} \equiv U(N, V, T)$$

is the observable “internal” energy.

From the above,

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

$$c_v \equiv \left(\frac{\partial U}{\partial T} \right)_{N, V} = - \frac{1}{k_B T^2} \left(\frac{\partial U}{\partial \beta} \right)_{N, V} = k_B \beta^2 \left(\frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{N, V} \quad \text{constant-volume heat capacity}$$

Separable Systems

The partition function for a system of two types of noninteracting particles, described by the Hamiltonian

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)}$$

with energy eigenvalues

$$E_{jk} = \varepsilon_j^{(1)} + \varepsilon_k^{(2)}$$

is

$$Q = Q^{(1)} Q^{(2)}$$

If the energy can be written as a sum of various (single-particle-like) contributions, the partition function is a product of the corresponding components.

Distinguishable vs. Indistinguishable Particles

The partition function for a system of N distinguishable particles is

$$Q = q^N$$

where q is the partition function of one particle.

The partition function for a system of N indistinguishable particles is

$$Q = q^N / N!$$

Partition Function for Polyatomic Molecules

The Hamiltonian of a molecule is often approximated by a sum of translational, rotational, vibrational and electronic contributions:

$$\hat{H} = \hat{H}^{\text{trans}} + \hat{H}^{\text{rot}} + \hat{H}^{\text{vib}} + \hat{H}^{\text{elec}}$$

Within this approximation the molecular partition function is

$$q = q^{\text{trans}} q^{\text{rot}} q^{\text{vib}} q^{\text{elec}}$$

Translational Partition function

Atom in box of volume V :

$$q^{\text{trans}}(V, T) = \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} V$$

Translational energy of an ideal gas:

$$U^{\text{trans}}(V, T) = \frac{3}{2} RT$$

Translational contribution to the heat capacity of an ideal gas:

$$c_v^{\text{trans}} = \frac{3}{2} R$$

Electronic Partition function

There is no general expression for electronic energies, thus one cannot write an expression for the electronic partition function. However, electronic excitation energies usually are large, so at ordinary temperatures

$$q^{\text{elec}}(V, T) \approx 1$$

Vibrational Partition Function for Diatomic Molecule

$$\varepsilon_v^{\text{vib}} = \left(v + \frac{1}{2}\right) \hbar \omega \quad (\text{harmonic oscillator approximation})$$

$$q^{\text{vib}} = \frac{e^{-\hbar\omega\beta/2}}{1 - e^{-\hbar\omega\beta}} = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}}, \quad \Theta_{\text{vib}} = \frac{\hbar\omega}{k_B} \quad \text{"vibrational temperature"}$$

Vibrational energy of diatomic molecule:

$$U^{\text{vib}} = N\hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega\beta} - 1} \right)$$

Vibrational contribution to heat capacity of diatomic molecule:

$$c_v^{\text{vib}} = R \left(\frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1 - e^{-\Theta_{\text{vib}}/T}\right)^2}$$

$$\text{As } T \rightarrow \infty, \quad c_v^{\text{vib}} \rightarrow R$$

Rotational Partition Function for Diatomic Molecule

$$\varepsilon_J^{\text{rot}} = \frac{\hbar^2 J(J+1)}{2I} \quad (\text{rigid rotor approximation, } (2J+1)\text{-fold degeneracy})$$

$$q^{\text{rot}} = \frac{8\pi^2 I k_B T}{h^2} = \frac{T}{\Theta_{\text{rot}}}, \quad \Theta_{\text{rot}} = \frac{h^2}{8\pi^2 I k_B} \quad \text{"rotational temperature"}$$

Rotational energy of diatomic molecule:

$$U^{\text{rot}} = Nk_B T$$

Rotational contribution to heat capacity of diatomic molecule:

$$c_v^{\text{rot}} = R$$

Symmetry factors:

If there are identical atoms in a molecule some rotational operations result in identical states. We introduce the “symmetry factor” σ to correct this overcounting.

$$q^{\text{rot}} = \frac{T}{\sigma \Theta_{\text{rot}}}$$

For homonuclear diatomic molecules at high temperature $\sigma=2$.

Polyatomic Molecules

n atoms, $3n$ degrees of freedom.

Nonlinear molecules:

3 Translational degrees of freedom

3 Rotational degrees of freedom

$3n-6$ Vibrational degrees of freedom

$$q^{\text{vib}} = \prod_{j=1}^{\alpha} q_j^{\text{vib}},$$

Linear molecules:

3 Translational degrees of freedom

2 Rotational degrees of freedom

$3n-5$ Vibrational degrees of freedom

$$\alpha = \begin{array}{l} 3n - 5 \text{ (linear)} \\ 3n - 6 \text{ (nonlinear)} \end{array}$$

Rotational partition function for linear polyatomic molecules

$$q^{\text{rot}} = \frac{T}{\sigma \Theta_{\text{rot}}}, \quad \Theta_{\text{rot}} = \frac{h^2}{8\pi^2 I k_B}$$

Symmetry factor:

The number of different ways the molecule can be rotated into an indistinguishable configuration.

Asymmetric molecules: $\sigma = 1$ (e.g. COS)

Symmetric molecules: $\sigma = 2$ (e.g. CO₂, HC≡CH)

Rotational partition function for nonlinear polyatomic molecules

Rotational properties of rigid bodies: three moments of inertia I_A, I_B, I_C .

$$I_A = I_B = I_C \quad \text{spherical top (e.g. CH}_4\text{)}$$

$$I_A = I_B \neq I_C \quad \text{symmetric top (e.g. NH}_3\text{)}$$

$$I_A \neq I_B \neq I_C \quad \text{asymmetric top (e.g. H}_2\text{O)}$$

$$\text{Spherical top: } q^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 I k_B T}{h^2} \right)^{\frac{3}{2}}$$

$$\text{Symmetric top: } q^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 I_A k_B T}{h^2} \right) \left(\frac{8\pi^2 I_C k_B T}{h^2} \right)^{\frac{1}{2}}$$

$$\text{Asymmetric top: } q^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 I_A k_B T}{h^2} \right)^{\frac{1}{2}} \left(\frac{8\pi^2 I_B k_B T}{h^2} \right)^{\frac{1}{2}} \left(\frac{8\pi^2 I_C k_B T}{h^2} \right)^{\frac{1}{2}}$$

The symmetry factor equals the number of pure rotational elements (including the identity) in the point group of a nonlinear molecule.

The Normal Mode Transformation

$$\hat{H} = \sum_{i=1}^{3n} \frac{\hat{p}_i^2}{2m_i} + V(\mathbf{r}_1, \mathbf{r}_2, \dots) \quad (\text{Cartesian atomic coordinates})$$

Expand the potential in a Taylor series about the minimum through quadratic terms:

$$V \approx \frac{1}{2} \sum_{i=1}^{3n} \sum_{j=1}^{3n} x_i K_{ij} x_j = \frac{1}{2} \mathbf{x}^T \cdot \mathbf{K} \cdot \mathbf{x} \quad (x_i = r_i - r_i^{\min} \quad \text{Cartesian displacement coordinates})$$

where $K_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$ force constant matrix

We will show in a simple way how one can obtain an independent mode form by doing a coordinate transformation. In practice, the normal mode transformation proceeds after the Hamiltonian is expressed in internal coordinates.

Transform to mass-weighted Cartesian coordinates $\mathbf{q}_i = \sqrt{m_i} x_i$

$$\text{Then } \frac{p_i^2}{2m} = \frac{1}{2} \mathbf{p}_i^2 \quad \text{and} \quad H = \sum_{i=1}^{3n} \frac{1}{2} \mathbf{p}_i^2 + \frac{1}{2} \sum_{i=1}^{3n} \sum_{j=1}^{3n} \mathbf{q}_i \tilde{\mathbf{K}}_{ij} \mathbf{q}_j$$

$$\tilde{\mathbf{K}}_{ij} = \frac{\partial^2 V}{\partial \mathbf{q}_i \partial \mathbf{q}_j} = m_i^{-\frac{1}{2}} m_j^{-\frac{1}{2}} \frac{\partial^2 V}{\partial x_i \partial x_j}$$

Introduce normal mode coordinates Q_i (with conjugate momenta P_i): $\mathbf{U} \cdot \mathbf{Q} = \mathbf{q}$

$$\mathbf{q} \cdot \tilde{\mathbf{K}} \cdot \mathbf{q} = \mathbf{Q}^T \cdot \mathbf{U}^T \cdot \tilde{\mathbf{K}} \cdot \mathbf{U} \cdot \mathbf{Q} = \mathbf{Q}^T \cdot \mathbf{\Lambda} \cdot \mathbf{Q}$$

$$\mathbf{U}^T \cdot \tilde{\mathbf{K}} \cdot \mathbf{U} = \mathbf{\Lambda}, \quad \text{or}$$

$$\tilde{\mathbf{K}} \cdot \mathbf{U} = \mathbf{U} \cdot \mathbf{\Lambda}$$

\mathbf{U} is the orthogonal matrix of eigenvectors, $\mathbf{\Lambda}$ is the diagonal matrix of eigenvalues.

$$\text{Now } H = \sum_{i=1}^{3n} \frac{1}{2} P_i^2 + \frac{1}{2} \sum_{i=1}^{3n} \omega_i^2 Q_i^2$$

The Equipartition Principle

Every quadratic term in the Hamiltonian of a system contributes $\frac{1}{2} k_B T$ to the internal energy U and $\frac{1}{2} k_B$ to the heat capacity c_v at high temperature.

Translation in one dimension: $\hat{H} = \frac{1}{2} \frac{\hat{p}^2}{m}$ (one quadratic term) $\Rightarrow \frac{1}{2} k_B$

Rotation about an axis: $\hat{H} = \frac{1}{2} \frac{d^2}{d\varphi^2}$ (one quadratic term) $\Rightarrow \frac{1}{2} k_B$

(linear molecules: 2 such terms, nonlinear molecules: 3 such terms)

Vibration: $\hat{H} = \frac{1}{2} \frac{\hat{p}^2}{m} + \frac{1}{2} m\omega^2 \hat{x}^2$ (two quadratic terms) $\Rightarrow k_B$

Diatomic molecule: $3\frac{1}{2} k_B$

Linear triatomic molecule: $6\frac{1}{2} k_B$

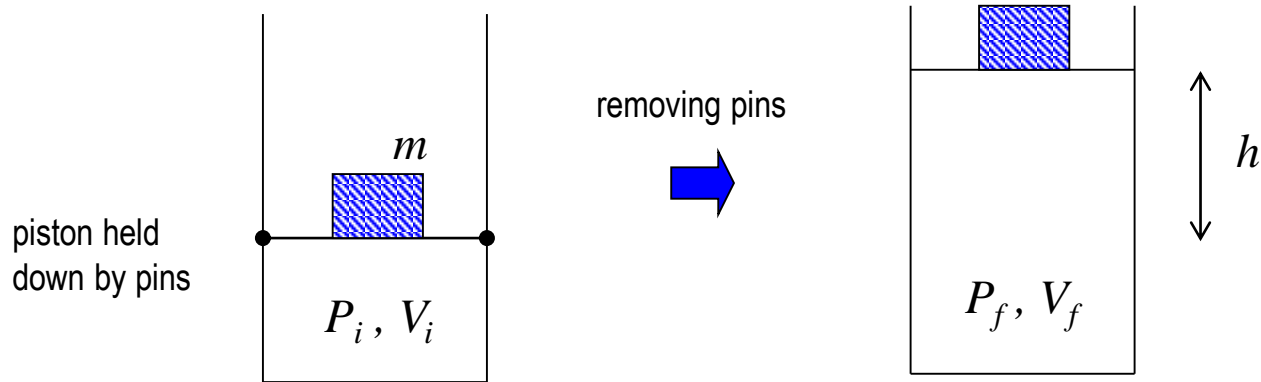
Nonlinear triatomic molecule: $6 k_B$

THE FIRST LAW OF THERMODYNAMICS

The first law is about conservation of energy
(in the form of work and heat)

Mechanical Work

Expansion of a gas



Work performed by the gas: $w = -P_{\text{ext}} \Delta V$

Infinitesimal volume change: $\delta w = -P_{\text{ext}} \delta V$

Convention: work done on the system is taken as positive.

Mechanical work:

$$w = -\int_{V_i}^{V_f} P_{\text{ext}}(V) dV$$

Reversible Processes

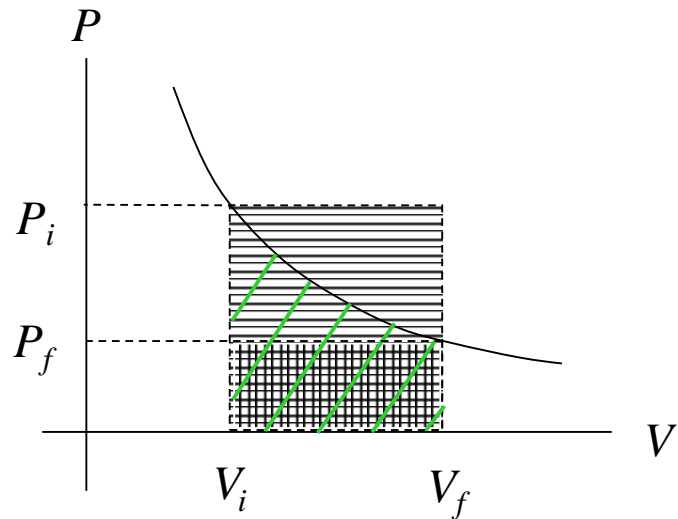
A process is called reversible if $P_{\text{system}} = P_{\text{ext}}$ at all times. The work expended to compress a gas along a reversible path can be completely recovered upon reversing the path.

- ❖ When the process is reversible the path can be reversed, so expansion and compression correspond to the same amount of work.
- ❖ To be reversible, a process must be infinitely slow.

A process is called reversible if $P_{\text{system}} = P_{\text{ext}}$ at all times.

$$w = -\int_{V_i}^{V_f} P(V) dV$$

Reversible Isothermal Expansion/Compression of Ideal Gas



$$w = -nRT \ln \frac{V_f}{V_i}$$

Reversible isothermal compression: minimum possible work

Reversible isothermal expansion: maximum possible work

Exact and Inexact Differentials

A state function is a property that depends solely on the state of the system. It does not depend on how the system was brought to that state.

When a system is brought from an initial to a final state, the change in a state function is independent of the path followed.

An infinitesimal change of a state function is an exact differential.

Internal energy U : state function

dU : exact differential

$$\int_i^f dU = U_f - U_i = \Delta U, \text{ independent of the path}$$

Work and heat are not state functions and do not correspond to exact differentials.

Of the three thermodynamic variables, only two are independent. It is convenient to choose V and T as the independent variables for U .

The First Law

The sum of the heat q transferred to a system and the work w performed on it equal the change ΔU in the system's internal energy.

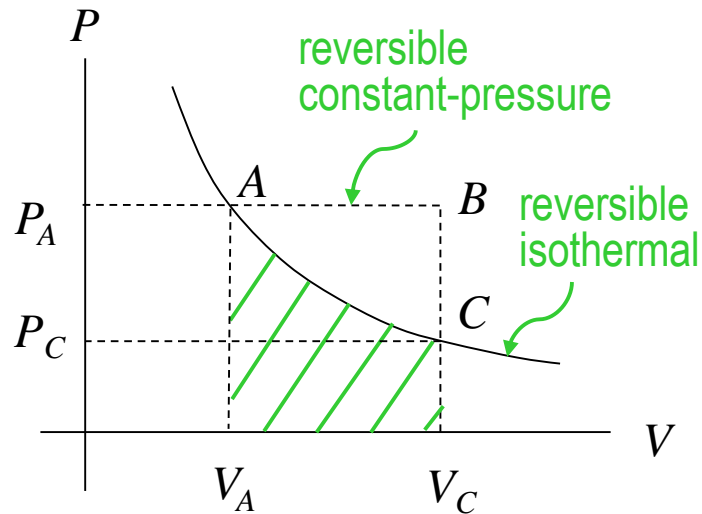
$$\Delta U = q + w$$

Postulate: The internal energy is a state function of the system.

Work and heat are not state functions and do not correspond to exact differentials.

$$dU = \bar{d}q - PdV$$

Work and Heat along Reversible Isothermal Expansion for an Ideal Gas, where $U=U(T)$



$$T_B = T_A \frac{V_C}{V_A}$$

$$w_{AC} = -nRT_A \ln \frac{V_C}{V_A}$$

$$w_{BC} = 0$$

$$w_{AB} = -P_A (V_B - V_A)$$

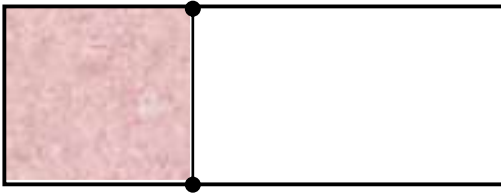
$$\Delta U_{AC} = 0 \Rightarrow q_{AC} = nRT_A \ln \frac{V_C}{V_A}$$

$$q_{BC} = \Delta U_{BC} = \int_{T_B}^{T_C} c_V dT$$

$$\Delta U_{AB} = \int_{T_A}^{T_B} c_V dT$$

$$q_{AB} = \Delta U_{AB} - w_{AB} = \int_{T_A}^{T_B} c_V dT + P_A (V_B - V_A)$$

Free Expansion



Suddenly remove the partition

No work, no heat!

$$\Delta U = 0$$

$$dU = c_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$U = U(T) \Leftrightarrow \Delta T = 0$$

For real, non-ideal gases these hold approximately, and $\left(\frac{\partial U}{\partial V} \right)_T$ is small.

Adiabatic Processes

A process is called adiabatic if no heat is transferred to or out of the system.

$$\Delta U = w_{\text{ad}}, \quad dU = dw_{\text{ad}}$$

$$dU = c_V dT = -PdV$$

$$= -\frac{nRT}{V} dV \quad (\text{ideal gas})$$

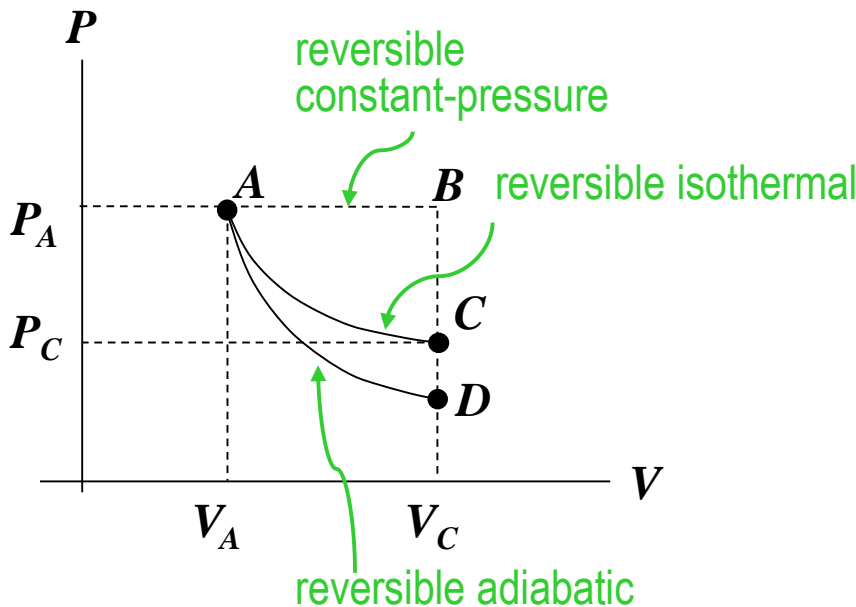
If $c_V(T)$ is known, this can be used to determine T (and thus also P) as a function of V .

For a monatomic ideal gas,

$$c_V = \frac{3}{2} nR \quad \text{independent of } T \Rightarrow$$

$$\left(\frac{T_D}{T_A}\right)^{\frac{3}{2}} = \frac{V_A}{V_D}$$

Adiabatic cooling!



Gases heat up when compressed adiabatically.

(This is why the pump used to inflate a tire becomes hot during pumping.)

Enthalpy

$$H \equiv U + PV$$

$$dH = dU + PdV + VdP = \delta q + VdP \quad \text{enthalpy function}$$

Heat capacity at constant pressure:

$$c_P = \left(\frac{\partial H}{\partial T} \right)_P$$

Ideal gas: $c_P = c_V + nR$

Heat transferred at constant pressure is enthalpy change.

Reversible Adiabatic Expansion of Ideal Gas Revisited

$$\delta q = c_V dT + PdV = c_P dT - VdP = 0$$

$$c_V dT = -PdV, \quad c_P dT = VdP$$

$$\frac{c_P}{c_V} d \ln V = -d \ln P$$

If $c_P / c_V \equiv \gamma$ is constant (e.g., monatomic ideal gas),

$$\left(\frac{V_2}{V_1} \right)^\gamma = \frac{P_1}{P_2}$$

For a monatomic ideal gas, $c_P = \frac{5}{2} nR$, $\gamma = \frac{5}{3}$

$$PV^{\frac{5}{3}} = \text{const.}$$

ENTROPY AND THE SECOND LAW

Processes evolve toward states of minimum energy and maximum disorder. These two tendencies are in competition.

The second law is about entropy and its role in determining whether a process will proceed spontaneously.

Entropy

A statement of the second law:

No process is possible whose sole effect is the absorption of heat from a reservoir and the conversion of this heat into work.

Postulate:

There exists a state function S called the entropy. This is such that, for a reversible process,

$$dS = \frac{\delta q}{T} \quad \oint dS = 0$$

$1/T$ is the integrating factor for δq .

S has units of R (or k_B). For a reversible process,

$$dU = TdS - PdV$$

Isolated system is a system that cannot exchange any matter or energy with the environment.

The second law: The entropy of an isolated system never decreases.

A spontaneous process that starts from a given initial condition always leads to the same final state. This final state is the equilibrium state.

Entropy of an Ideal Gas

$$dU = c_v dT = TdS - PdV = TdS - \frac{nRT}{V} dV \Rightarrow$$

$$dS = c_v \frac{dT}{T} + nR \frac{dV}{V} \Rightarrow$$

$$S = \int_{T_0}^T c_v(T) d \ln T + nR \int_{V_0}^V d \ln V = f(T) - f(T_0) + nR \ln \frac{V}{V_0}$$

$$= S(T, V) \quad \text{independent of the path!}$$

$$dH = c_p dT = TdS + VdP = TdS + \frac{nRT}{P} dP \Rightarrow$$

$$dS = c_p \frac{dT}{T} - nR \frac{dP}{P} \Rightarrow$$

$$S = \int_{T_0}^T c_p(T) d \ln T - nR \int_{P_0}^P d \ln P = g(T) - g(T_0) - nR \ln \frac{P}{P_0}$$

$$= S(T, P)$$

The Clausius Principle

The Clausius principle states that

No process is possible whose sole result is the transfer of heat from a cooler body to a hotter body.

The Clausius principle is another statement of the second law.



$$dU = dU_A + dU_B = 0 \quad (\text{isolated system})$$

$$dS = dS_A + dS_B = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} = dU_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right)$$

According to Clausius' principle, if $T_A > T_B$ then heat will flow from A to B, i.e.,

$$dS > 0$$

A spontaneous process evolves in the direction of increasing entropy.

Reversible vs. Spontaneous (Irreversible) Processes

In an isolated system $\dot{d}q = 0$.

Reversible process: $dS = \frac{\dot{d}q}{T}$.

Spontaneous (irreversible) process: $dS > \frac{\dot{d}q}{T}$.

In general, $dS \geq \frac{\dot{d}q}{T}$.

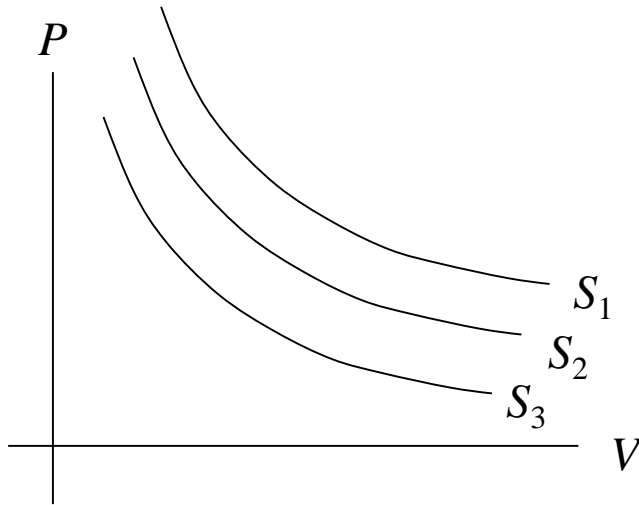
A reversible adiabatic process is an isentropic process, $dS = 0$.

The Caratheodory Principle

This is yet another statement of the second law. It states that

In the neighborhood (however close) of any equilibrium state of a system (of any number of thermodynamic coordinates) there exist states that cannot be reached by reversible adiabatic processes.

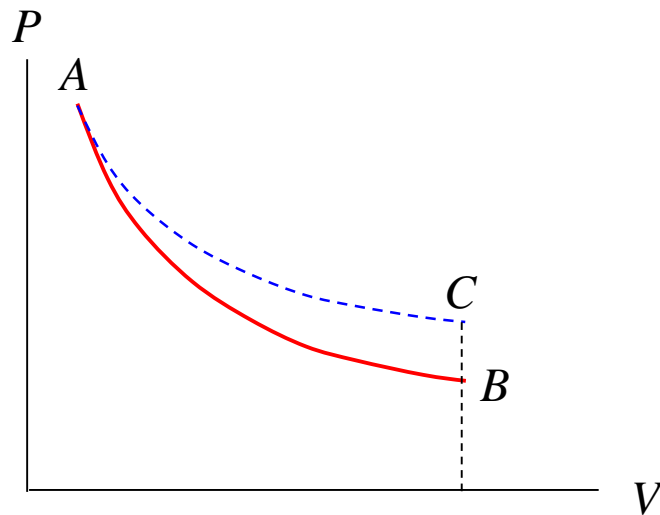
Caratheodory's statement is equivalent to the existence of the entropy function.



Family of isentropic (constant S) surfaces that don't intersect.

Proof of Existence of Non-Intersecting Adiabatic Surfaces

Suppose B can be reached from A by a reversible adiabatic process. Let's suppose C can also be reached from A via a reversible adiabatic process.



Consider the process $A \rightarrow B \rightarrow C \rightarrow A$.

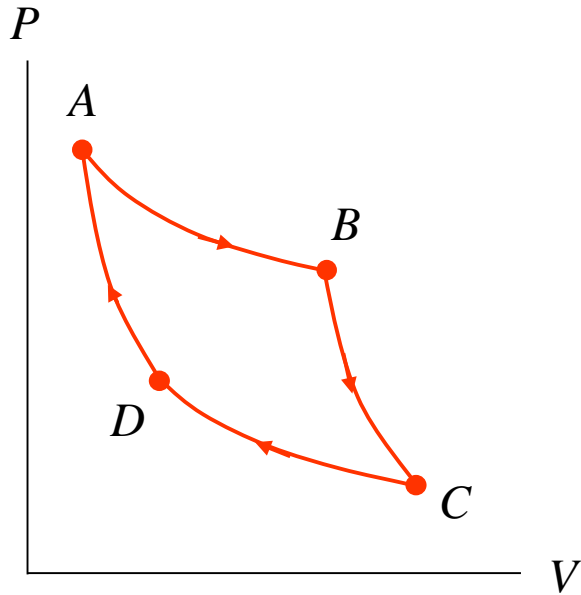
$$\Delta U_{A \rightarrow B \rightarrow C \rightarrow A} = 0 = q_{B \rightarrow C} + w_{A \rightarrow B, C \rightarrow A}$$

$$q_{B \rightarrow C} > 0 \quad (\text{heat absorption}) \Rightarrow$$

$$w_{A \rightarrow B, C \rightarrow A} = -q_{B \rightarrow C} < 0$$

So in this cycle there is heat absorbed that is converted into work. This is in contradiction with the second law. We arrived at this contradiction by assuming there are two reversible adiabatic processes starting from point A .

The Carnot Cycle



AB : reversible isothermal at temperature T_1

BC : reversible adiabatic

CD : reversible isothermal at temperature $T_2 < T_1$

DA : reversible adiabatic

$$\Delta U_{ABCD} = 0 \Rightarrow q_{AB} + q_{CD} = -w > 0$$

(the system does work)

Efficiency of Carnot engine:

$$\eta = \frac{|w|}{q_{AB}} = 1 - \frac{|q_{CD}|}{q_{AB}}$$

Entropy changes:

$$\Delta S_{AB} = \int_A^B \frac{dq}{T} = \frac{q_{AB}}{T_1}, \quad \Delta S_{CD} = \frac{q_{CD}}{T_2} = -\Delta S_{AB} \Rightarrow \frac{q_{CD}}{q_{AB}} = -\frac{T_2}{T_1}$$

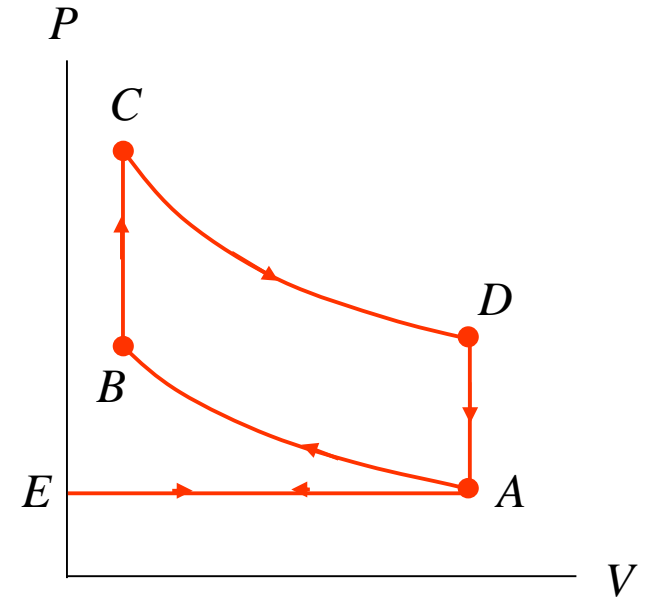
$$\eta = 1 - \frac{T_2}{T_1} < 1 \quad (\text{unless } T_2 = 0)$$

One can never utilize all the thermal energy given to the engine by converting it into mechanical work.

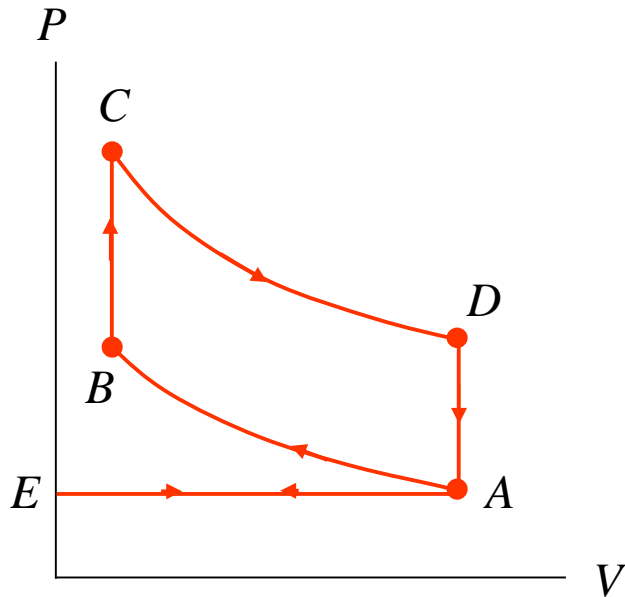
The Internal Combustion Engine

In the gasoline engine, the cycle involves six processes, four of which require motion of the piston and are called strokes. The idealized description of the engine is the Otto cycle.

1. Intake stroke. A mixture of gasoline vapor and air is drawn into the cylinder (EA).
2. Compression stroke. The mixture of gasoline vapor and air is compressed until its pressure and temperature rise considerably (AB).
3. Ignition. Combustion of the hot mixture is caused by an electric spark. The resulting combustion products attain a very high pressure and temperature, but the volume remains unchanged (BC).
4. Power stroke. The hot combustion products expand and push the piston out, thus expanding adiabatically (CD).
5. Valve exhaust. An exhaust valve allows some gas to escape until the pressure drops to that of the atmosphere (DA).
6. Exhaust stroke. The piston pushes almost all the remaining combustion products out of the cylinder (AE).



Thermodynamics of the Otto Cycle



Reversible adiabatic compression AB: $T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$

BC is reversible absorption of heat q_h from a series of reservoirs whose temperatures range from T_B to T_C :

$$q_h = \int_{T_B}^{T_C} c_V dT.$$

If we assume c_V is constant, $q_h = c_V (T_C - T_B)$.

Reversible adiabatic expansion CD: $T_C V_C^{\gamma-1} = T_D V_D^{\gamma-1}$ or $T_C V_B^{\gamma-1} = T_D V_A^{\gamma-1}$

DA is reversible rejection of heat q_c to a series of reservoirs whose temperatures range

from T_D to T_A : $q_c = \int_{T_D}^{T_A} c_V dT = -c_V (T_D - T_A)$.

$$\eta = 1 - \frac{|q_c|}{q_h} = 1 - \frac{T_D - T_A}{T_C - T_B} = 1 - \left(\frac{V_B}{V_A} \right)^{\gamma-1}$$

V_B / V_A : compression ratio

Other Ideal Gas Engines

See <http://www.ac.wvu.edu/~vawter/PhysicsNet/Topics/ThermLaw2/Entropy/GasCycleEngines.html>

copied in 444-web-page/Ideal Heat Engine Gas Cycles.htm

Entropy of Reversible Isothermal Expansion of an Ideal Gas

Reversible isothermal expansion: $\bar{d}q_{\text{sys}} = dU_{\text{sys}} - \bar{d}w_{\text{sys}}$

But $dU_{\text{sys}} = 0 \Rightarrow \bar{d}q_{\text{sys}} = PdV$

$$\Delta S_{\text{sys}} = \int_1^2 \frac{\bar{d}q_{\text{sys}}}{T} = \int_{V_1}^{V_2} \frac{PdV}{T} = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1} > 0$$

The heat entering the system was absorbed from the environment. Then

$$\bar{d}q_{\text{env}} = -\bar{d}q_{\text{sys}} \Rightarrow \Delta S_{\text{env}} = -\Delta S_{\text{sys}}, \quad \Delta S_{\text{univ}} = 0.$$

Entropy of Spontaneous Expansion of an Ideal Gas

Spontaneous expansion: $q_{\text{sys}} = \Delta U_{\text{sys}} = w_{\text{sys}} = 0$

Entropy is a state function, so the entropy change of the system has the same value as that during a reversible (isothermal) expansion:

$$\Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} > 0$$

Because no heat is absorbed from the environment,

$$\delta q_{\text{env}} = 0 \Rightarrow \Delta S_{\text{env}} = 0, \quad \Delta S_{\text{univ}} > 0.$$

The entropy of the system increased, but the entropy of the environment remained unchanged.

Statistical Mechanical Definition of Entropy

$$S_{\text{ensemble}} = k_B \ln W$$

Completely ordered ensemble: $a_1 = 1, a_2 = a_3 = \dots = 0 \Rightarrow S_{\text{ensemble}} = 0$

Maximum disorder: $a_1 = a_2 = a_3 = \dots$ (set that maximizes W)

$$S_{\text{sys}} = \frac{1}{A} S_{\text{ensemble}}$$

$$S_{\text{sys}} = \frac{1}{A} S_{\text{ensemble}}$$

Use $W = \frac{A!}{\prod_j a_j!}$ and apply Stirling's approximation.

$$\ln W = \ln A! - \sum_j \ln a_j! \approx A \ln A - A - \sum_j (a_j \ln a_j - a_j)$$

$$S_{\text{ensemble}} = k_B A \ln A - k_B \sum_j a_j \ln a_j$$

Use populations $p_j = \frac{a_j}{A}$

$$S_{\text{ensemble}} = k_B A \ln A - k_B \sum_j A p_j \ln A p_j$$

$$= k_B A \ln A - k_B A \sum_j p_j \ln A - k_B A \sum_j p_j \ln p_j$$

$$S_{\text{sys}} = -k_B \sum_j p_j \ln p_j$$

Pure and Mixed States

If all replicas of our system in a particular ensemble are in the same state n , i.e.,

$p_n = 1, p_{i \neq n} = 0$ then $S = 0$. This is called a pure ensemble.

Note: the quantum state n need not be an eigenstate of the Hamiltonian.

If the members of the ensemble are in different quantum states, i.e.,

$p_i < 1$ for all i , then $S > 0$. This is called a mixed ensemble.

The canonical ensemble is a mixed ensemble.

Entropy of the Canonical Ensemble

$$p_i = Q^{-1} e^{-\beta E_i}$$

$$S = -k_B Q^{-1} \sum_i e^{-\beta E_i} (-\beta E_i - \ln Q) = k_B \beta U + k_B \ln Q$$

$$S = \frac{U}{T} + k_B \ln Q$$

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

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

Entropy of Monatomic Ideal Gas

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

$$\left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_{N,V} = \frac{3}{2} \frac{N}{T}. \text{ Using Stirling's approximation to } \ln N!,$$

$$S = \frac{5}{2} nR + nR \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \frac{\bar{V}}{N_A} \right]$$

Molecular Interpretation of Work and Heat

$$U = \sum_j p_j E_j, \quad p_j = \frac{e^{-\beta E_j}}{Q} \Rightarrow$$

$$dU = \sum_j p_j dE_j + \sum_j E_j dp_j$$

variation of energy levels
without changing populations;
can be done by changing
the volume.

change populations without
changing energy eigenvalues;
can be done by heating
or cooling

$$dU = \sum_j p_j \left(\frac{\partial E_j}{\partial V} \right)_N dV + \sum_j E_j dp_j = -PdV + \delta q$$

$$Q = \sum_j e^{-\beta E_j}, \quad \left(\frac{\partial Q}{\partial V} \right)_{N,\beta} = -\beta \sum_j e^{-\beta E_j} \left(\frac{\partial E_j}{\partial V} \right)_N$$

$$P = -\sum_j p_j \left(\frac{\partial E_j}{\partial V} \right)_N = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta}$$

$$\delta q = \sum_j E_j dp_j$$

Example: Monatomic ideal gas

$$Q = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}N} V^N \quad \Rightarrow \quad \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} = \frac{N}{V}$$

$$P = k_B T \frac{N}{V} = nR \frac{T}{V} \quad \text{ideal gas law!}$$

We see that the ideal gas law is obtained by using relations obtained for a gas of non-interacting particles.

The Boltzmann Factor: Determination of the Lagrange Multiplier

$$S = -k_B \sum_j p_j \ln p_j \quad dS = -k_B \sum_j (\ln p_j dp_j + dp_j) = -k_B \sum_j \ln p_j dp_j$$

because $\sum_j dp_j = 0$

$$dS = -k_B \sum_j (-\beta E_j - \ln Q) dp_j = \beta k_B \sum_j E_j dp_j = \beta k_B d\bar{q} \equiv \frac{d\bar{q}}{T} \Rightarrow$$

$$\beta k_B = \frac{1}{T}$$

THE THIRD LAW

The third law is about the impossibility of attaining the absolute zero of temperature in a thermodynamic system.

Entropy as a Function of Temperature

$$dU = TdS - PdV \quad \Rightarrow \quad \left(\frac{\partial U}{\partial T} \right)_V = c_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} c_V(T) d \ln T \quad \text{under constant } V$$

$$dH = TdS + VdP \quad \Rightarrow \quad \left(\frac{\partial H}{\partial T} \right)_P = c_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} c_P(T) d \ln T \quad \text{under constant } P$$

The third law:

Absolute zero is not attainable via a finite series of processes.

or, according to the Nernst-Simon statement,

The entropy change associated with any isothermal reversible process of a condensed system approaches zero as the temperature approaches zero.

$$dS = \frac{c_V}{T} dT \quad \text{at constant } V$$

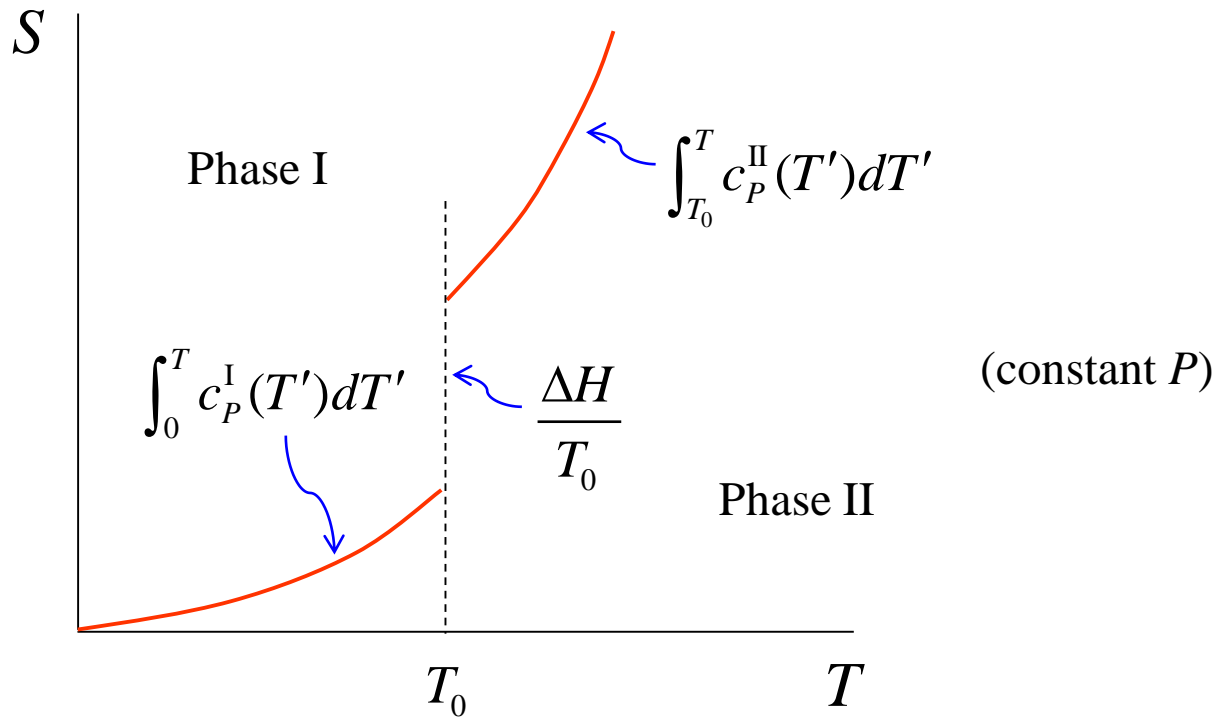
Crystals: $c_V \propto T^3$ as $T \rightarrow 0 \Rightarrow dS \propto T^2 dT$ as $T \rightarrow 0$

$$S = -k_B \sum_j p_j \ln p_j$$

The entropy of a system that has a non-degenerate ground state vanishes at the absolute zero.

First-Order Phase Transitions

Many thermodynamic variables are discontinuous across first-order phase transitions.



Helmholtz and Gibbs “Free” Energies

$A \equiv U - TS$ Helmholtz free energy

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$A = A(T, V)$$

$G \equiv A + PV = U - TS + PV$ Gibbs free energy

$$dG = -SdT - PdV + PdV + VdP = -SdT + VdP$$

$$G = G(T, P)$$

Reversible isothermal process under constant volume: $dA = 0$

Reversible isothermal process under constant pressure: $dG = 0$

Legendre Transforms

It is often desirable to express a thermodynamic function in terms of different independent variables. Most often this new desirable variable is the first derivative of a fundamental function with respect to one of its undesirable independent variables; for example,

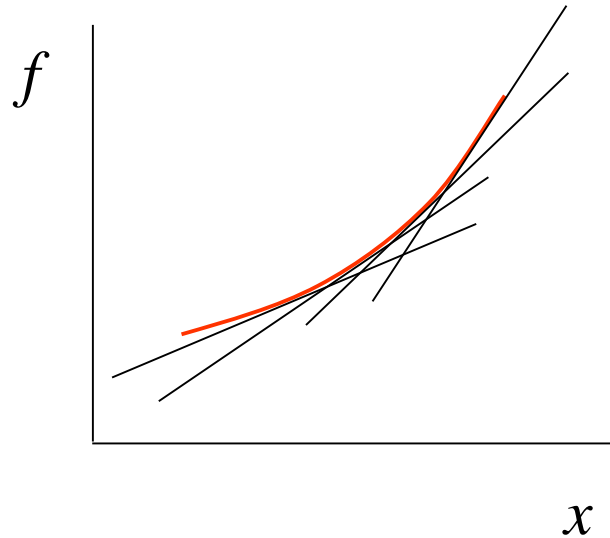
$$U = U(S, V)$$

$$dU = TdS - PdV, \quad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

We are seeking a general tool for finding a new function that contains the same information as the original fundamental thermodynamic function, but where the “undesirable” variable has been eliminated in favor of the “desirable” one. In the previous example,

We seek a new function $H = H(S, P)$ that is equivalent to U but which depends on the variable P rather than V .

General Theory of Legendre Transformation



Given a function $f(x)$, we seek an equivalent function (i.e., one containing the same information as f) whose independent variable is df/dx .

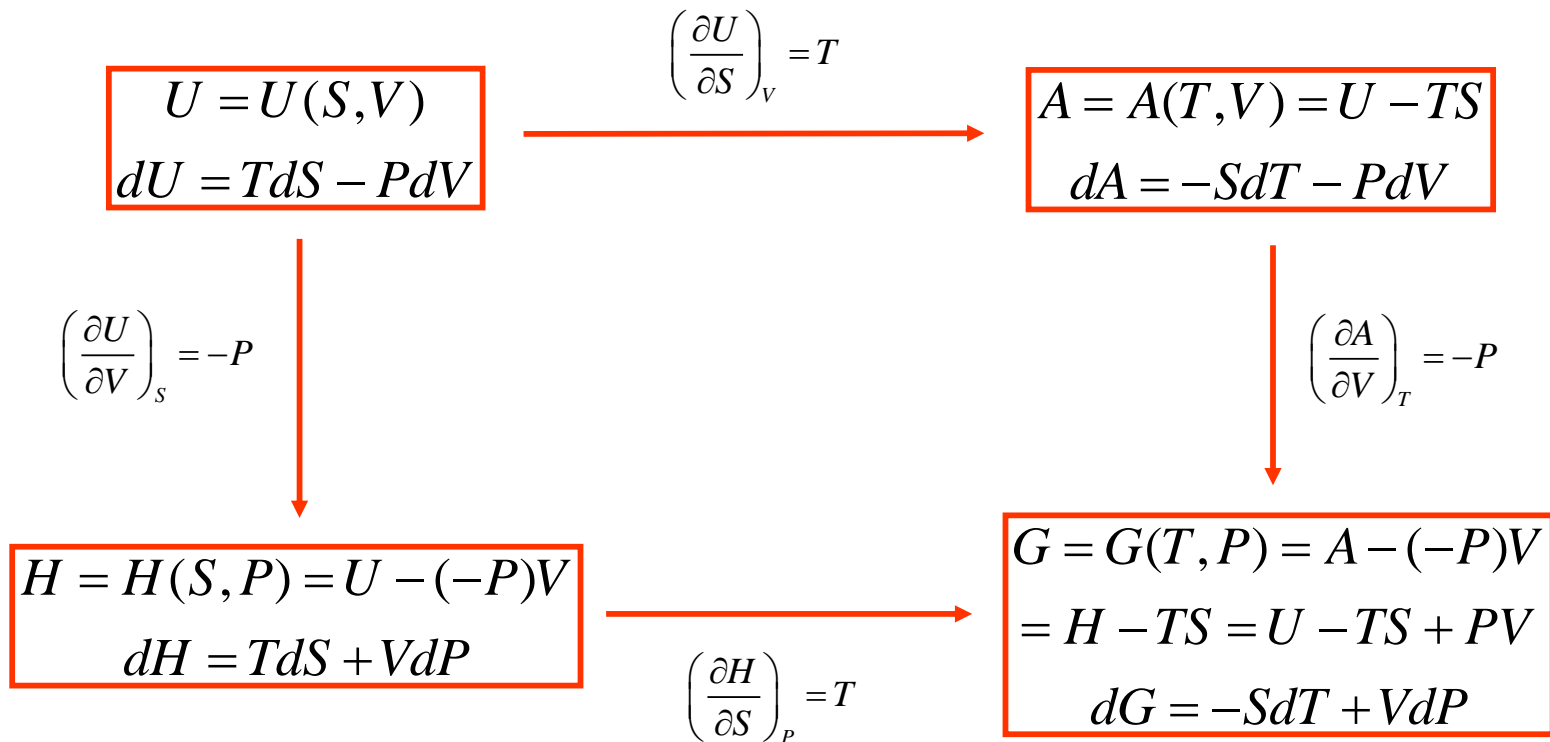
The curve $f(x)$ can be reconstructed from the family of its tangent lines.

A tangent line can be specified by its slope $f' \equiv \chi$ (new independent variable) and intercept ψ .

Notice $\chi = f' = \frac{f - \psi}{x} \Rightarrow \boxed{\psi = f - x f'(x)}$ “Legendre transform of f ”

We solve $f' \equiv \chi(x)$ for x and substitute in the above relation to obtain $\psi = \psi(x)$. This is possible if f' is single-valued, i.e., $f'' \neq 0$ at all x .

Application of Legendre Transform Theory



Maxwell's Relations

$$f(x_1, x_2)$$

$$df = y_1 dx_1 + y_2 dx_2$$

$$y_1 = \left(\frac{\partial f}{\partial x_1} \right)_{x_2} \quad y_2 = \left(\frac{\partial f}{\partial x_2} \right)_{x_1}$$

$$\left(\frac{\partial y_2}{\partial x_1} \right)_{x_2} = \left(\frac{\partial y_1}{\partial x_2} \right)_{x_1}$$

Conversely, if the Maxwell relation is satisfied, one can conclude that df is an exact differential.

Examples

$$dU = TdS - PdV$$

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad P = - \left(\frac{\partial U}{\partial V} \right)_S \quad \Rightarrow \quad \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$dA = -SdT - PdV$$

$$-S = \left(\frac{\partial A}{\partial T} \right)_V, \quad -P = \left(\frac{\partial A}{\partial V} \right)_T \quad \Rightarrow \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$dH = TdS + VdP$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$dG = -SdT + VdP$$

$$- \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

Applications of Maxwell's Relations

Entropy of a gas:

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\text{At constant } T, \quad dS = \left(\frac{\partial S}{\partial V} \right)_T dV = \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$S_2 - S_1 = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T} \right)_V dV \quad \text{along an isothermal process}$$

$$\text{Ideal gas: } \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V} \quad \Rightarrow \quad S_2 - S_1 = nR \ln \frac{V_2}{V_1}$$

Internal energy of a gas:

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial U}{\partial V} \right)_T = -P + T \left(\frac{\partial S}{\partial V} \right)_T = -P + T \left(\frac{\partial P}{\partial T} \right)_V$$

$$\text{At constant } T, \quad dU = \left(\frac{\partial U}{\partial V} \right)_T dV = \left[-P + T \left(\frac{\partial P}{\partial T} \right)_V \right] dV$$

$$U_2 - U_1 = \int_{V_1}^{V_2} \left[-P + T \left(\frac{\partial P}{\partial T} \right)_V \right] dV \quad \text{along an isothermal process}$$

We may choose a sufficiently large value of V_1 such that U_1 is given by the ideal gas law, then calculate the internal energy at a different volume where the gas does not exhibit ideal behavior.

Pfaffian Forms

Extensive variable

Intensive variable

Work

V (gas volume)

$-P$

$-P dV$

L (wire length)

F (force)

$F dL$

A (film area)

S (surface tension)

$-S dA$

M (magnetic dipole moment)

H (magnetic field)

$H dM$

...

...

...

$$dU = TdS + \sum_i Y_i dX_i$$

Pfaffian form

X_i : extensive variable

Y_i : intensive variable

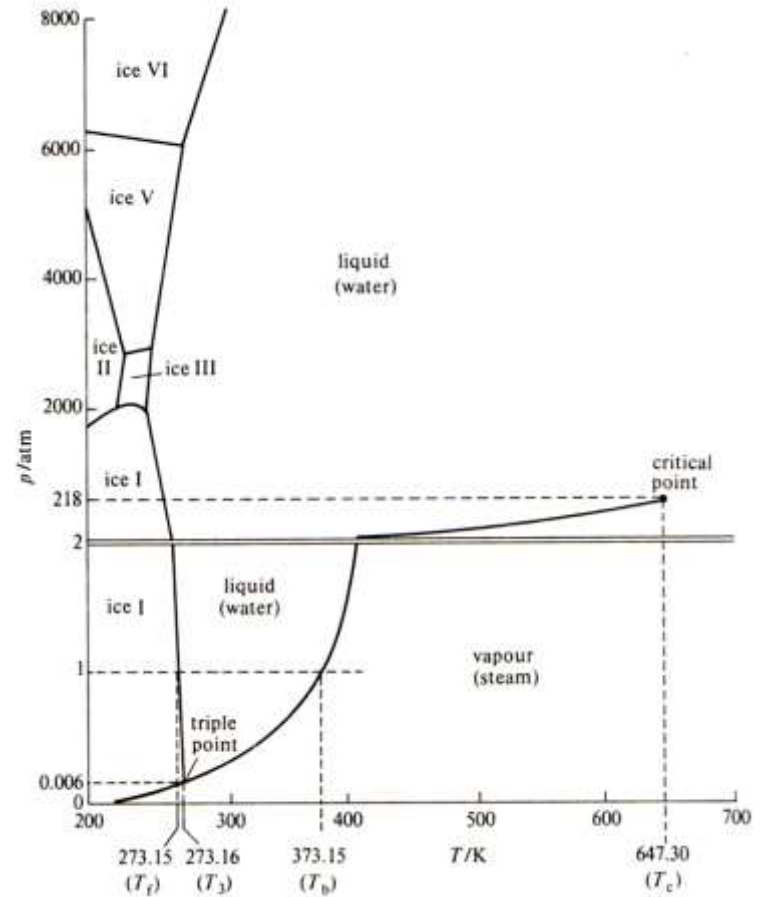
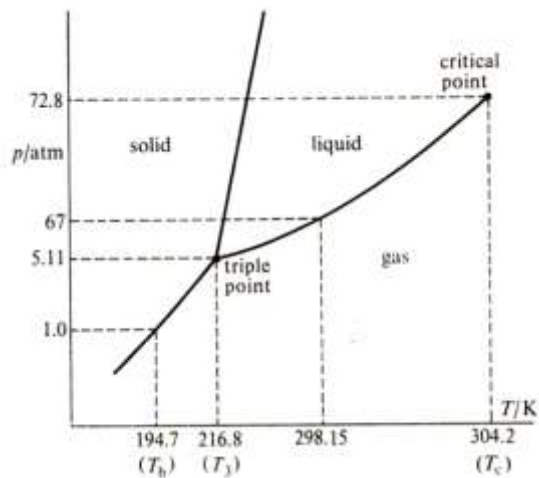
PHASE EQUILIBRIUM

What is the equilibrium state of a multi-component system?

Phase Diagrams

Water

Carbon Dioxide (Typical Case)



Phase transitions (melting, freezing, boiling, sublimation, etc.)

Chemical Potential

Intensive variable μ such that

$$\bar{d}w_{\text{chem}} = \sum_j \mu_j dn_j \quad \text{"chemical work"}$$

(The sum is over all components of a system and n_j are the mole numbers.)

$$dU = TdS - PdV + \sum_j \mu_j dn_j$$

$$dH = TdS + VdP + \sum_j \mu_j dn_j$$

$$dA = -SdT - PdV + \sum_j \mu_j dn_j$$

$$dG = -SdT + VdP + \sum_j \mu_j dn_j$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_{j \neq i}}$$

$$= \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

Pure substance: $G(P,T,n) = n g(P,T) \Rightarrow \mu = g(P,T)$

The chemical potential of a pure substance is the molar Gibbs free energy.

General Conditions of Equilibrium

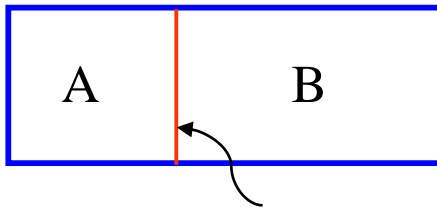
An isolated system tends to attain the state of maximum entropy with respect to its internal (extensive) degrees of freedom, subject to the given external constraints.

$$dS = 0, \quad d^2S < 0$$

Consequence:

The thermodynamic potentials attain minimum values with respect to their internal extensive variables at equilibrium, subject to the given external constraints.

I. Thermal Equilibrium



rigid, diathermal wall
impermeable to matter

Constraints:

$$V^A = \text{const.}, \quad V^B = \text{const.}, \quad U = U^A + U^B = \text{const.}$$

"Internal variable": U^A

$$U^A = U^A(S^A, V^A) \quad \text{and} \quad S = S^A(U^A, V^A) + S^B(U^B, V^B)$$

Since the volumes cannot change,

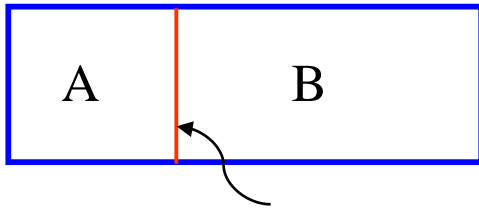
$$dS = \left(\frac{\partial S^A}{\partial U^A} \right)_{V^A} dU^A + \left(\frac{\partial S^B}{\partial U^B} \right)_{V^B} dU^B = \left[\left(\frac{\partial S^A}{\partial U^A} \right)_{V^A} - \left(\frac{\partial S^B}{\partial U^B} \right)_{V^B} \right] dU^A$$

From $dU = TdS - PdV$ we find $\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T}$ and therefore

$$dS = \left(\frac{1}{T^A} - \frac{1}{T^B} \right) dU^A$$

At equilibrium $dS = 0$ for any dU^A . It follows that $T^A = T^B$

II. Thermal and Mechanical Equilibrium



movable, diathermal wall
impermeable to matter

Constraints:

$$V = V^A + V^B = \text{const.}, \quad U = U^A + U^B = \text{const.}$$

"Internal variables": U^A, V^A

$$\begin{aligned} dS &= \left(\frac{\partial S^A}{\partial U^A} \right)_{V^A} dU^A + \left(\frac{\partial S^A}{\partial V^A} \right)_{U^A} dV^A + \left(\frac{\partial S^B}{\partial U^B} \right)_{V^B} dU^B + \left(\frac{\partial S^B}{\partial V^B} \right)_{U^B} dV^B \\ &= \left[\left(\frac{\partial S^A}{\partial U^A} \right)_{V^A} - \left(\frac{\partial S^B}{\partial U^B} \right)_{V^B} \right] dU^A + \left[\left(\frac{\partial S^A}{\partial V^A} \right)_{U^A} - \left(\frac{\partial S^B}{\partial V^B} \right)_{U^B} \right] dV^A \end{aligned}$$

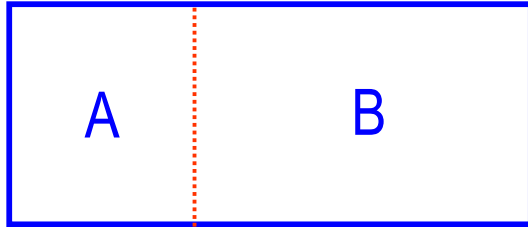
From $dU = TdS - PdV$ we find $\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T}$, $\left(\frac{\partial S}{\partial V} \right)_U = \frac{P}{T}$ and therefore

$$dS = \left(\frac{1}{T^A} - \frac{1}{T^B} \right) dU^A + \left(\frac{P^A}{T^A} - \frac{P^B}{T^B} \right) dV^A.$$

At equilibrium $dS = 0$ for any dU^A, dV^A . It follows that

$$T^A = T^B, \quad P^A = P^B$$

III. Equilibrium with Respect to Matter Flow



Rigid, diathermal
wall permeable to substance 1

Internal variables: U^A , n_1^A

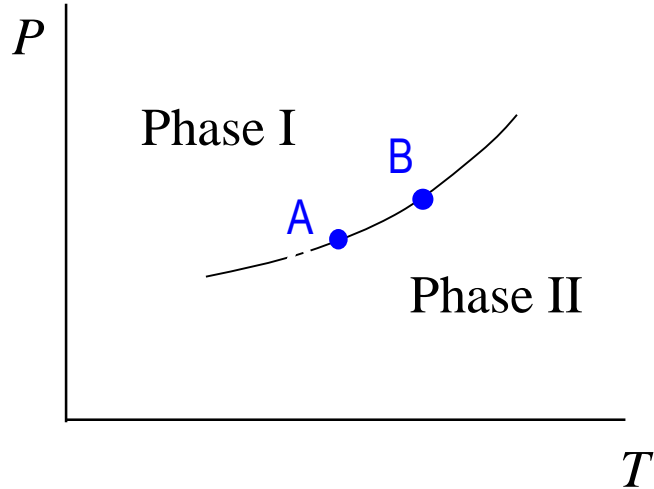
$$dS = \left(\frac{\partial S^A}{\partial U^A} \right)_{V^A, n_1^A} dU^A + \left(\frac{\partial S^A}{\partial n_1^A} \right)_{V^A, U^A} dn_1^A + \left(\frac{\partial S^B}{\partial U^B} \right)_{V^B, n_1^B} dU^B + \left(\frac{\partial S^B}{\partial n_1^B} \right)_{V^B, U^B} dn_1^B$$

$$dU = TdS - PdV + \sum_j \mu_j dn_j \quad \Rightarrow \quad \left(\frac{\partial S}{\partial n_1} \right)_{U, V} = -\frac{\mu_1}{T}$$

$$dS = \left(\frac{1}{T^A} - \frac{1}{T^B} \right) dU^A - \left(\frac{\mu_1^A}{T^A} - \frac{\mu_1^B}{T^B} \right) dn_1^A$$

At equilibrium $T^A = T^B$, $\mu_1^A = \mu_1^B$

1st Order Phase Transitions: The Clausius-Clapeyron Equation



$$d\mu^I = \mu_B^I - \mu_A^I = -\bar{S}^I dT + \bar{V}^I dP$$

$$d\mu^{II} = \mu_B^{II} - \mu_A^{II} = -\bar{S}^{II} dT + \bar{V}^{II} dP$$

$$(\bar{V}^{II} - \bar{V}^I) dP = (\bar{S}^{II} - \bar{S}^I) dT \quad \Rightarrow \quad \frac{dP}{dT} = \frac{\Delta\bar{S}^{I \rightarrow II}}{\Delta\bar{V}^{I \rightarrow II}}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}}$$

Clapeyron equation

Liquid-to-vapor transition

$$\Delta\bar{S}^{l\rightarrow g} > 0, \quad \Delta\bar{V}^{l\rightarrow g} > 0 \quad \Rightarrow \quad \frac{dP}{dT} > 0$$

Increase in pressure causes conversion to the higher-density liquid phase.

Solid-to-liquid transition

$$\Delta\bar{S}^{s\rightarrow l} > 0$$

$$\text{If } \Delta\bar{V}^{s\rightarrow l} > 0 \quad \text{then} \quad \frac{dP}{dT} > 0$$

$$\text{If } \Delta\bar{V}^{s\rightarrow l} < 0 \quad \text{then} \quad \frac{dP}{dT} < 0. \quad \text{This is the case with water.}$$

The Clapeyron equation is an expression of Le Chatelier's principle.

Approximation for liquid-vapor phase transition:

$$\bar{V}^g \gg \bar{V}^l, \quad \bar{V}^g \approx \frac{RT}{P} \text{ (ideal gas), so}$$

$$\frac{1}{P} \frac{dP}{dT} = \frac{\Delta \bar{H}^{l \rightarrow g}}{RT^2}$$

Clausius-Clapeyron approximation

Statistical Mechanical Calculation of Chemical Potential

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{P,T} = \left(\frac{\partial A}{\partial n} \right)_{T,V} = \dots$$

$$A = U - TS = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} - T \left[k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q \right]$$

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

$$\mu = -k_B T \left(\frac{\partial \ln Q}{\partial n} \right)_{T,V} = -RT \left(\frac{\partial \ln Q}{\partial N} \right)_{T,V}$$

Chemical Potential of Ideal Gas

$$Q = \frac{q^N}{N!} \Rightarrow \ln Q = N \ln q - \ln N! \approx N \ln q - (N \ln N - N)$$

$$\frac{\partial \ln Q}{\partial N} = \ln \frac{q}{N}$$

$$PV = nRT = \frac{n}{N_A} N_A RT = N k_B T \Rightarrow \frac{V}{N} = \frac{k_B T}{P}$$

$$\mu = -RT \ln \frac{q}{V} \frac{k_B T}{P} = -RT \ln \frac{q}{V} k_B T + RT \ln P \Rightarrow$$

$$\mu = -RT \ln \frac{q}{V} \frac{k_B T}{P^0} + RT \ln \frac{P}{P^0}, \text{ or}$$

$$\mu = \mu_0 + RT \ln \frac{P}{P_0}$$

P^0 standard pressure (10^5 Pa)

SOLUTIONS

We consider a two-component system with mole numbers n_1 and n_2 .

$$dG = VdP - SdT + \mu_1 dn_1 + \mu_2 dn_2$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \quad \text{at constant } P \text{ and } T$$

Imagine increasing the mole numbers from 0 to their final values by varying a dimensionless parameter λ :

$$dn_1 = n_1 d\lambda, \quad dn_2 = n_2 d\lambda$$

$$G = \int_0^{n_1} \mu_1 dn_1 + \int_0^{n_2} \mu_2 dn_2 = \int_0^1 (\mu_1 n_1 + \mu_2 n_2) d\lambda = \mu_1 n_1 + \mu_2 n_2$$

$$G = G_1 + G_2 = \bar{G}_1 n_1 + \bar{G}_2 n_2$$

\bar{G}_i : partial molar free energies

$$\bar{G}_i = \mu_i$$

The partial molar free energy is the chemical potential of the substance, i.e., an intensive variable. However, the partial molar free energies generally depend on the mole fraction $n_1/(n_1 + n_2)$. This is so because the partial derivatives

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

are functions of all the variables, including n_j .

Using a similar procedure we can write

$$V = V_1 + V_2 = \bar{V}_1 n_1 + \bar{V}_2 n_2 \quad (\bar{V}_i : \text{partial molar volumes})$$

The partial molar volumes depend on the mole fraction of the particular substance in the solution and are not additive when substances are mixed! This statement applies generally to any extensive variable. Of course extensive variables still scale linearly with the total number of moles, provided the mole fraction of each substance remains fixed.

Euler Relations

The internal energy U is a function of extensive variables, $U = U(S, V, n_1, n_2, \dots)$.

Based on the previous remarks, U is a homogeneous first order property, i.e.,

$$U(\lambda S, \lambda V, \lambda n_1, \lambda n_2, \dots) = \lambda U(S, V, n_1, n_2, \dots)$$

Differentiating with respect to λ ,

$$\begin{aligned} U(S, V, n_1, n_2, \dots) &= \frac{\partial}{\partial \lambda} U(\lambda S, \lambda V, \lambda n_1, \lambda n_2, \dots) \\ &= \frac{\partial U(\lambda S, \lambda V, \lambda n_1, \lambda n_2, \dots)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda n_1, \lambda n_2, \dots)}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} \\ &+ \frac{\partial U(\lambda S, \lambda V, \lambda n_1, \lambda n_2, \dots)}{\partial(\lambda n_1)} \frac{\partial(\lambda n_1)}{\partial \lambda} + \dots \end{aligned}$$

This is true for any value of λ . For $\lambda = 1$,

$$U(\lambda S, \lambda V, \lambda n_1, \lambda n_2, \dots) = \lambda U(S, V, n_1, n_2, \dots)$$

$$\frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \frac{\partial U}{\partial n_1} n_1 + \dots = U \quad \Rightarrow$$

$$U = TS - PV + \sum_i \mu_i n_i$$

This is called Euler's relation for the internal energy.

Other Euler relations:

$$H = U + PV \Rightarrow H = TS + \sum_i \mu_i n_i$$

$$A = U - TS \Rightarrow A = -PV + \sum_i \mu_i n_i$$

$$G = A + PV \Rightarrow G = \sum_i \mu_i n_i$$

The Gibbs-Duhem Relation

Differentiating the Euler relation for dG ,

$$dG = \sum_j \mu_j dn_j + \sum_j n_j d\mu_j$$

Using the relation

$$dG = -SdT + VdP + \sum_j \mu_j dn_j$$

we obtain the Gibbs-Duhem relation

$$SdT - VdP + \sum_j n_j d\mu_j = 0$$

This result can also be obtained from the Euler relation for dU :

$$dU = TdS + SdT - PdV - VdP + \sum_j \mu_j dn_j + \sum_j n_j d\mu_j$$

Using the relation

$$dU = TdS - PdV + \sum_j \mu_j dn_j$$

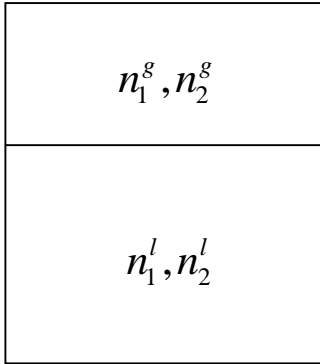
we find

$$SdT - VdP + \sum_j n_j d\mu_j = 0$$

For a one-component system we recover the known result

$$-SdT + VdP = nd\mu = dG$$

Phase Equilibrium in Multicomponent Systems



Two-component liquid at equilibrium with its vapor.
At constant P and T ,

$$dG = \left(\frac{\partial G}{\partial n_1^l} \right)_{P, T, n_2^l, n_1^g, n_2^g} dn_1^l + \left(\frac{\partial G}{\partial n_1^g} \right)_{P, T, n_1^l, n_2^l, n_2^g} dn_1^g$$

$$+ \left(\frac{\partial G}{\partial n_2^l} \right)_{P, T, n_1^l, n_1^g, n_2^g} dn_2^l + \left(\frac{\partial G}{\partial n_2^g} \right)_{P, T, n_1^l, n_2^l, n_1^g} dn_2^g$$

Since $dn_1^l + dn_1^g = 0$, $dn_2^l + dn_2^g = 0$, and $\left(\frac{\partial G}{\partial n_1^l} \right)_{P, T, n_2^l, n_1^g, n_2^g} = \mu_1^l$, etc.

$$\mu_1^l = \mu_1^g, \quad \mu_2^l = \mu_2^g$$

Assuming the vapor behaves as an ideal gas, the chemical potential of substance j in the solution is

$$\mu_j^l = \mu_j^g = \mu_j^0(T) + RT \ln \frac{P_j}{P^0}$$

For the pure substance j ,

$$\mu_j^{l*} = \mu_j^{g*} = \mu_j^0(T) + RT \ln \frac{P_j^*}{P^0}$$

because $\mu_j^0(T)$ doesn't depend on mole fractions. It follows that

$$\mu_j^l - \mu_j^{l*} = RT \ln \frac{P_j}{P_j^*}$$

Ideal Solutions and Raoult's Law

If the partial vapor pressure of each component in a solution obeys the relation

$$P_j = x_j P_j^*$$

where $x_j = \frac{n_j}{\sum_i n_i}$ is the mole fraction of component j in the liquid phase,

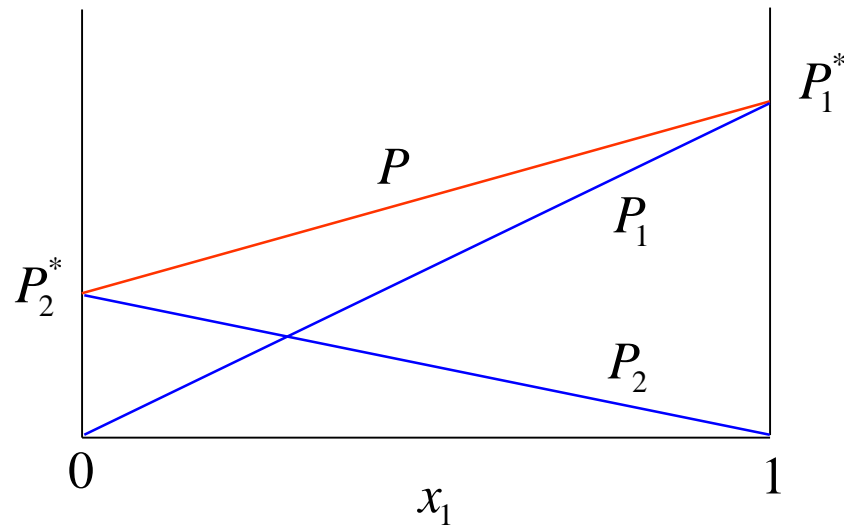
the solution is called ideal. Ideal solutions follow Raoult's law,

$$\mu_j^{\text{sol}} - \mu_j^* = RT \ln x_j$$

Here μ_j^{sol} is the chemical potential of (liquid) component j in the solution and μ_j^* is the chemical potential of the pure substance.

Vapor Pressure of Ideal Two-Component Solutions

$$P = P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = x_1 P_1^* + (1 - x_1) P_2^* = x_1 (P_1^* - P_2^*) + P_2^* \quad (\text{linear in } x_1)$$



The mole fraction of component 1 in the liquid phase is

$$x_1 = \frac{P - P_2^*}{P_1^* - P_2^*}$$

Calculate the mole fraction y_1 of component 1 in the vapor phase at a given value P of the vapor pressure using Dalton's law of partial pressures:

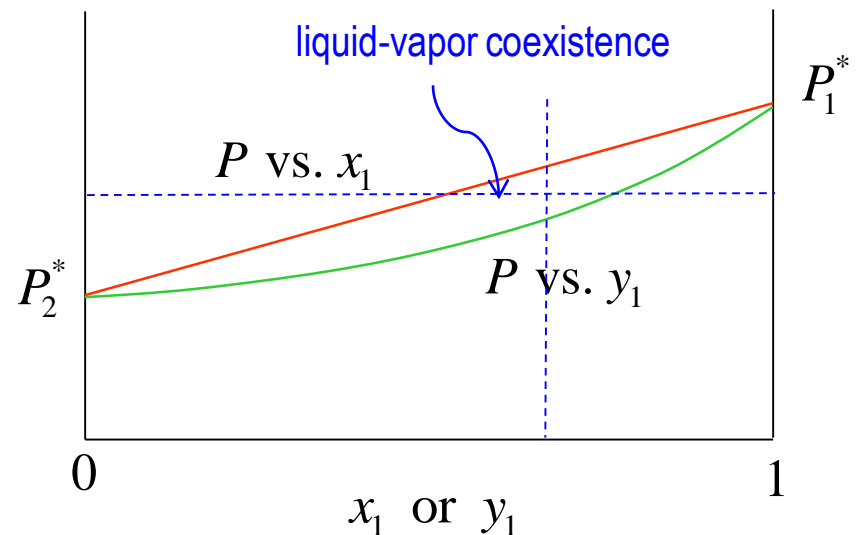
$$y_1 = \frac{P_1}{P} \quad (\text{Dalton's law})$$

$$= \frac{x_1 P_1^*}{x_1 P_1^* + x_2 P_2^*} = \frac{P - P_2^*}{P_1^* - P_2^*} \frac{P_1^*}{P} = \frac{P_1^*}{P_1^* - P_2^*} \left(1 - \frac{P_2^*}{P} \right)$$

x_1 depends linearly on P .

y_1 depends nonlinearly

(hyperbolically) on P (and on x_1)!



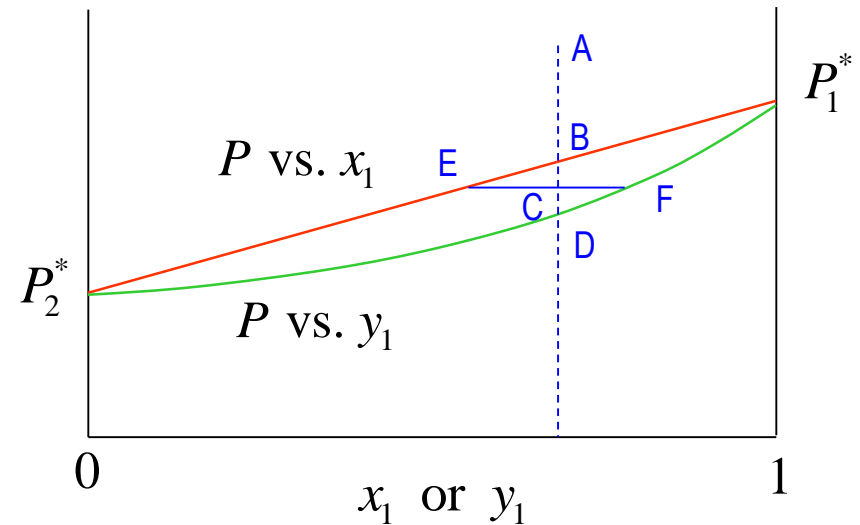
How much liquid vs. vapor is there at a pressure P^C , given that the overall mole fraction of component 1 is x_1^B ?

Mole fractions in liquid and vapor phases:

$$x_1^E = \frac{n_1^l}{n_1^l + n_2^l} = \frac{n_1^l}{n^l}, \quad y_1^F = \frac{n_1^g}{n_1^g + n_2^g} = \frac{n_1^g}{n^g} \quad \text{or} \quad n_1^l = n^l x_1^E, \quad n_1^g = n^g y_1^F$$

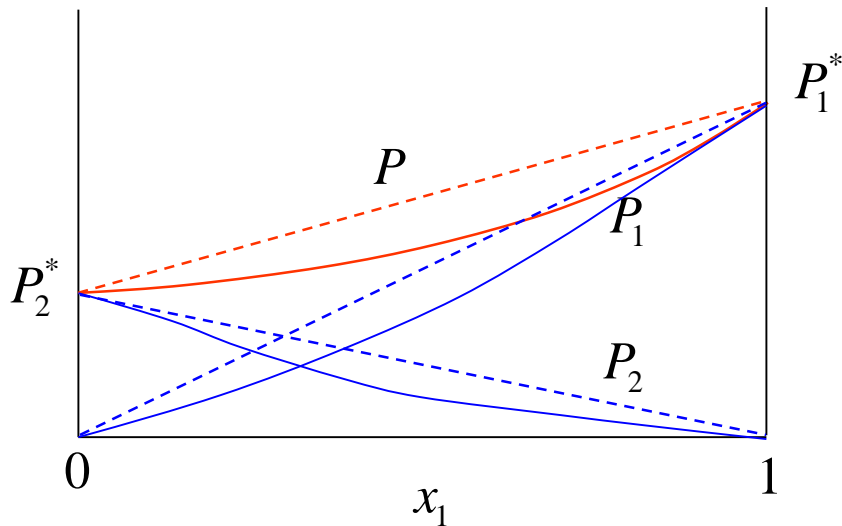
$$x_1^B = \frac{n_1^l + n_1^g}{n^l + n^g} \Rightarrow x_1^B (n^l + n^g) = n_1^l + n_1^g = n^l x_1^E + n^g y_1^F$$

$$n^l (x_1^B - x_1^E) = n^g (y_1^F - x_1^B) \quad \text{"lever rule"}$$

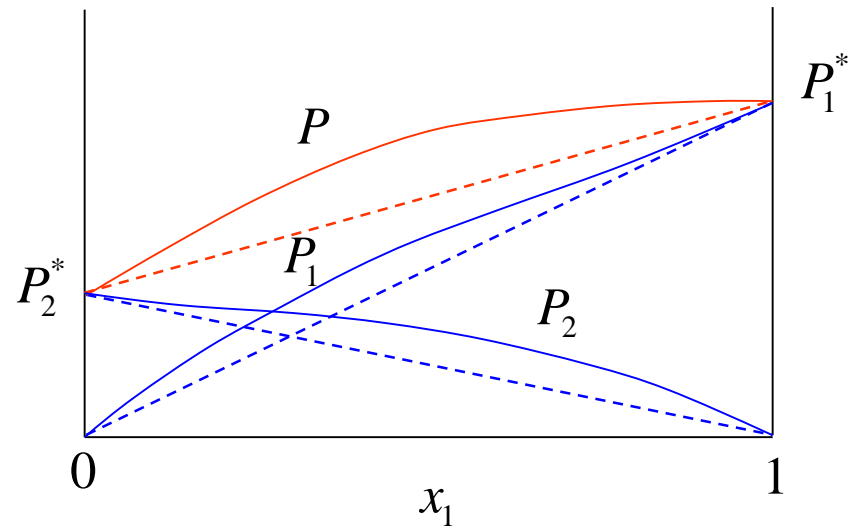


Non-Ideal Solutions

$$P_j \neq x_j P_j^*$$



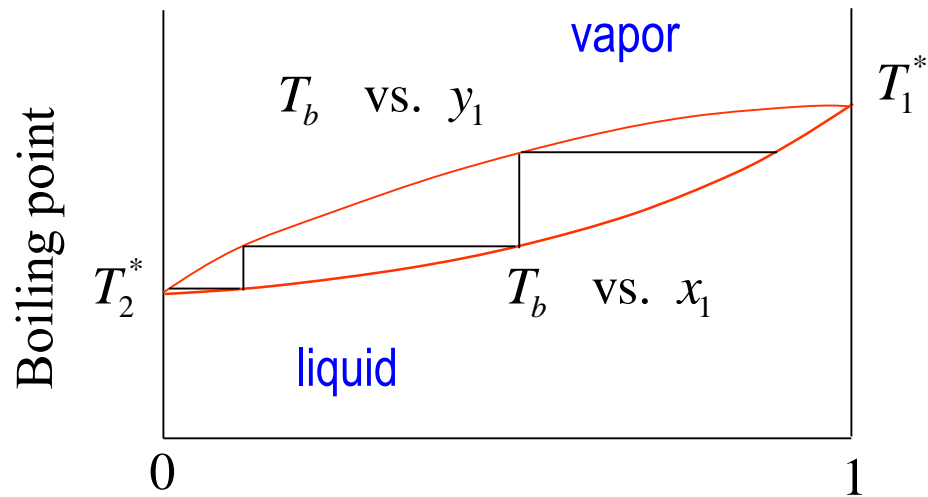
attractive interactions between
different molecules dominate



repulsive interactions between
different molecules dominate

$$P_j \square x_j P_j^* \text{ as } x_j \rightarrow 1 \text{ only}$$

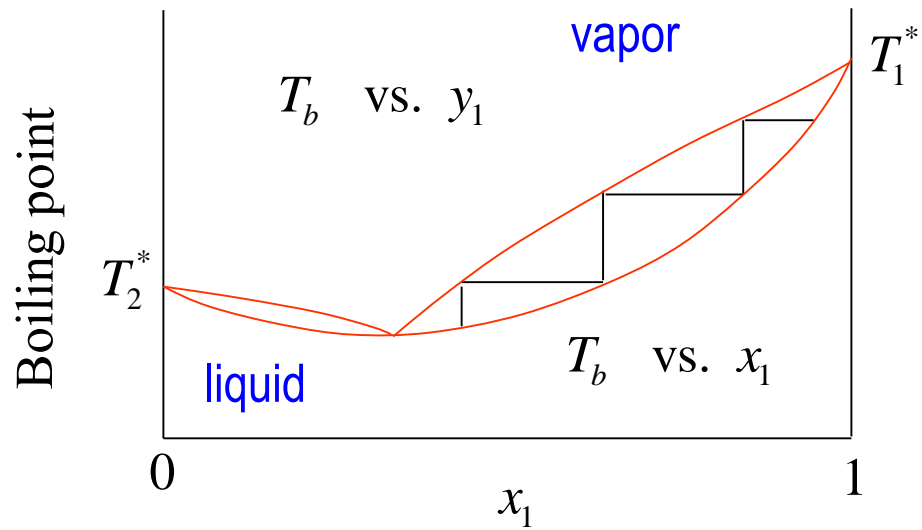
Temperature-Composition Diagrams



Substance labeled 2 is assumed to have a lower boiling point. The vapor is richer than the solution in the more volatile substance 2, thus $y_1 < x_1$.

Fractional distillation exploits this principle.

Azeotropes



Fractional distillation cannot separate the two components.

Activity

For any solution (ideal or not),

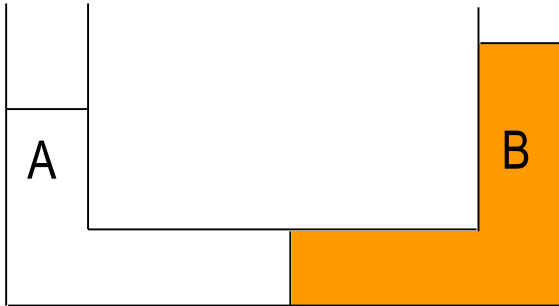
$$\mu_j^l - \mu_j^{l*} = RT \ln \frac{P_j}{P_j^*}$$

For ideal solutions $\frac{P_j}{P_j^*} = x_j$

For nonideal solutions $\frac{P_j}{P_j^*} \equiv a_j$ "activity of component j in the solution"

$$\mu_j^l = \mu_j^{l*} + RT \ln a_j$$

Solid-Liquid Solutions



A: water

B: water + sugar

Solutions separated by membrane permeable to water only.

$\mu_j^A = \mu_j^B$ for every substance that appears on both sides and

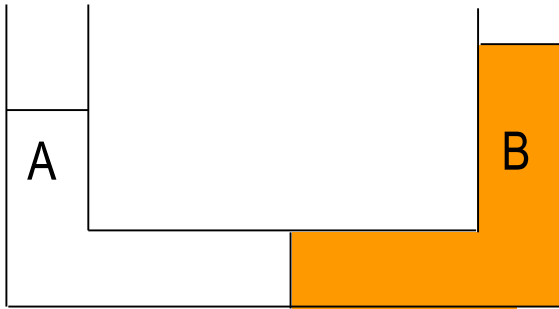
$$\mu_w^A = \mu_w^*$$

$$\mu_w^B = \mu_w^* + RT \ln a_w$$

These cannot be equal with $a_w \neq 1$ unless $\mu_w^A \neq \mu_w^B$.

The only way for this to happen is to have $P^A \neq P^B$.

Osmotic Pressure



$$\mu_w^A(T, P) = \mu_w^*(T, P)$$

$$\mu_w^B(T, P + \Pi) = \mu_w^*(T, P + \Pi) + RT \ln a_w$$

$$a_w = \frac{P_w}{P_w^*}. \text{ But } \left(\frac{\partial \mu_w^*}{\partial P} \right)_T = \bar{V}_w^*, \text{ so } \mu_w^*(T, P + \Pi) - \mu_w^*(T, P) = \int_P^{P+\Pi} \bar{V}_w(P') dP'$$

Assuming \bar{V}_w is independent of pressure for the liquid,

$$\int_P^{P+\Pi} \bar{V}_w(P') dP' = \bar{V}_w \Pi \quad \text{so } \bar{V}_w \Pi + RT \ln a_w = 0$$

For a dilute solution $a_w \approx x_w = 1 - x_s \Rightarrow$

$$\ln a_w \approx \ln(1 - x_s) \approx -x_s \Rightarrow \Pi \bar{V}_w \approx RTx_s$$

$$x_s \approx \frac{n_s}{n_w} \Rightarrow \Pi V_w \approx RTn_s$$

It follows that the osmotic pressure of dilute solutions is given by the relation

$$\boxed{\Pi = cRT}$$

Additional Definitions

Coefficient of Thermal Expansion

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Isothermal Compressibility Factor

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

KINETIC THEORY OF GASES

Root-Mean-Square Velocity

$\mathbf{u} = (u_x, u_y, u_z)$ velocity vector of a gas molecule

From the equipartition principle, $\left\langle \frac{\mathbf{p}^2}{2m} \right\rangle = \frac{3}{2} k_B T \Rightarrow$

$$\left\langle u^2 \right\rangle^{\frac{1}{2}} \equiv u_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$

Velocity Distribution

Recall that the probability of having translational energy

$$E = \frac{1}{2} m (u_x^2 + u_y^2 + u_z^2)$$

is given by the Boltzmann factor

$$P(E) \propto e^{-m(u_x^2 + u_y^2 + u_z^2)/2k_B T}$$

The probability of having a velocity component u_x in the x direction is Gaussian:

$$p_x(u_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mu_x^2/2k_B T}$$

From this, $\langle u_x \rangle = 0$ and $\langle u_x^2 \rangle = \int_{-\infty}^{\infty} u_x^2 p_x(u_x) = \frac{k_B T}{m}$

The Maxwell-Boltzmann Distribution

Calculate the probability distribution $f(u)$ for a molecule to have a velocity modulus

$$u = \left(u_x^2 + u_y^2 + u_z^2 \right)^{\frac{1}{2}}$$

by converting to spherical polar coordinates and integrating over angles:

$$f(u)du = u^2 du \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-mu^2/2k_B T}$$

$$f(u) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} u^2 e^{-mu^2/2k_B T}$$

Average speed: $\langle u \rangle = \int_{-\infty}^{\infty} u f(u) du = \sqrt{\frac{8k_B T}{\pi m}} \Rightarrow \langle u \rangle = \sqrt{\frac{8k_B T}{\pi m}}$

Most Probable Speed

The maximum of the Maxwell-Boltzmann distribution lies at

$$\frac{d}{du} f(u) = 0$$

which is satisfied for

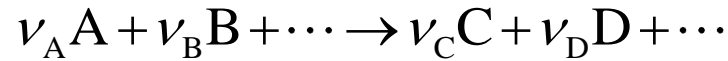
$$u_{\text{mp}} = \sqrt{\frac{2k_B T}{m}}$$

Velocity Distribution and Reaction Rates

The shape of the Maxwell-Boltzmann distribution has important implications for chemical reactions. Even though the maximum of the curve depends weakly on temperature, the fraction of molecules with velocities higher than a critical value depends exponentially on the temperature. Thus a relatively small increase of temperature can have a large effect on the rate of a chemical reaction.

REACTION RATES

Chemical Reactions



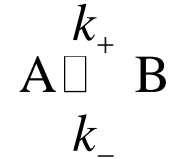
$$-\frac{1}{\nu_A} \frac{d[A]}{dt} = -\frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_C} \frac{d[C]}{dt} = \frac{1}{\nu_D} \frac{d[D]}{dt} = \dots = k[A]^\alpha [B]^\beta \dots$$

Exponents: reaction order

First order reactions: $-\frac{d[A]}{dt} = k[A] \quad [A] = [A]_0 e^{-kt}$

Second order reactions: $-\frac{d[A]}{dt} = k[A]^2 \quad \frac{1}{[A]} = \frac{1}{[A]_0} + kt$

1st Order Reactions



$$\frac{d[A]}{dt} = -k_+[A] + k_-[B] = -\frac{d[B]}{dt}$$

Steady state (dynamic equilibrium):

$$\frac{d[A]}{dt} = 0 \Rightarrow \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} \equiv K = \frac{k_+}{k_-}$$

At all times, $[A] + [B] = [A]_0$

$$k_+[A]_{\text{eq}} = k_-[B]_{\text{eq}} = k_-([A]_0 - [A]_{\text{eq}}) \Rightarrow (k_+ + k_-)[A]_{\text{eq}} = k_-[A]_0$$

At all times, $[A] + [B] = [A]_0$

Steady state (dynamic equilibrium):

$$\frac{d[A]}{dt} = 0 \Rightarrow \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} \equiv K = \frac{k_+}{k_-}$$

$$k_+[A]_{\text{eq}} = k_-[B]_{\text{eq}} = k_-([A]_0 - [A]_{\text{eq}}) \Rightarrow (k_+ + k_-)[A]_{\text{eq}} = k_-[A]_0$$

$$\frac{d[A]}{dt} = -k_+[A] + k_-([A]_0 - [A]) = -(k_+ + k_-)[A] + (k_+ + k_-)[A]_{\text{eq}}$$

$$-\frac{d[A]}{dt} = (k_+ + k_-)([A] - [A]_{\text{eq}})$$

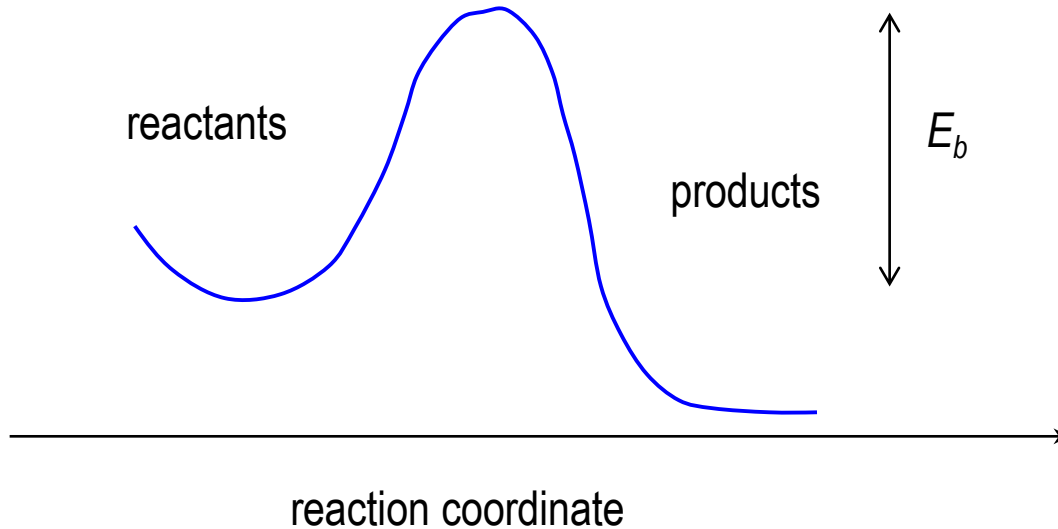
$$-\frac{d}{dt}([A] - [A]_{\text{eq}}) = (k_+ + k_-)([A] - [A]_{\text{eq}})$$

$$[A] - [A]_{\text{eq}} = ([A]_0 - [A]_{\text{eq}}) e^{-(k_+ + k_-)t}$$

Temperature Dependence of Rate Constants

In most cases under common conditions, $k = A e^{-E_a/RT}$ Arrhenius equation

E_a : activation energy



Transition State Theory

Assumption: All trajectories that reach the barrier top lead to products.

$$k^{\text{TST}} = \frac{\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp e^{-\beta H(x,p)} \frac{p}{m} \delta(x - x_b) \theta(p)}{\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp e^{-\beta H(x,p)}}$$

$$\text{Numerator} = \int_0^{\infty} dp e^{-\beta H(x_b,p)} \frac{p}{m} = \int_0^{\infty} dp e^{-\beta p^2/2m} e^{-\beta E_b} \frac{p}{m} = \frac{e^{-\beta E_b}}{\beta}$$

$$\text{Denominator} = Q_r^{\text{cl}} \quad (\text{partition function of reactants})$$

Assuming the potential is harmonic about the minimum,

$$Q_r^{\text{cl}} \square \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp e^{-\beta \left[\frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 (x-x_0)^2 \right]} = \frac{2\pi}{\beta \omega_0}$$

$$k^{\text{TST}} = \frac{\omega_0}{2\pi} e^{-\beta E_b}$$

Taking into account degrees of freedom orthogonal to the reaction coordinate,

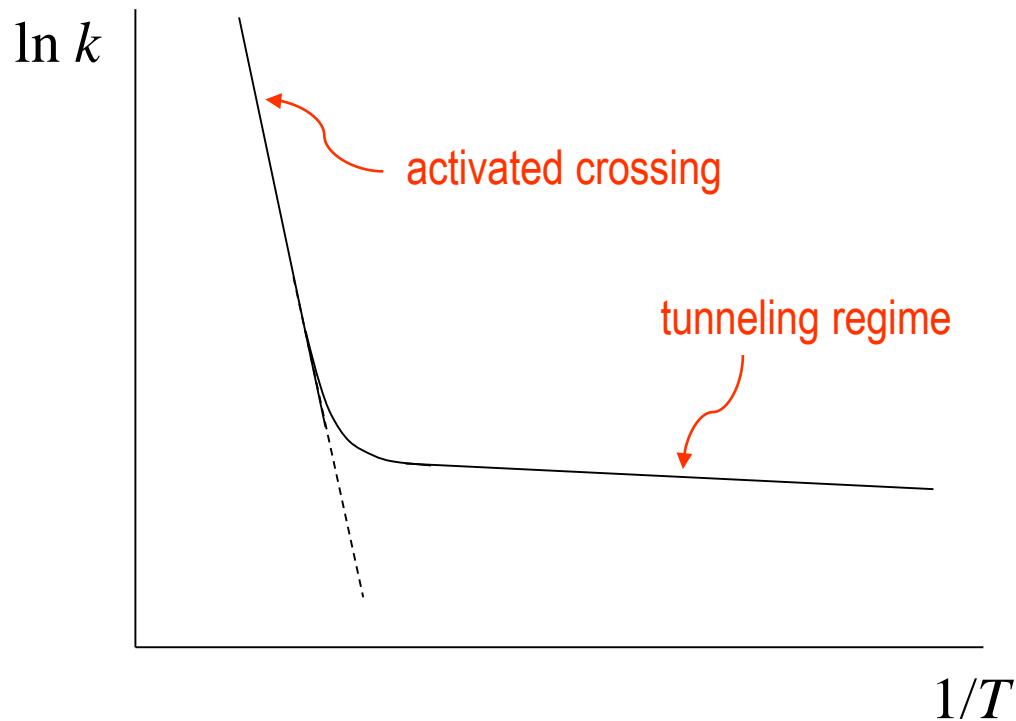
$$k^{\text{TST}} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_r} e^{-\beta E_b}$$

Q^\ddagger : partition function of stable modes at the transition state

Q_r : partition function of reactants

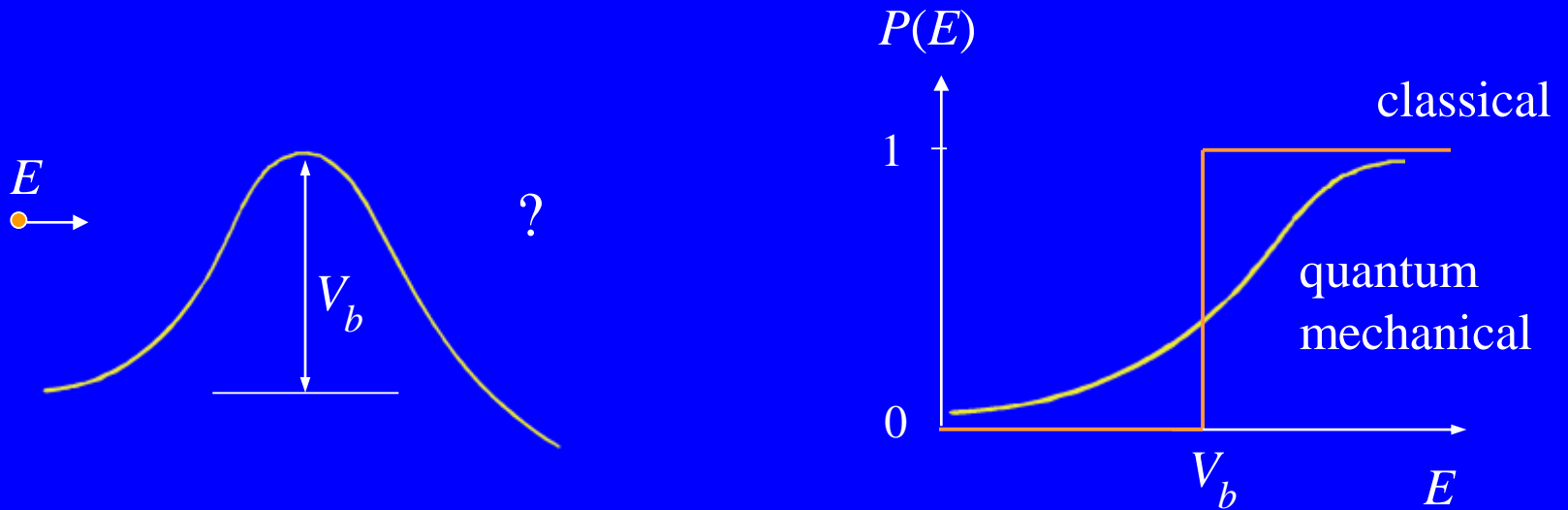
Corrections to Classical Transition State Theory

1. Recrossing of transition state region (negative corrections)
2. Quantum mechanical effects (primarily tunneling)



Tunneling

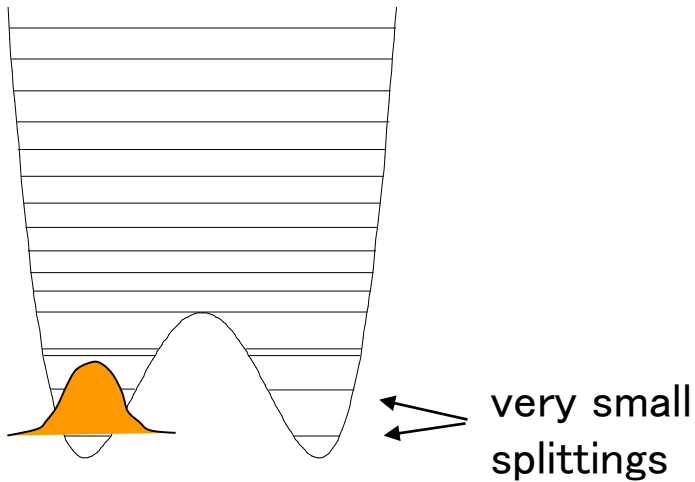
Preliminaries



$$P_{\text{tunneling}}(E) \approx \exp\left\{-\frac{1}{\hbar} \int \sqrt{2m[V(x) - E]} dx\right\}$$

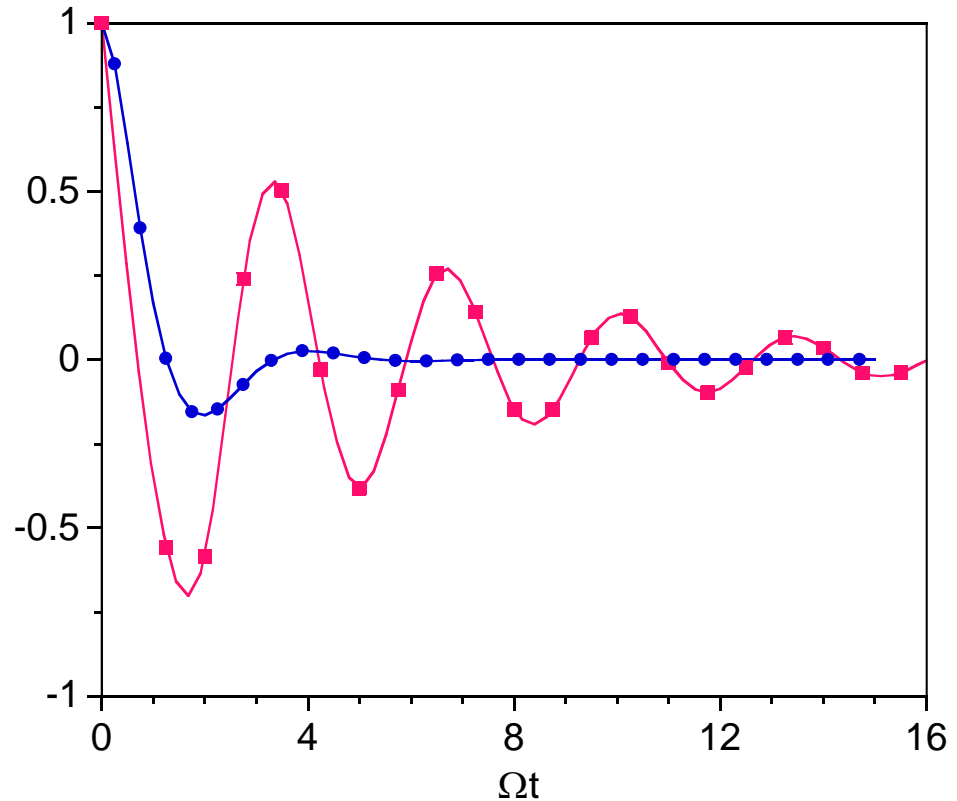
- Tunneling is important in the kinetics of light particles (primarily e^- , H, H^+ , D, ...)
- Tunneling effects are sensitive to isotopic substitution

Time evolution in double wells



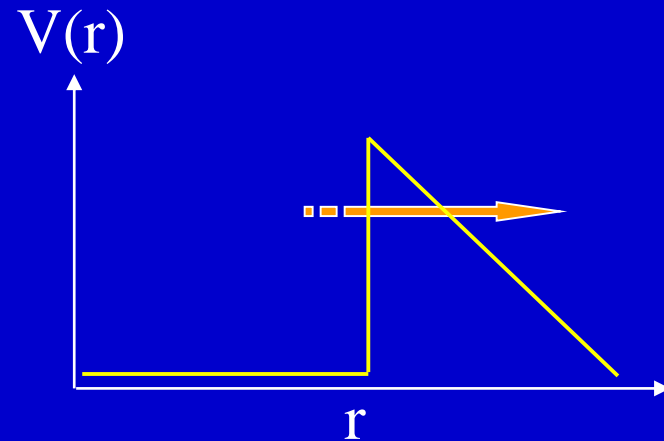
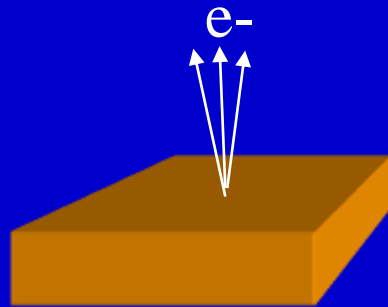
- Isolated symmetric double well: constant amplitude tunneling oscillations
- Asymmetry quenches tunneling

- Symmetric double well in a dissipative medium: quenched tunneling oscillations



Early history

- 1927 Hund suggested that quantum mechanical tunneling may play an important role in some chemical reactions.
- 1928 Fowler and Nordheim observed velocities of electrons emitted by metals that were too small.



R. H. Fowler and L. Nordheim, *Proc. Roy. Soc. A* **119**, 173 (1928)

1932 The discovery of deuterium provided ample evidence for quantum tunneling and motivated theoretical and experimental work on isotope effects.

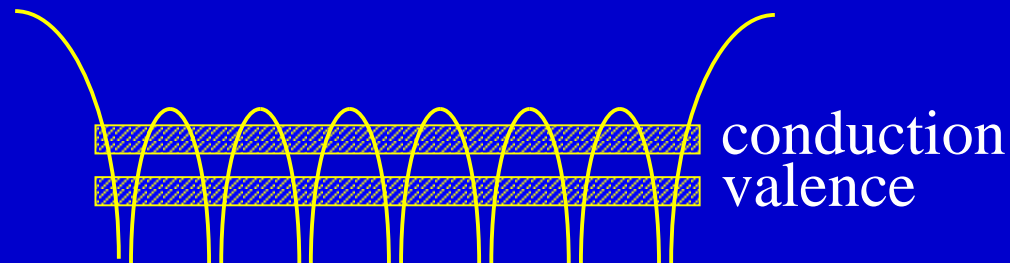
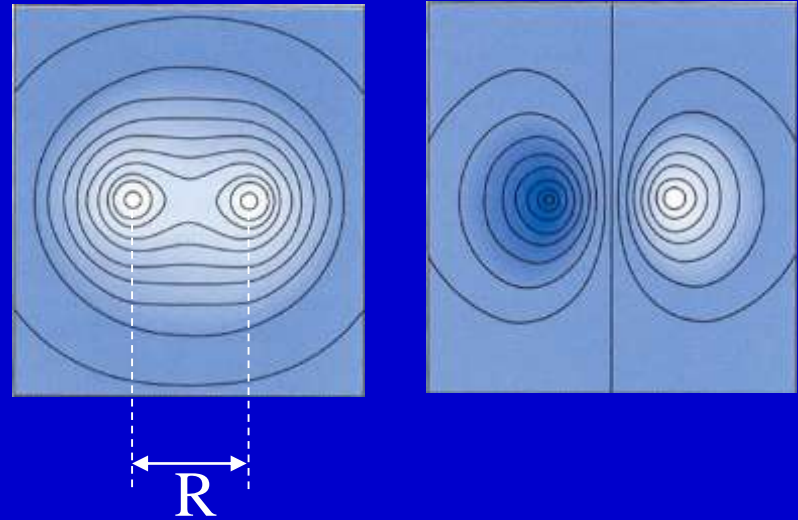
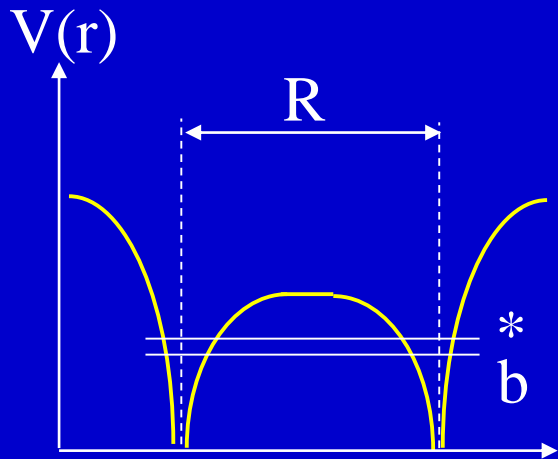


1933 Kinetic information from *ortho/para*-H₂ interconversion revealed considerable deviations from Arrhenius behavior indicative of tunneling

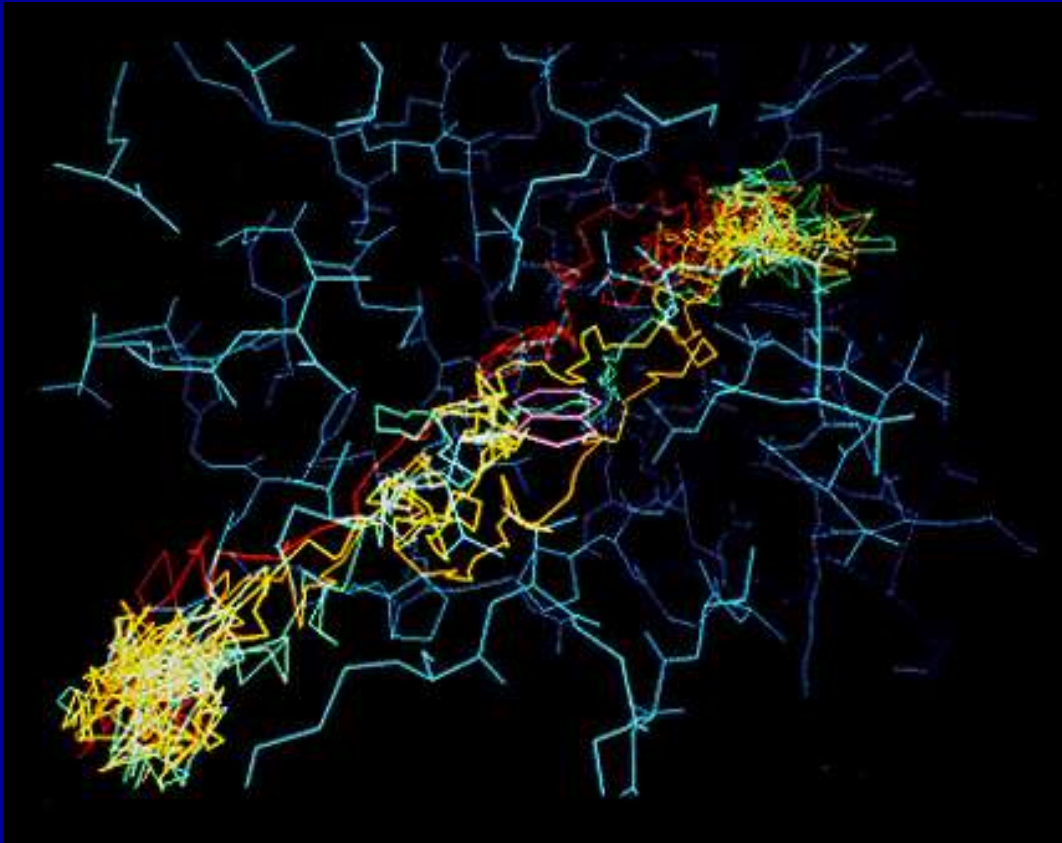
1934 Observation of tunneling splittings in NH₃

1956 H⁺/D⁺ abstraction from 2-ethoxycarbonylcyclopentanone

Chemical bonding, conjugated systems and band structure



Electron tunneling in biomolecules

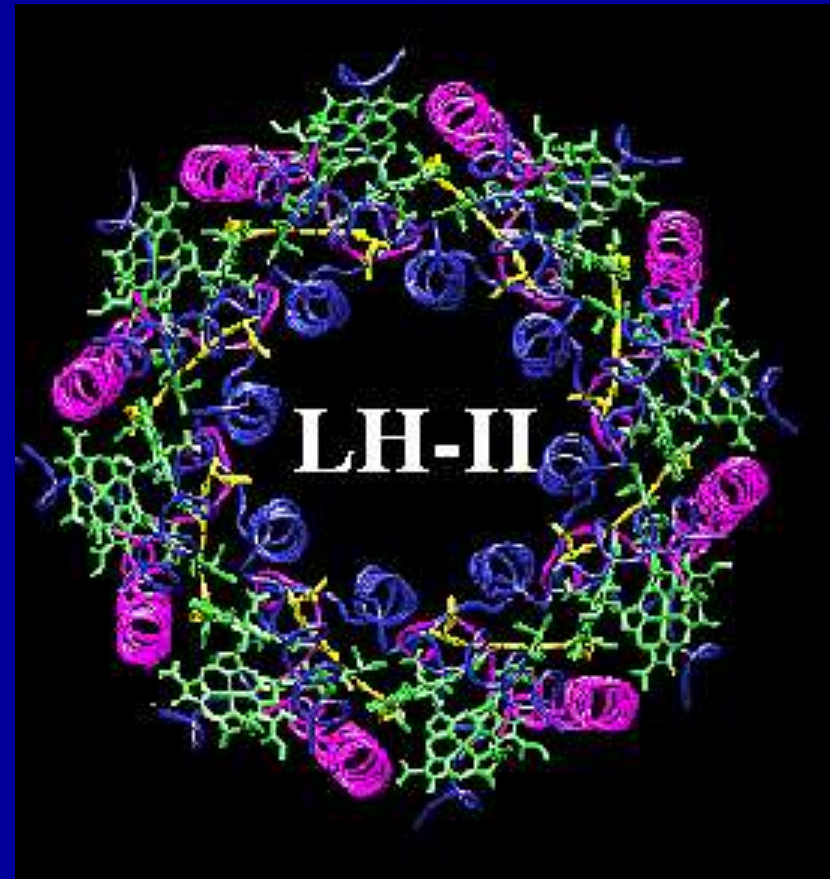


Quantum paths for the tunneling electron in ruthenium-modified myoglobin. The heme and ruthenium redox centers are separated by 28 Angstroms.

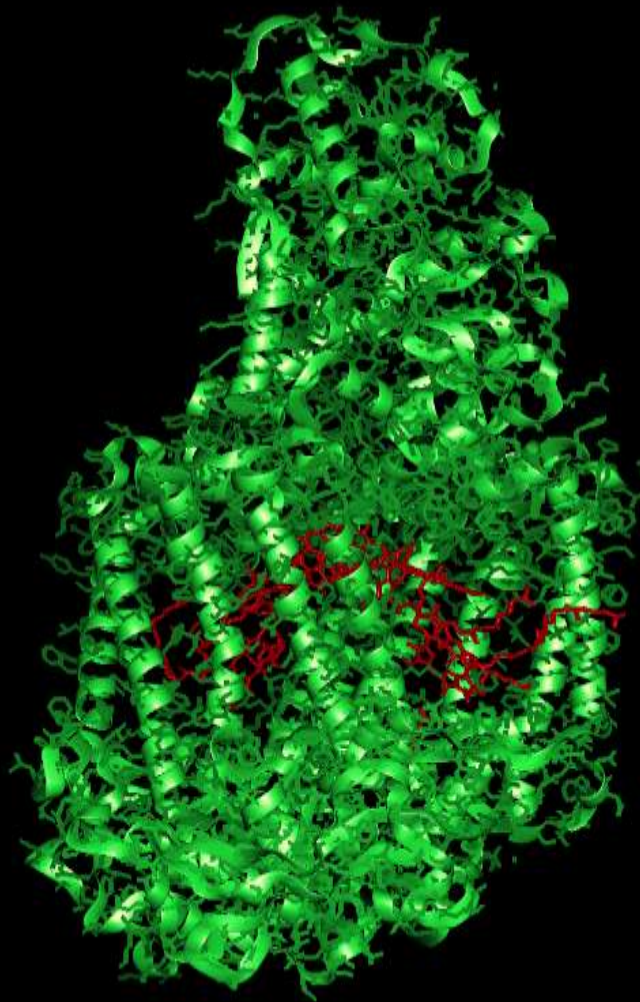
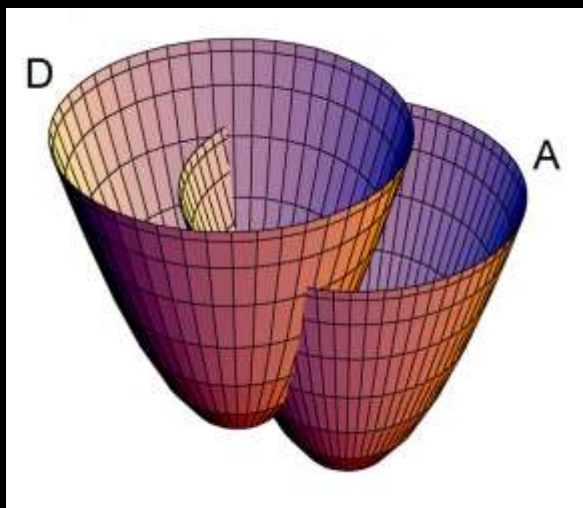
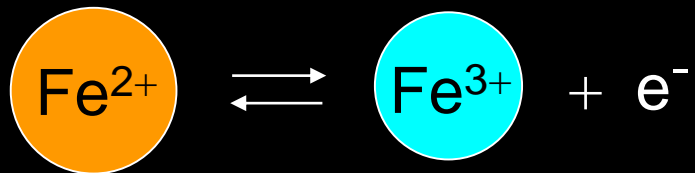
KA. Kuki A. and P. G. Wolynes, *Science* 1987, 236, 1647-1652.

Exciton tunneling in molecular aggregates

Exciton tunneling in symmetric molecular aggregates leads to a type of band structure and delocalized states.

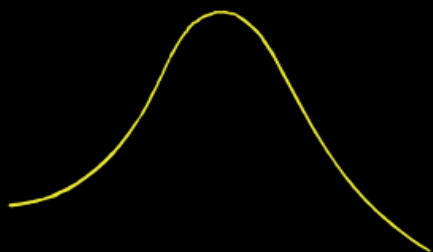


Nuclear tunneling in electron transfer

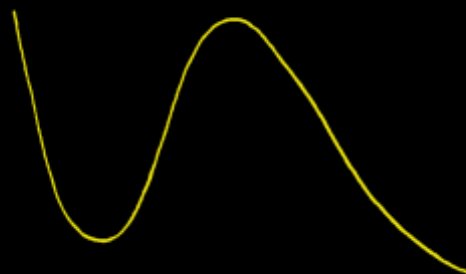


R. A. Marcus,
1992 Nobel Prize in Chemistry.

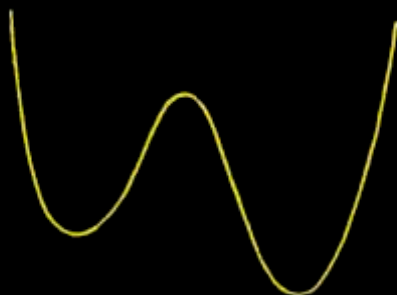
Tunneling of atoms



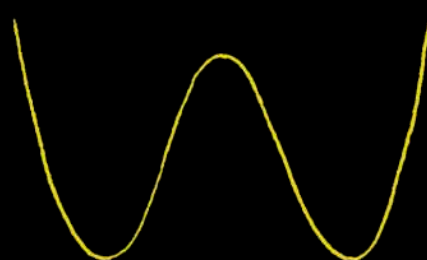
scattering
bimolecular reactions



predissociation
unimolecular decay



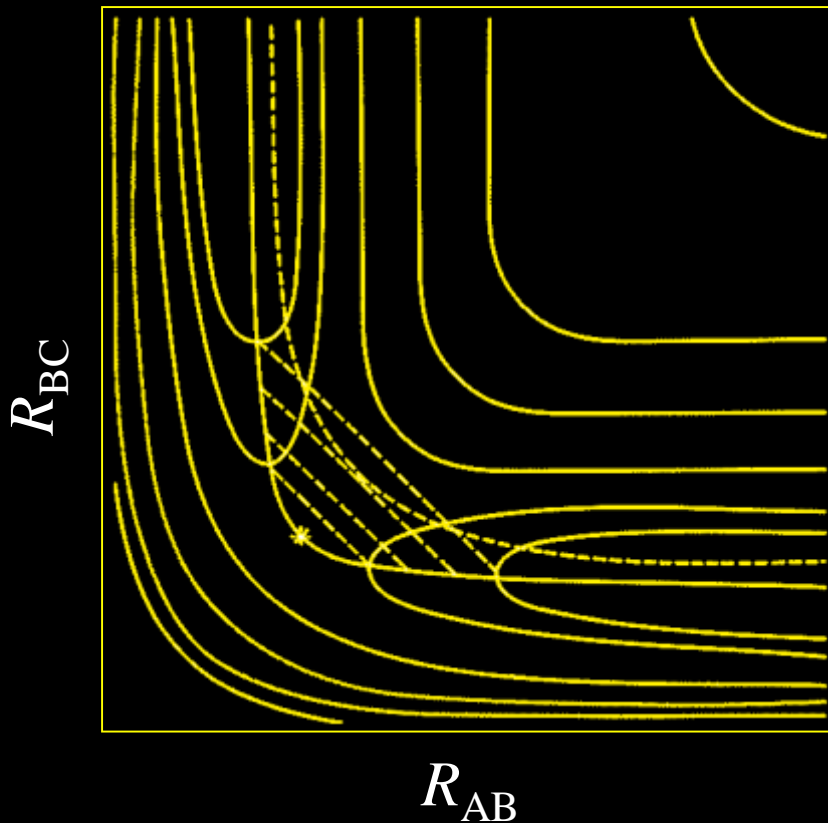
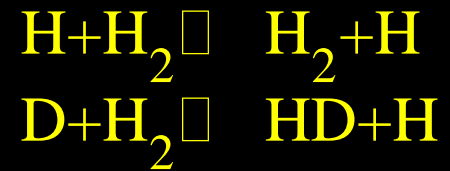
asymmetric
isomerizations



symmetric
isomerizations

enhancement
of tunneling

Tunneling effects in bimolecular reactions

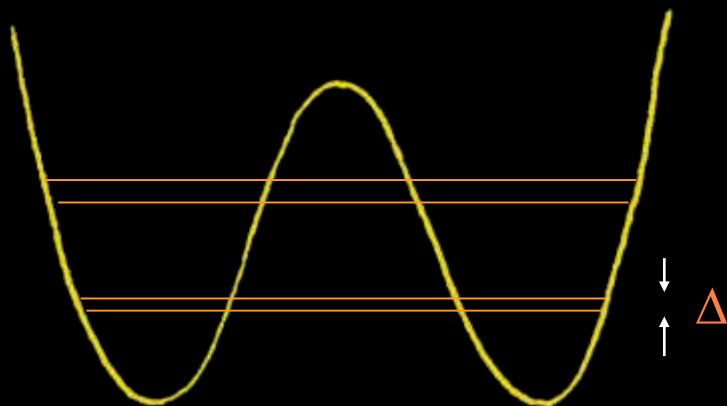


(observed through interconversion of *ortho*- and *para*-forms)

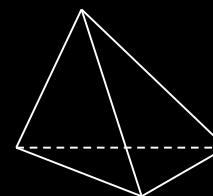
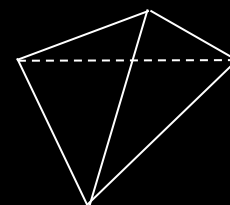
Potential surface curvature
("corner cutting")

Tunneling effects in molecular spectroscopy

Tunneling leads to splitting of rovibrational levels in symmetric isomerizations. The splitting is observed spectroscopically in the microwave region.



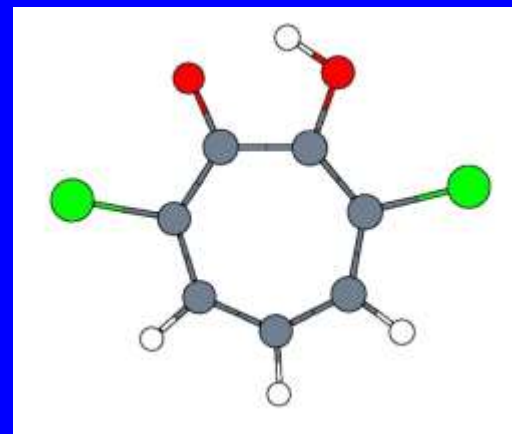
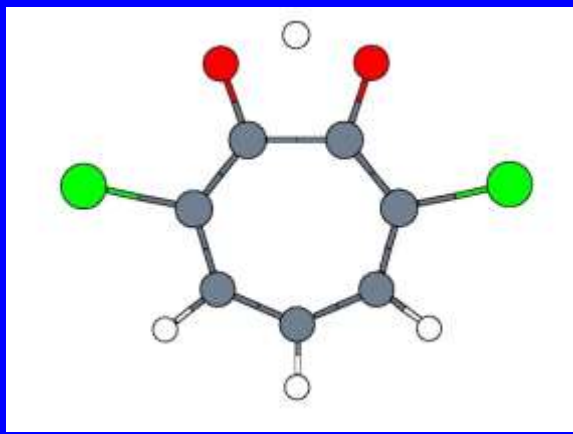
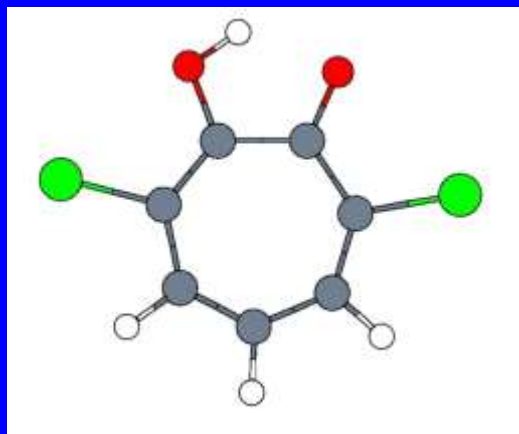
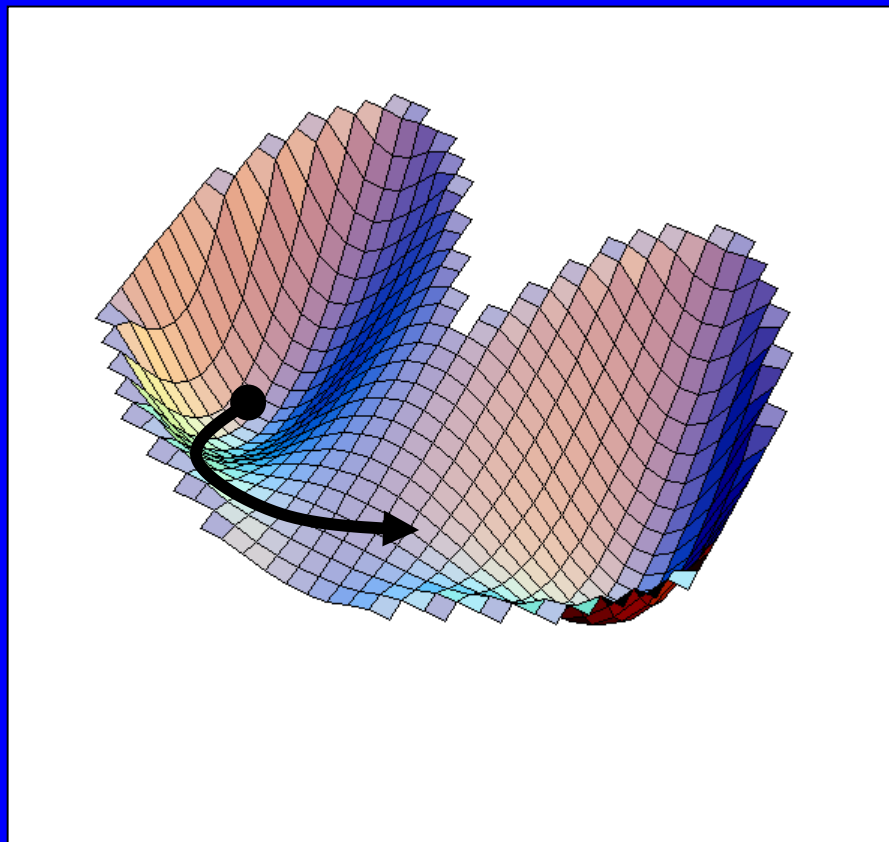
Inversion of NH_3



C. E. Cleeton and N. H. Williams,
Phys. Rev. 45, 234 (1934).

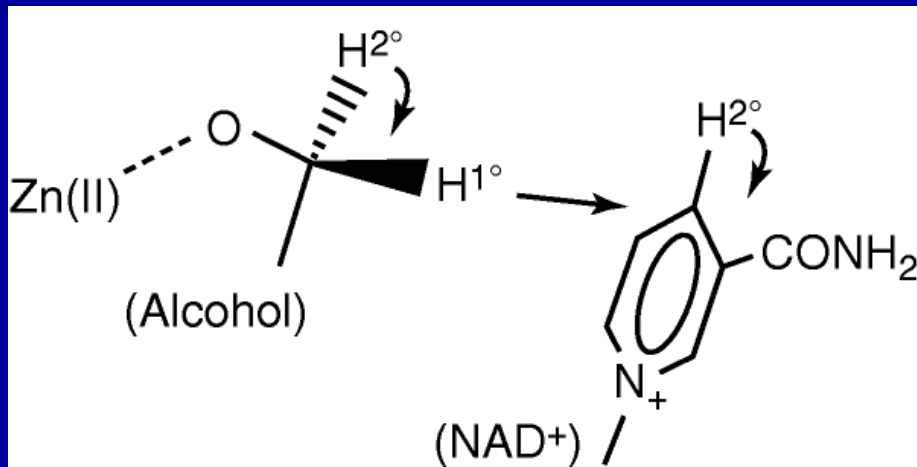
H tunneling in hydrogen-bonded molecules

3,7-dichlorotropolone



Tunneling in enzymes

Tunneling plays a significant role in hydrogen transfer at enzyme active sites.

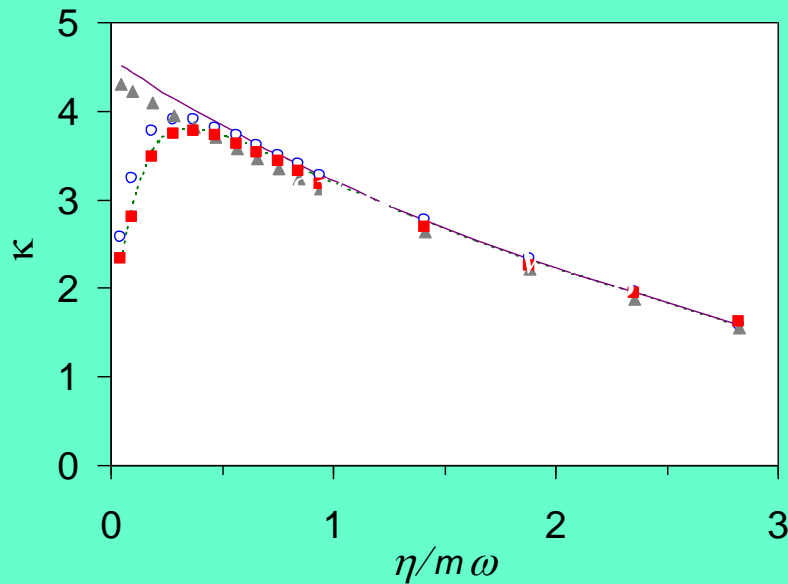


Motion of the primary (1°) and secondary (2°) hydrogens in the reaction of alcohol dehydrogenase.

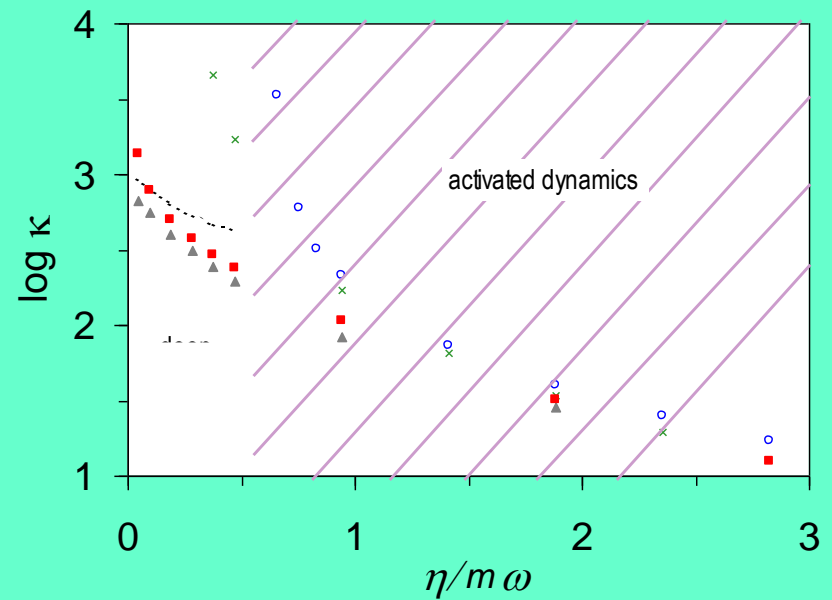
A. Kohen, R. Cannio, S. Bartolucci and J.P. Klinman (1999), *Nature* **399**, 496-499.

Tunneling in the condensed phase

$$k_{\text{qm}} = \kappa k_{\text{qm}}^{\text{TST}}$$



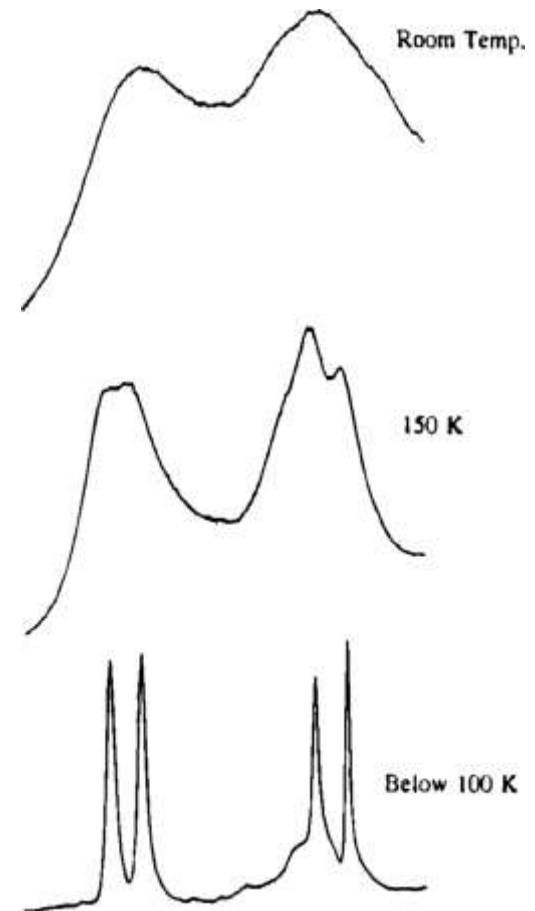
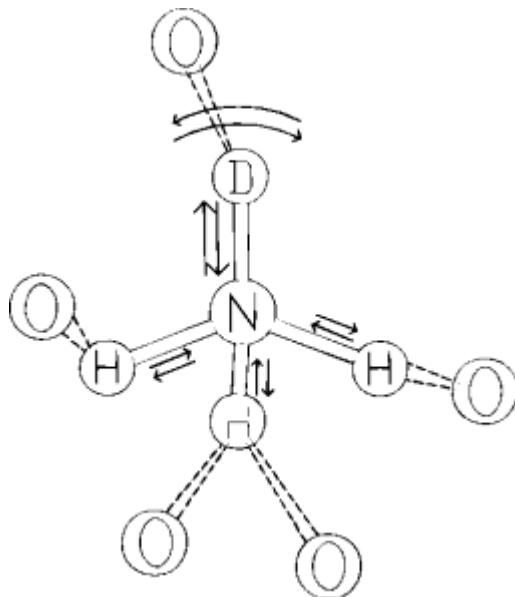
Intermediate T



Low T

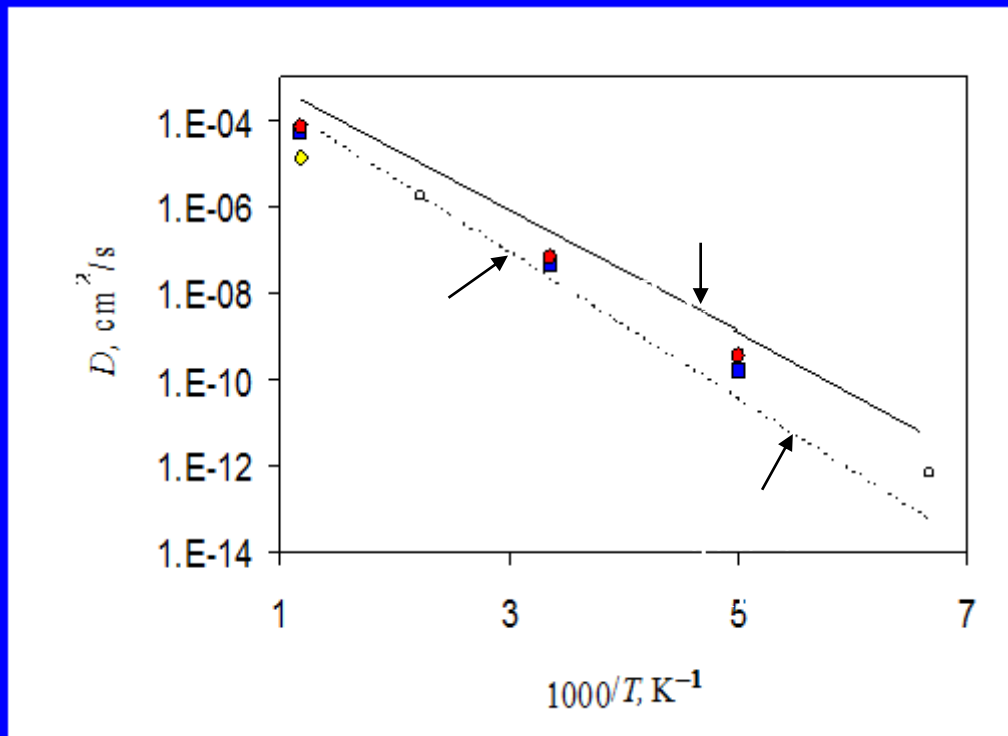
Rotational tunneling in crystals

At low temperatures (4-50K) the rotation of ammonium ions in ionic salts is dominated by tunneling.



Competing effects in kinetics

Diffusion of H and D in crystalline Si



Inverse isotope effect!

Theoretical treatments of tunneling

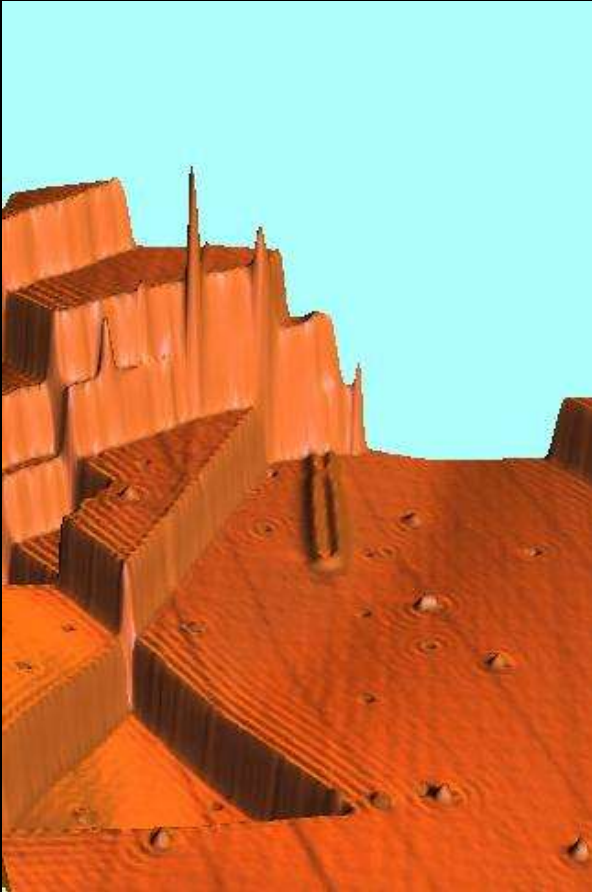
- Full solution of the quantum mechanical wave equation
- Instanton theory (tunneling in imaginary time / inverted potential)
- Tunneling corrections to classical trajectory calculations from semiclassical expressions
- Quantum mechanical solution of simplified models (master equations, harmonic bath approximations,...)
- Path integral or quantum Monte Carlo calculations in select situations (e.g., tunneling splittings)

Scanning Tunneling Microscopy

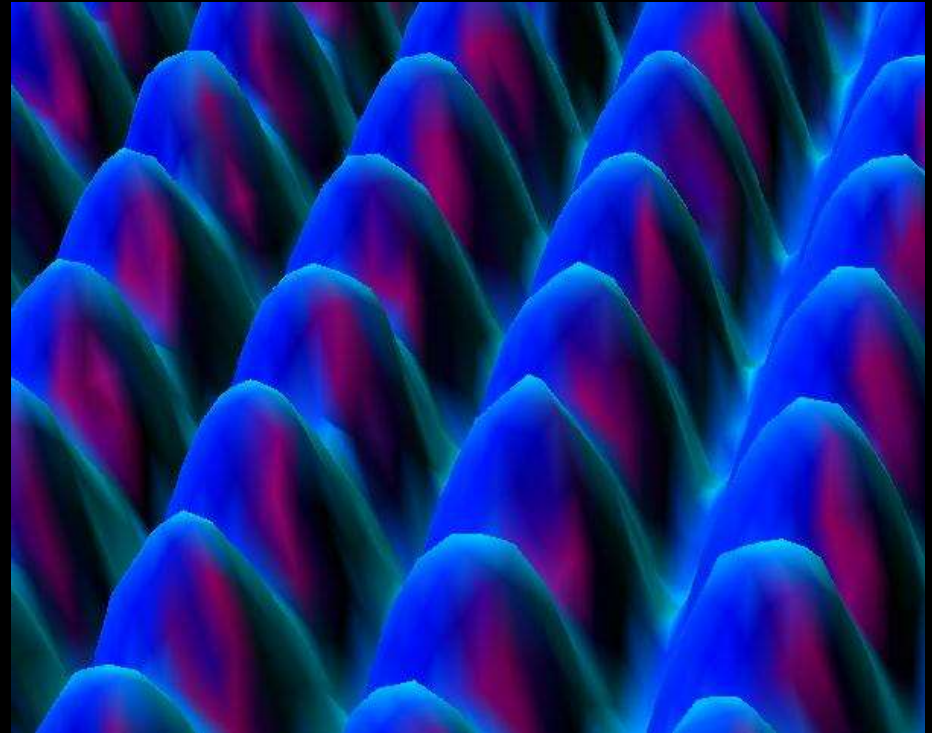
A tip is scanned over a surface at a distance of a few atomic diameters in a point-by-point and line-by-line fashion. At each point the tunneling current between the tip and the surface is measured. The tunneling current decreases exponentially with increasing distance and thus, through the use of a feedback loop, the vertical position of the tip can be adjusted to a constant distance from the surface.

Gerd Binnig and Heinrich Rohrer, IBM Research Laboratory, Zurich, shared the Physics Nobel prize in 1986 for their discovery of STM.

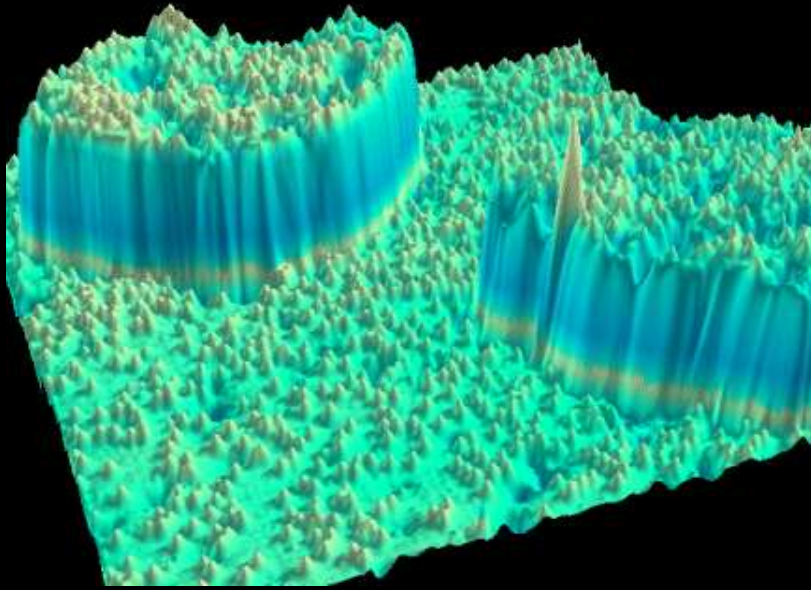
Imaging surfaces



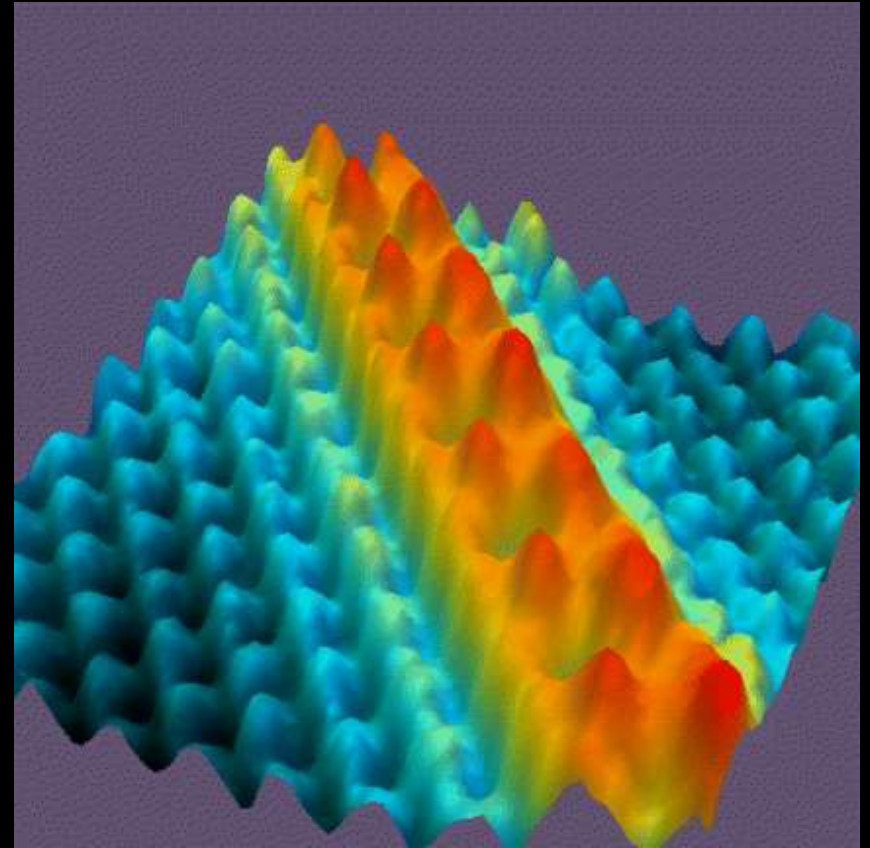
Cu surface (electron standing waves on surface steps)



Unreconstructed (110) Ni surface

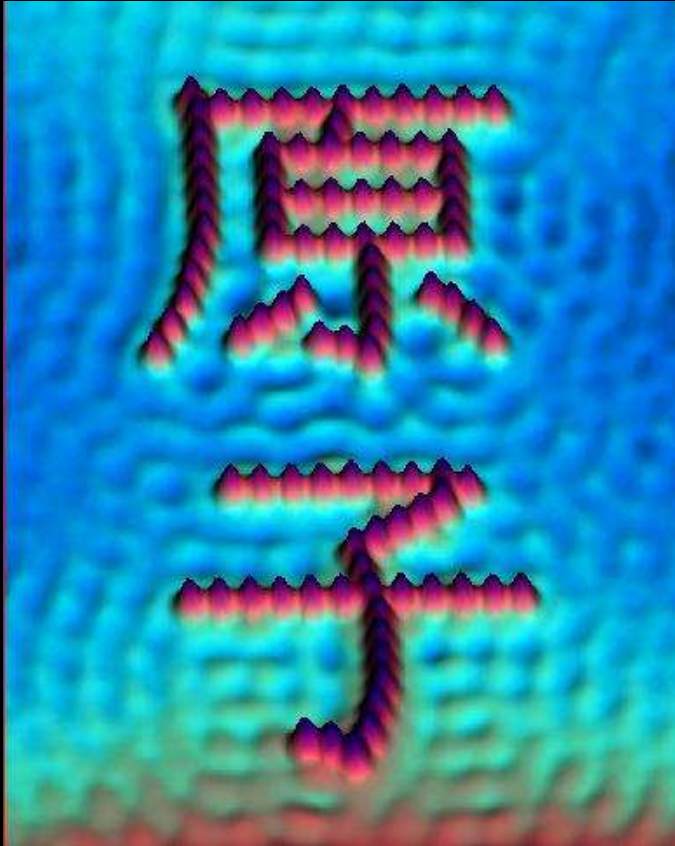


Cr impurities on a Fe (001)
surface

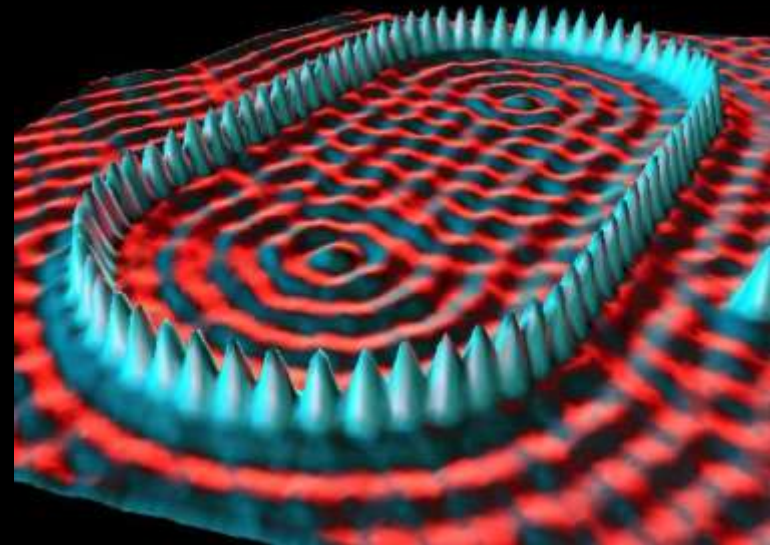


Zig-zag chain of Cs atoms
on the GaAs(110) surface.

Nanoengineering with STM



Spelling “atom” in
Japanese. Fe on Cu



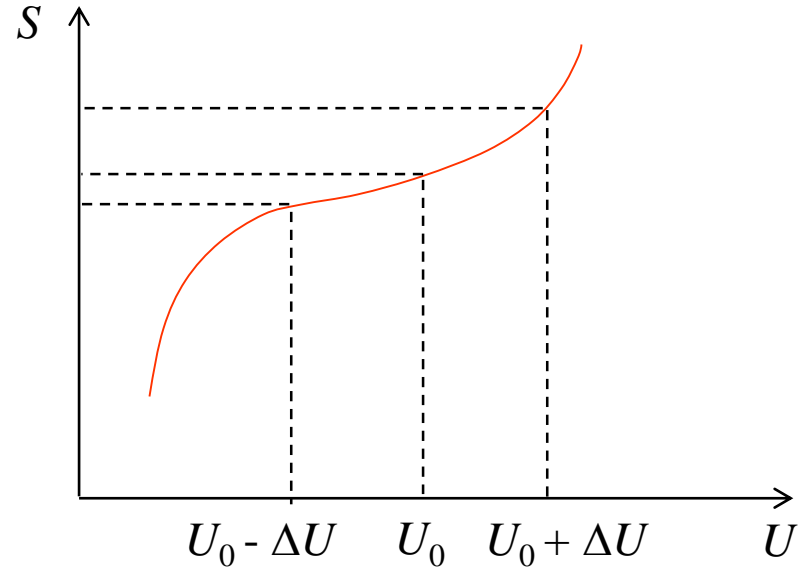
Stadium quantum corral:
Fe on Cu

STABILITY CRITERIA AND PHASE TRANSITIONS

Concavity of the Entropy

Imagine a system whose entropy function of a system has the shape shown in the figure. Consider two identical such systems, each with internal energy U_0 and entropy $2S(U_0)$. Suppose we remove energy ΔU from the first system and put it in the second system. The new entropy will be

$$S(U - \Delta U) + S(U + \Delta U) > 2S(U)$$

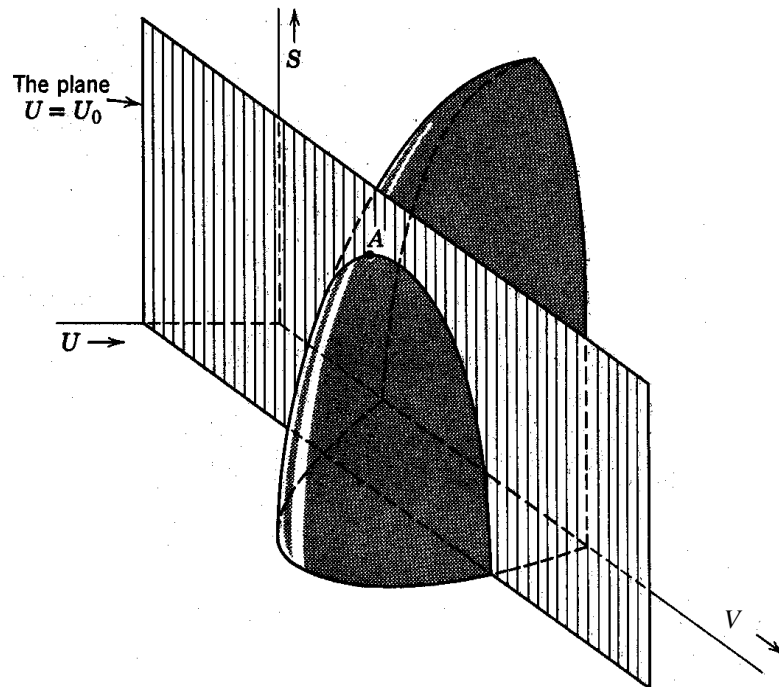


Since this rearrangement of the energy results in a larger entropy, it should occur spontaneously if the two systems are connected through a diathermal wall. This way the system will break up into two systems of different thermodynamic properties. This process is a phase transition.

The instability leading to phase separation is a consequence of the assumed convex shape of S over a range of U . In stable thermodynamic systems the entropy function is a concave function, i.e., $d^2 S < 0$ with respect to the extensive variables U and V .

Stability Conditions for Thermodynamic Potentials

The concavity condition for the entropy implies the convexity of the internal energy function with respect to its extensive variables S and V , as illustrated in the figure.



Adapted from H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd Edition.

The other thermodynamic potentials are functions of extensive as well as intensive variables. Because intensive variables are introduced through negative terms in the Legendre transform of the internal energy, the resulting thermodynamic potentials are concave functions of their intensive variables (but they are still convex functions of their extensive variables). For example,

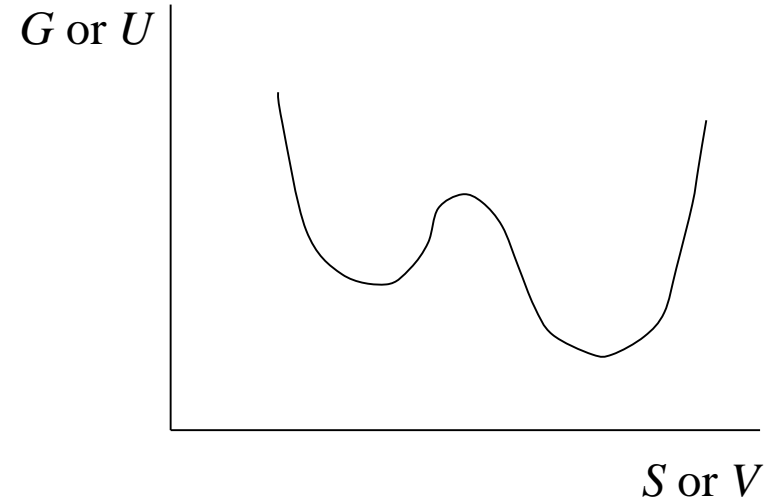
$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T \geq 0, \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_P \leq 0$$

A consequence of the first of these relations is

$$-\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 A}{\partial V^2}\right)_T \geq 0 \quad \Rightarrow \quad \kappa_T > 0$$

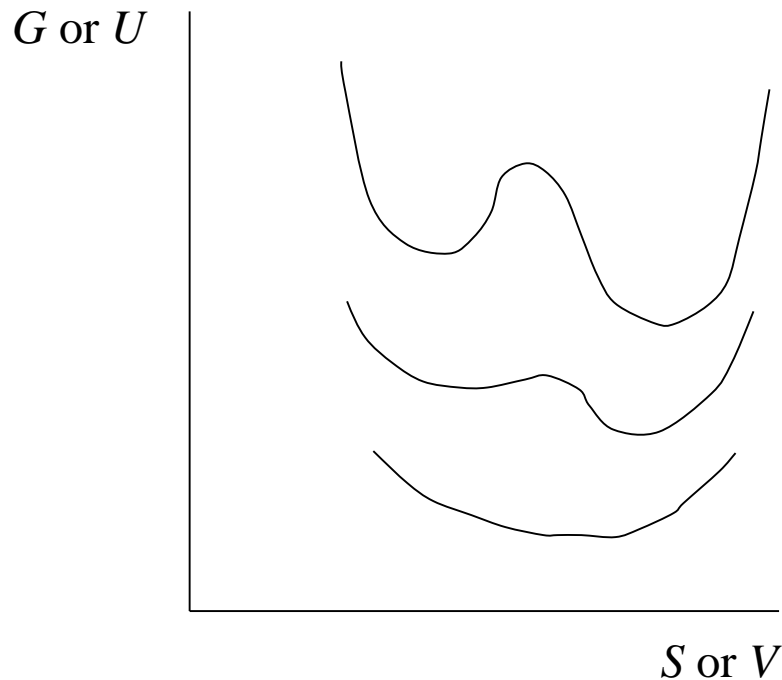
First Order Phase Transitions

Failure of stability criteria:
If the fundamental thermodynamic function of a system is unstable, fluctuations may take the system over the local maximum, and the system breaks up into more than one phases.



Second Order Phase Transitions and Critical Phenomena

The two stable minima responsible for a first order phase transition coalesce at the critical point, giving rise to a second order phase transition.



Critical phenomena are accompanied by huge density fluctuations, which give rise to the observed “critical opalescence”.

SUPERFLUIDITY AND BOSE-EINSTEIN CONDENSATION

The History of Superfluid ^4He

1908: ^4He was first liquified (5.2 K).

Unusual properties were observed: strange flow, expansion upon cooling below 2.2 K.

1928: Sharp maximum in the density with a discontinuity in slope at ~ 2.2 K. Two phases.

1932: The specific heat diverges at 2.17 K; the curve has a λ shape (“lambda transition”). Normal and superfluid phases identified.

1930s-1940s:

Remarkable transport properties of superfluid ^4He studied extensively.

- Viscosity drops by many orders of magnitude; the system flows through capillaries.
- The superfluid forms extended thin films over large surfaces.
- The superfluid does not rotate upon rotating its container.
- It appears the superfluid flows without friction!

The Phenomenon of Superfluidity

A group of phenomena including:

- Frictionless flow
- Persistent current
- Heat transfer without a thermal gradient

Bose-Einstein Condensation (BEC)

Einstein predicted that if a gas of bosons were cooled to a sufficiently low temperature, all the atoms would gather in the lowest energy state.

In 1995, Cornell and Wieman produced the first condensate of 2000 Rb atoms at 20 nK. Ketterle produced a condensate of Na with more atoms and observed interference patterns.

BEC is intimately connected with superfluidity, but is not a necessary condition for this group of phenomena.

Recent Nobel prizes:

2001: Cornell, Wieman and Ketterle for BEC

2003: Leggett for theory of superfluids

Condensate fraction: $n_0 = \frac{N_0}{N}$

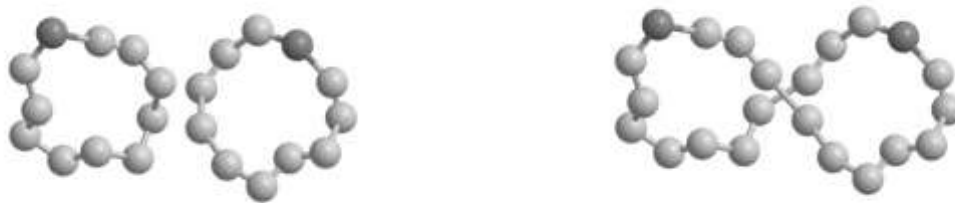
(N_0 : number of particles in the zero momentum state)

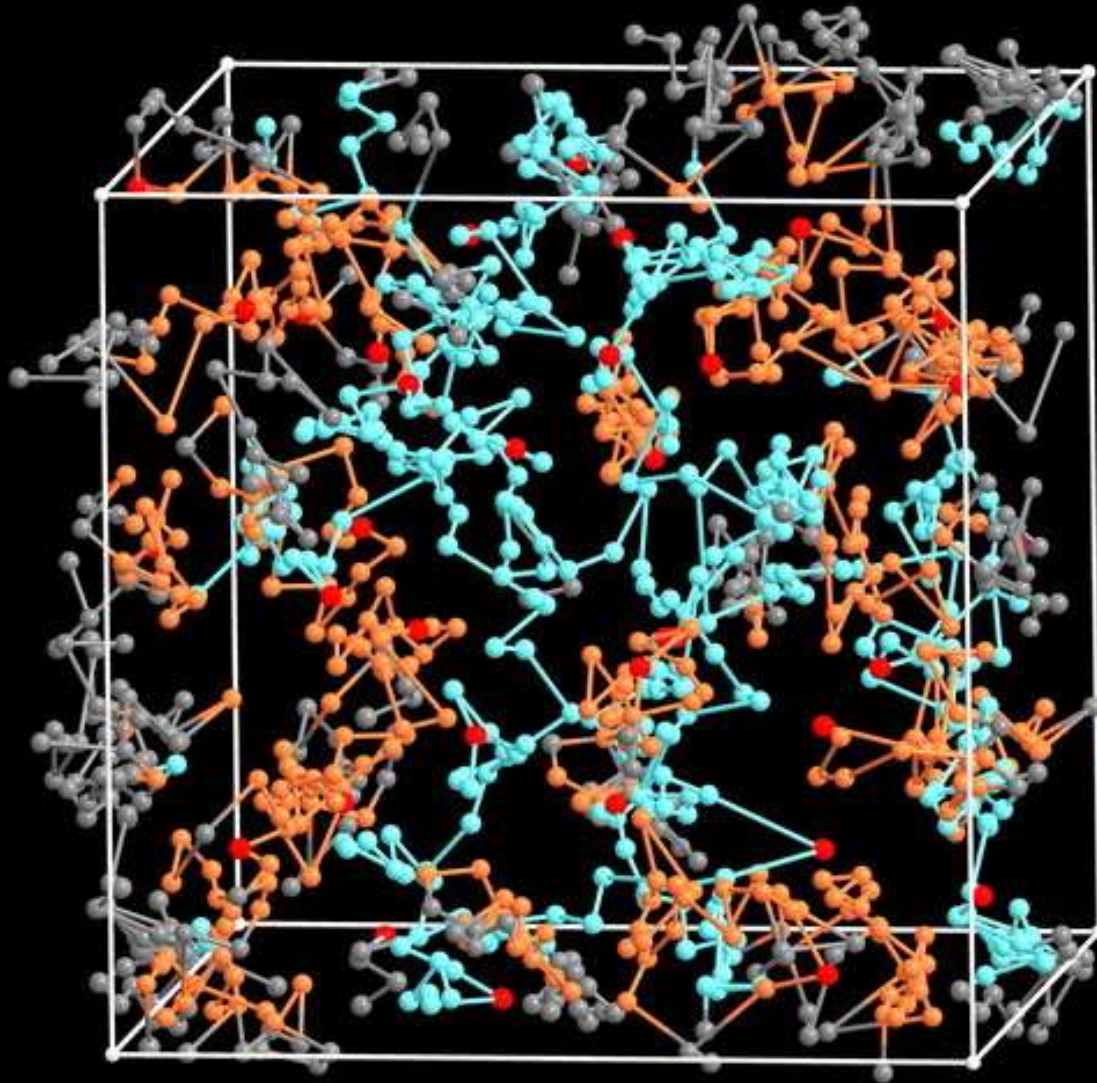
In the strongly interacting ^4He superfluid the condensate fraction is small (about 7% at $T = 0$)

The Quantum-Classical Isomorphism

A single quantum mechanical particle is isomorphic to a “necklace” of N classical “beads” that are connected with one another via harmonic springs and which experience a potential equal to $1/N$ of the actual potential felt by the quantum particle.

Quantum statistical effects of identical bosons or fermions manifest themselves in the exchange of beads, which causes the necklaces of different particles to cross-link.





A snapshot of ^4He at 1.2 K. Each ^4He atoms is represented in the simulation through 20 "pair-propagator" beads. The blue beads correspond to linked necklaces.

The End