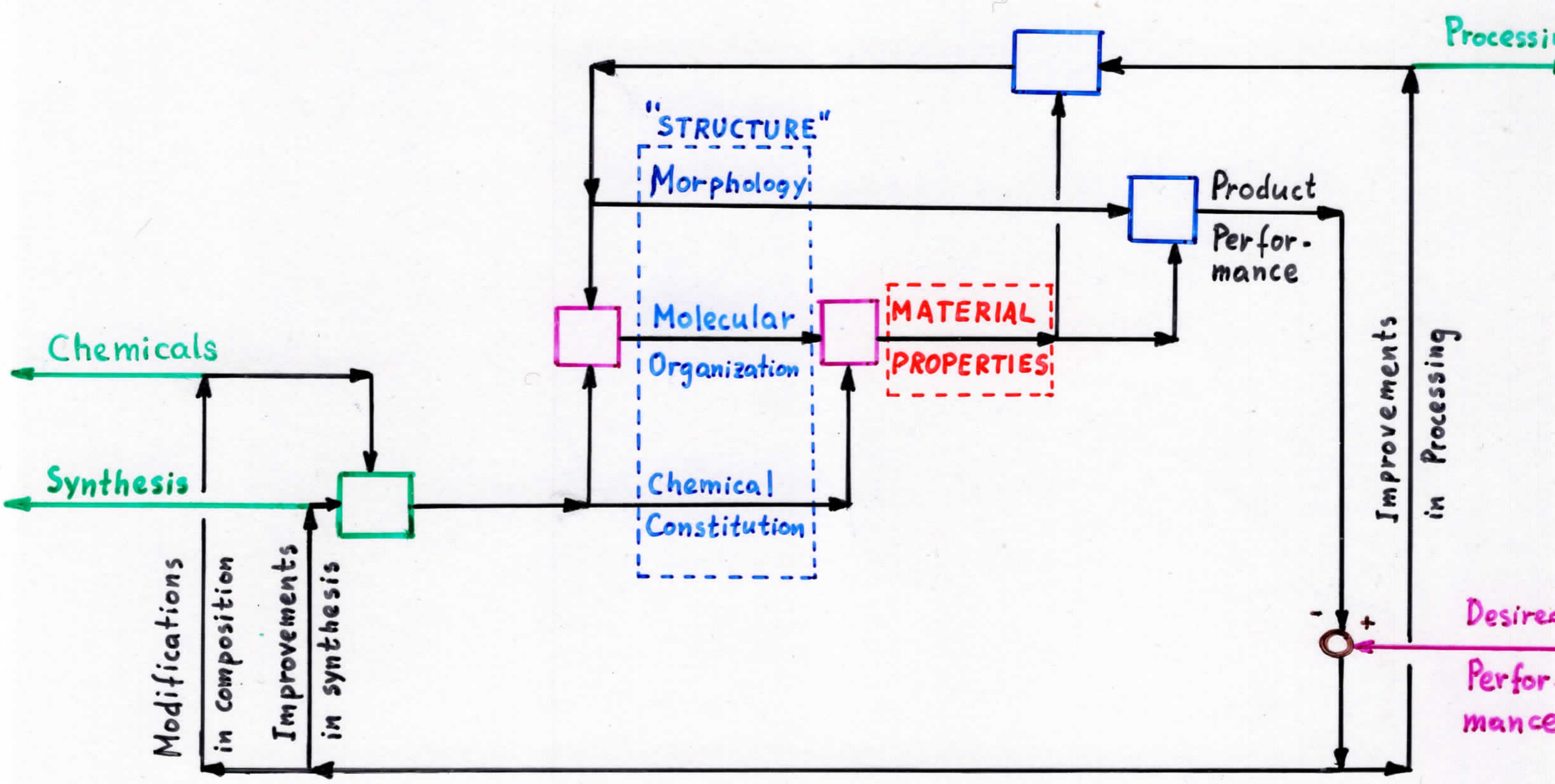
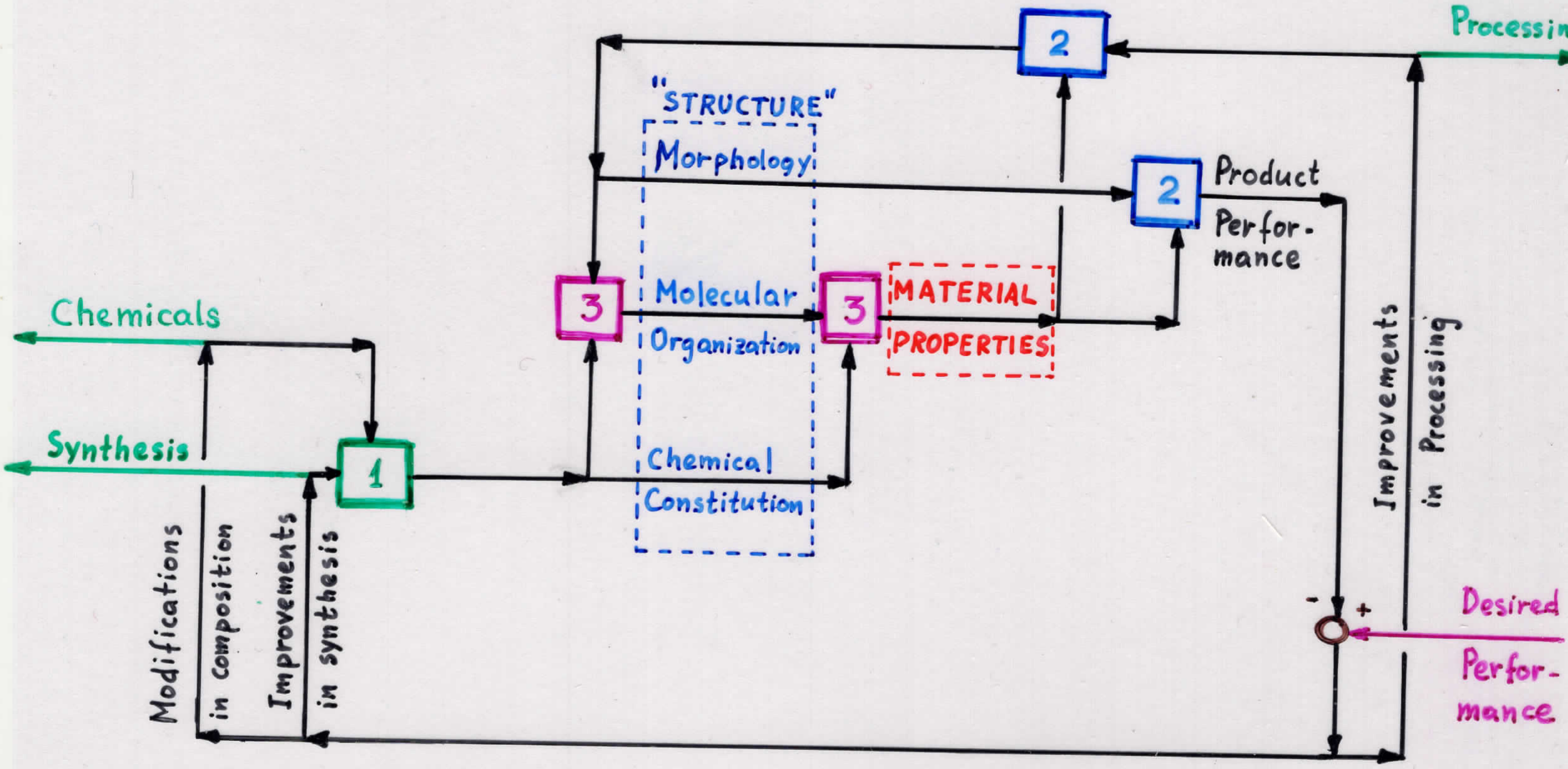
THE MATERIALS DESIGN PROBLEM



KNOWLEDGE NEEDED FOR ADDRESSING THE MATERIALS DESIGN PROBLEM



1: Chemistry, Reaction Engineering

2: Continuum Engineering Science

Thermodynamics
Momentum, heat, mass transport
Chemical kinetics, catalysis
Continuum mechanics, rheology
Electromagnetic theory

3: "Structure - Property Relations"

Material Properties

Thermodynamic

density, heat capacity, solubility.

phase diagrams for single component and multicomponent systems.

sorption isotherms, surface and interfacial tension.

Mechanical

elastic constants, strength, fracture toughness.

Transport and Rheological

viscosity, diffusivity

spectrum of relaxation times governing viscoelastic response.

Electrical, Optical, Magnetic

Electrical conductivity.

Dielectric and magnetic susceptibilities

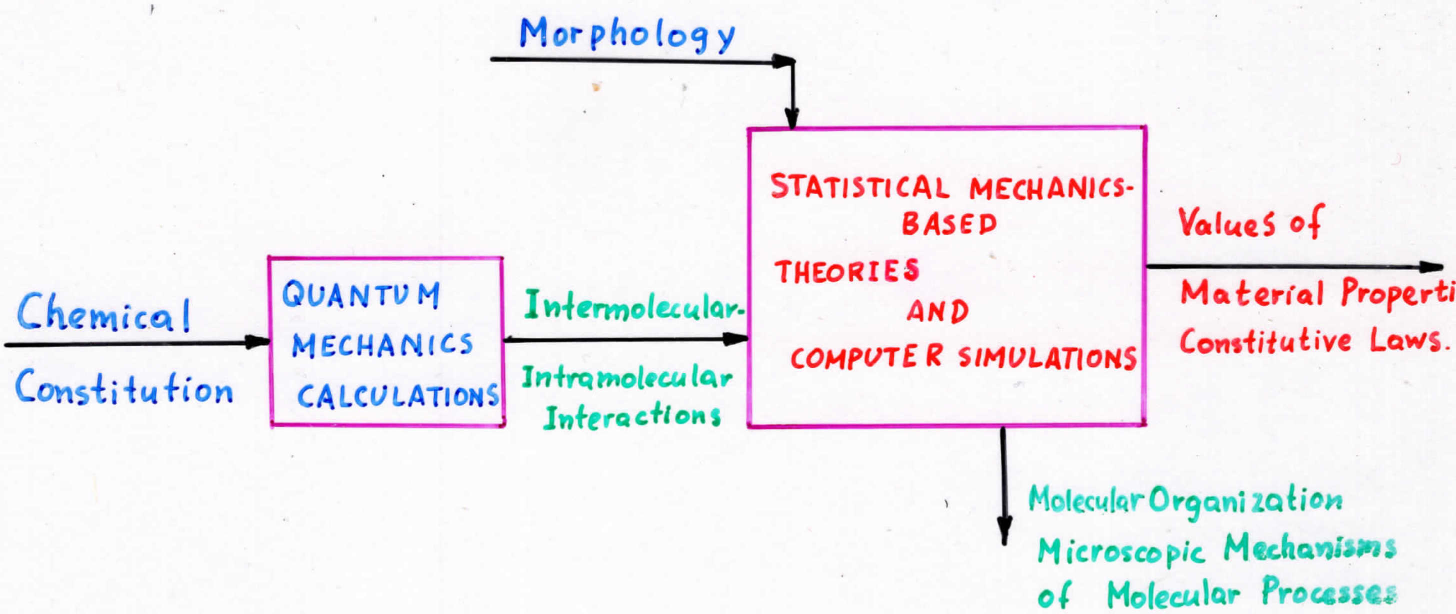
Chemical

Rate constants for chemisorption phenomena, catalytic reactions.

Chemical equilibrium constants.

Even in cases where accurate prediction of property values is impossible, materials design efforts are greatly aided by functional relations for the description of macroscopic behavior, in which microscopic structure enters through parameters (e.g. equations of state, constitutive equations)

Prediction of Properties Based on Molecular Modeling


Morphology

Chemical Constitution

QUANTUM MECHANICS CALCULATIONS

Intermolecular- Intramolecular Interactions

STATISTICAL MECHANICS-BASED THEORIES AND COMPUTER SIMULATIONS

Values of Material Properti Constitutive Laws.

Molecular Organization

Microscopic Mechanisms of Molecular Processes

THEORIES

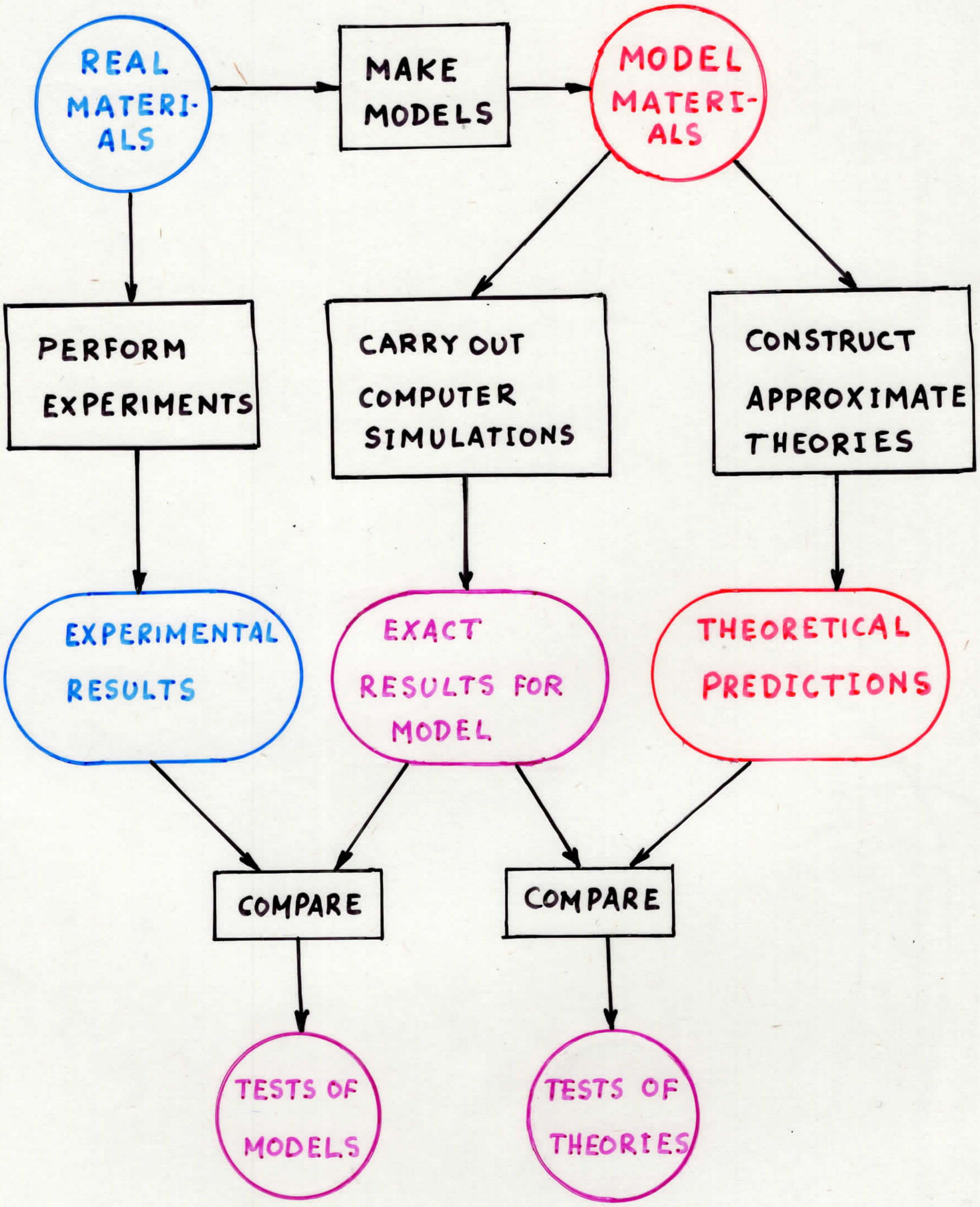
- Cast in the form of (systems of) algebraic or differential equations that can be solved analytically or numerically.
- Introduce simplifying approximations into the statistical mechanical treatme

COMPUTER SIMULATIONS (computer experiments)

- Involve the explicit creation of microstates, which may
  - sample distribution in configuration space dictated by an ensemble (MC)
  - trace temporal evolution of a material system under given constraints (MD
- Capable, in principle, of providing an "exact" solution to the statistical mechanics for given molecular geometry and energetics.
- May involve approximations

THEORIES	COMPUTER SIMULATIONS
• typically approximate	can be exact (up to testable numerical error)
• general (molecular constitution appears in the form of parameters)	typically system-specific (different computer experiments have to be run for different species)
• often postulate molecular mechanisms	can reveal molecular mechanisms.
• their application typically requires modest computational resources	can be exceedingly demanding computationally. (e.g. "brute force" atomistic MD simulation can only be carried out for systems of length scale ~ 100 Å over time scales ~1 μs using conventional algorithms on a *Beowulf cluster*)

Addressing real-life materials in a manner that combines realism of representation, rigor of formulation, and computational tractability requires a carefully designed hierarchy of theoretical and simulation approaches.



Connection between experiment, theory, and computer simulation.
(after Allen & Tildesley, 1987)

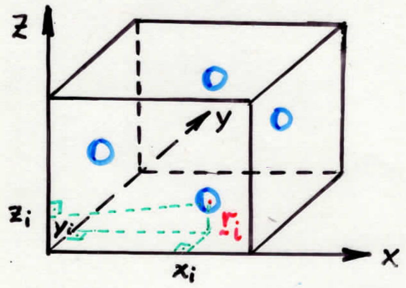
INTRODUCTION TO CLASSICAL STATISTICAL MECHANICS

Trajectories in Phase Space.

Complete description of microstate of a system

Quantum Mechanics: Ψ, a function of position coordinates of all nuclei and electrons.

Classical Mechanics: Generalized coordinates, $\underset{\sim}{q}$
Generalized momenta, $\underset{\sim}{p}$



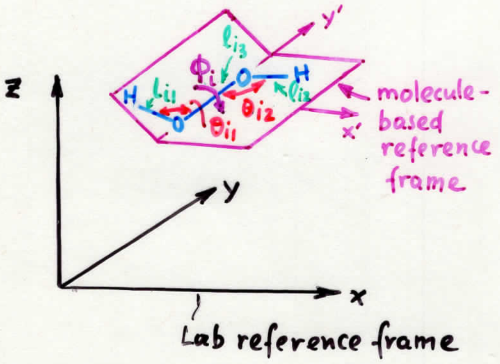
N molecules

Generalized coordinates can be the Cartesian coordinates of interaction sites.

e.g., monatomic gas:

$$\underset{\sim}{q} \equiv \underset{\sim}{r} = (\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots, \underset{\sim}{r}_N)$$

3-d position vector (x_1, y_1, z_1)



Bond lengths, bond angles, torsion angles can be used as generalized coordinates.

e.g., liquid H_2O_2 (fully flexible representation):

$$\underset{\sim}{q} = (\underset{\sim}{q}_1, \underset{\sim}{q}_2, \ldots, \underset{\sim}{q}_N)$$

with $\underset{\sim}{q}_i = (x_i, y_i, z_i, \psi_{i1}, \psi_{i2}, \psi_{i3}, l_{i1}, l_{i2}, l_{i3}, \theta_{i1}, \theta_{i2}, \phi_i)$

x_i, y_i, z_i: coordinates of center of O-O bond.

$\psi_{i1}, \psi_{i2}, \psi_{i3}$: angles describing orientation of molecule-based frame wrt. lab frame.

In this discussion, number of generalized coordinates will be assumed equal to 3N.

$$\underset{\sim}{q} \equiv (\underset{\sim}{q}_1, \underset{\sim}{q}_2, \cdots, \underset{\sim}{q}_i, \cdots, \underset{\sim}{q}_N) = (q_{11}, q_{12}, q_{13}, q_{21}, q_{22}, q_{23}, \cdots, q_{i1}, q_{i2}, q_{i3}, \cdots, q_{N1}, q_{N2}, q_{N3})$$

3N generalized coordinates, or "configurational degrees of freedom"

Potential energy: $\mathcal{V}(\underset{\sim}{q})$ Conservative system

$\mathcal{V}$ is obtainable, in principle, as a function of all nuclear coordinates via Quantum mechanics. (Born-Oppenheimer approximation).

time derivative

Kinetic energy: $\mathcal{K}(\underset{\sim}{q}, \dot{\underset{\sim}{q}})$

Lagrangian: $\mathcal{L}(\underset{\sim}{q}, \dot{\underset{\sim}{q}}) = \mathcal{K}(\underset{\sim}{q}, \dot{\underset{\sim}{q}}) - \mathcal{V}(\underset{\sim}{q})$

Definition of generalized momenta: $$\underset{\sim}{p} \equiv \frac{\partial}{\partial \dot{\underset{\sim}{q}}} \mathcal{L}(\underset{\sim}{q}, \dot{\underset{\sim}{q}}) \qquad (3.1)$$

← gradient vector wrt. $\dot{\underset{\sim}{q}}$

Hamiltonian, $$\mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p}) \equiv \dot{\underset{\sim}{q}} \cdot \underset{\sim}{p} - \mathcal{L}(\underset{\sim}{q}, \dot{\underset{\sim}{q}}) \qquad (3.2)$$

For fluid described in terms of the coordinates of interaction sites $(\underset{\sim}{q} \equiv \underset{\sim}{r})$ we have:

$$\mathcal{K} = \sum_{i=1}^{N} \frac{1}{2} m_i (\dot{\underset{\sim}{r}}_i)^2 \quad , \quad \mathcal{V} = \mathcal{V}(\underset{\sim}{r}_1, \cdots, \underset{\sim}{r}_N)$$

$$\underset{\sim}{p}_i = \frac{\partial}{\partial(\dot{\underset{\sim}{r}}_i)} \mathcal{L}(\underset{\sim}{r}_1, \cdots, \underset{\sim}{r}_N, \dot{\underset{\sim}{r}}_1, \cdots, \dot{\underset{\sim}{r}}_N) = m_i \dot{\underset{\sim}{r}}_i$$

$$\mathcal{H} = \sum_{i=1}^{N} \dot{\underset{\sim}{r}}_i \cdot (\dot{\underset{\sim}{r}}_i m_i) - \sum_{i=1}^{N} \frac{1}{2} m_i (\dot{\underset{\sim}{r}}_i)^2 + \mathcal{V}(\underset{\sim}{r}_1, \cdots, \underset{\sim}{r}_N)$$

or $$\mathcal{H}(\underset{\sim}{q},p) = \underset{\text{Kinetic Energy}}{\sum_{i=1}^{N} \frac{\underset{\sim}{p}_i^{2}}{2m_i}} + \underset{\text{Potential energy}}{\mathcal{V}(\underset{\sim}{r}_1,\dots,\underset{\sim}{r}_N)}$$

Gives total energy as a function of coordinates and momenta.

(3.3)

Consider a system evolving in time subject only to interactions among its constituent particles, i.e. in the absence of interactions with the environment. (isolated system).

The time evolution of such a system is dictated by Hamilton's equations:

$$\dot{\underset{\sim}{p}}_\ell \equiv \frac{\partial \underset{\sim}{p}_\ell}{\partial t} = -\frac{\partial \mathcal{H}}{\partial \underset{\sim}{q}_\ell} \qquad (3.4)$$

denotes gradient vector

$(\ell = 1, 2, \dots, N)$

$$\dot{\underset{\sim}{q}}_\ell \equiv \frac{\partial \underset{\sim}{q}_\ell}{\partial t} = \frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_\ell} \qquad (3.5)$$

Interpretation in the case of a Cartesian description:

$\dot{\underset{\sim}{p}}_\ell = -\frac{\partial \mathcal{H}}{\partial \underset{\sim}{r}_\ell} = -\frac{\partial \mathcal{V}}{\partial \underset{\sim}{r}_\ell} = \underset{\sim}{F}_\ell$, total force on ℓ. (Newton's 2nd law).

$\dot{\underset{\sim}{r}}_\ell = \frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_\ell} = \frac{\partial \mathcal{K}}{\partial \underset{\sim}{p}_\ell} = \frac{\underset{\sim}{p}_\ell}{m_\ell}$, or $\underset{\sim}{p}_\ell = m_\ell \dot{\underset{\sim}{r}}_\ell$ (definition of momentum

Given $(\underset{\sim}{q}, \underset{\sim}{p})$ at a given time, Hamilton's equations enable the calculation of $\underset{\sim}{q}$ and $\underset{\sim}{p}$ at all future and past times.

For a conservative system, $\mathcal{H}$ is a constant of the motion.

$$\frac{\partial \mathcal{H}}{\partial t} = \sum_{i=1}^{N} \frac{\partial \mathcal{H}}{\partial \underset{\sim}{q}_i} \cdot \frac{\partial \underset{\sim}{q}_i}{\partial t} + \sum_{i=1}^{N} \frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_i} \cdot \frac{\partial \underset{\sim}{p}_i}{\partial t} \overset{\text{Hamilton's eqs.}}{=} \sum_{i=1}^{N} \left(\frac{\partial \mathcal{H}}{\partial \underset{\sim}{q}_i} \cdot \frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_i} - \frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_i} \cdot \frac{\partial \mathcal{H}}{\partial \underset{\sim}{q}_i} \right) = 0$$

$\mathcal{H}(\underset{\sim}{p}, \underset{\sim}{q}) = E$, a constant. (conservation of energy). (3.6)

Microscopic Degrees of freedom

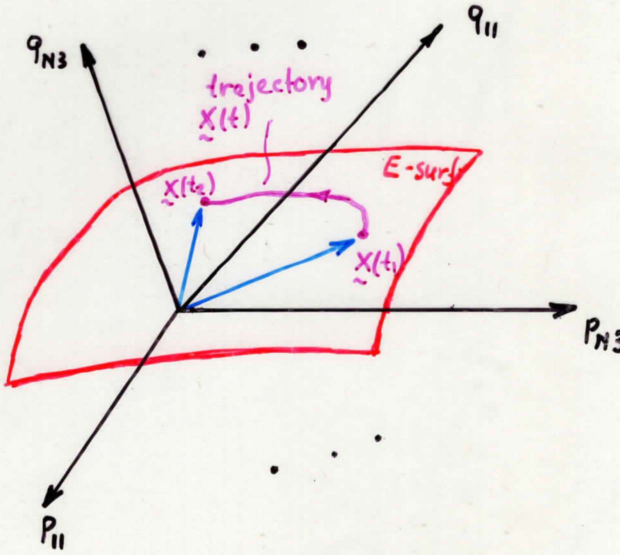
$$\underset{\sim}{X} = (\underset{\sim}{p}, \underset{\sim}{q}) = (\underbrace{\underset{\sim}{p}_1, \underset{\sim}{p}_2, \cdots, \underset{\sim}{p}_N}, \underbrace{\underset{\sim}{q}_1, \underset{\sim}{q}_2, \cdots, \underset{\sim}{q}_N})$$

$\underset{\sim}{X}$ takes values from a 6N-dimensional vector space:	take values from a 3N-dimensional vector space:	take values from a 3N-dimensional vector space:
PHASE SPACE	MOMENTUM SPACE	CONFIGURATION SPACE

The equation $\mathcal{H}(\underset{\sim}{p}, \underset{\sim}{q}) = E$ defines a (6N-1)-dimensional hypersurface in phase space, corresponding to energy value E.

The solution to Hamilton's equations under given initial conditions defines a trajectory in phase space.

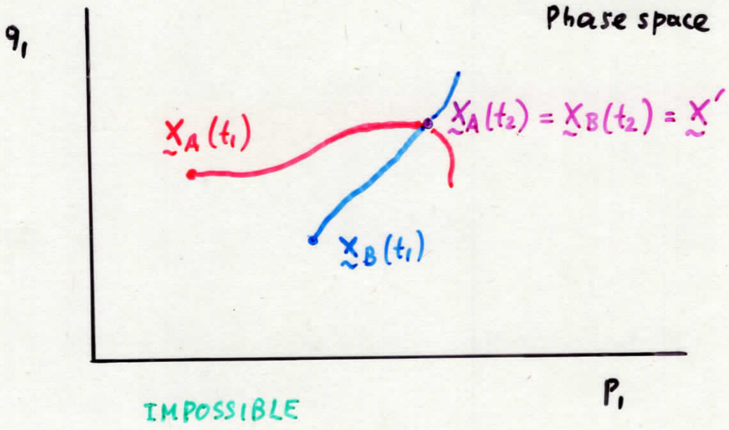
$\underset{\sim}{p} = \underset{\sim}{p}(t)$, $\underset{\sim}{q} = \underset{\sim}{q}(t)$ or $\underset{\sim}{X} = \underset{\sim}{X}(t)$



For macroscopic systems, dimensionality of phase space is $\mathcal{O}(10^{23})$!

Topology of Trajectories in Phase Space.

1. Let $\underset{\sim}{X}_A(t_1)$ and $\underset{\sim}{X}_B(t_1)$ the state points at time t_1 of two N-particle systems characterized by the same Hamiltonian $\mathcal{H}(\underset{\sim}{p},\underset{\sim}{q})$, and let $\underset{\sim}{X}_A(t_1) \neq \underset{\sim}{X}_B(t_1)$.
   Then, the trajectories traced by the systems A and B in phase space will never meet at any future (or past) time.



Statement:

$$\underset{\sim}{X}_A(t_1) \neq \underset{\sim}{X}_B(t_1) \Rightarrow \underset{\sim}{X}_A(t) \neq \underset{\sim}{X}_B(t) \;\forall t$$

Proof:

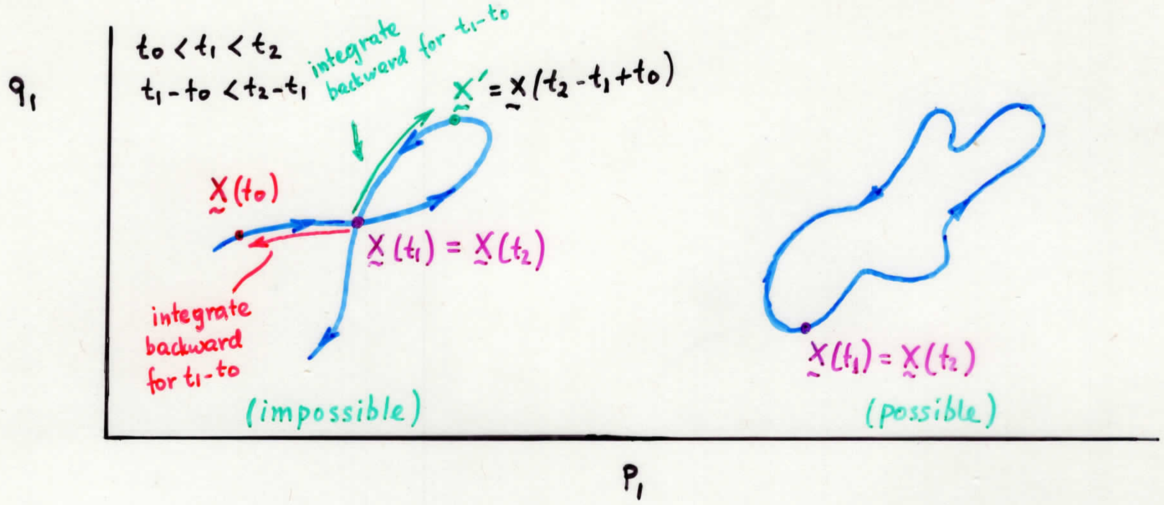
Assume that, at some time t_2, the two trajectories meet at a point $\underset{\sim}{X}'$, so that $\underset{\sim}{X}_A(t_2) = \underset{\sim}{X}_B(t_2) = \underset{\sim}{X}'$.

Consider system A. By integrating Hamilton's equations for that system from time t_2 to time t_1, with initial condition $\underset{\sim}{X}_A(t_2) = \underset{\sim}{X}'$, we reach phase-space point $\underset{\sim}{X}_A(t_1)$.

Consider system B. By integrating Hamilton's equations for that system from time t_2 to time t_1, with initial condition $\underset{\sim}{X}_B(t_2) = \underset{\sim}{X}'$, we reach phase-space point $\underset{\sim}{X}_B(t_1)$.

The Hamiltonian is the same, therefore Hamilton's equations are identical for the two systems. Necessarily, then, one must have $\underset{\sim}{X}_A(t_1) = \underset{\sim}{X}_B(t_1)$, as these points are reached by integrating the same equations for the same time with the same initial condition. But this contradicts our hypothesis. Therefore, the two trajectories do not meet at any t_2. (REDUCTIO AD ABSURDUM

2. The trajectory $\underset{\sim}{X}(t)$, traced by a conservative system on a constant energy hypersurface as time evolves, can never intersect itself. It can, however, form a closed loop.



Proof

Assume that a trajectory $\underset{\sim}{X}(t)$ intersects itself without forming a closed loop. This means that, for two distinct times $t_2 > t_1$, the trajectory goes through the same point in phase space, $\underset{\sim}{X}(t_1) = \underset{\sim}{X}(t_2)$, and that there are trajectory points not lying on the path traced between times t_1 and t_2. Let $\underset{\sim}{X}(t_0)$ be such a point, corresponding to time $t_0 < t_1$, such that $t_1 - t_0 < t_2 - t_1$.

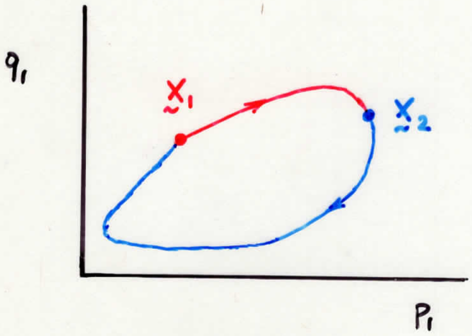
If we start at $\underset{\sim}{X}(t_1)$ and integrate Hamilton's equations backwards for an interval $t_1 - t_0$, we reach point $\underset{\sim}{X}(t_0)$.

On the other hand, if we start at $\underset{\sim}{X}(t_2)$ and integrate Hamilton's equations backwards for an interval $t_1 - t_0$, we will reach a point $\underset{\sim}{X}'$ lying on the path traced between times t_1 and t_2.

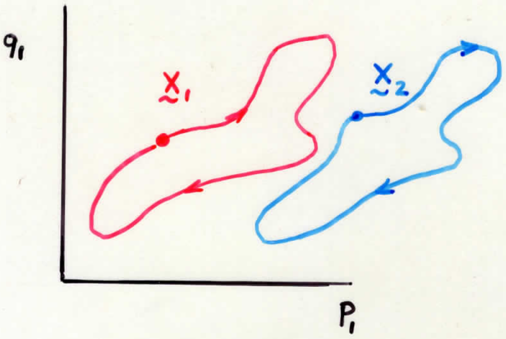
Given that $\underset{\sim}{X}(t_1) = \underset{\sim}{X}(t_2)$, $\underset{\sim}{X}(t_0)$ and $\underset{\sim}{X}'$ must coincide. This, however, is impossible, because it contradicts our original hypothesis that $\underset{\sim}{X}(t_0)$ lies outside the path traced between t_1 and t_2.

Therefore, the trajectory $\underset{\sim}{X}(t)$ cannot intersect itself.

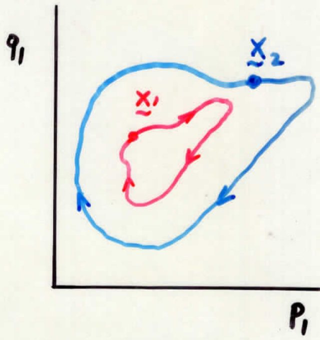
3. Given two different points in phase space, the trajectories emanating from these points will either be parts of the same large trajectory, or never intersect each other.



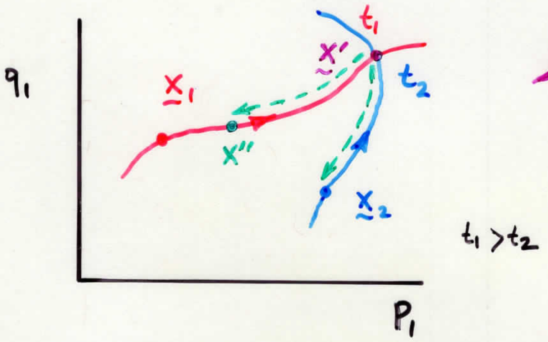
POSSIBLE



POSSIBLE



POSSIBLE



IMPOSSIBLE

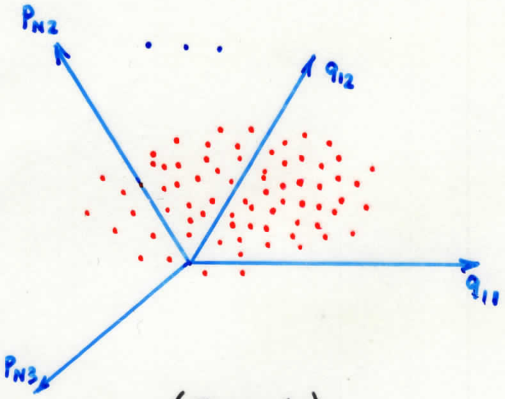
To prove the impossibility of an intersection:

Assume that the trajectory emanating from $\underset{\sim}{X}_1$ (i.e. the trajectory $\underset{\sim}{X}(t)$ obtained through integration of Hamilton's equations with initial condition $\underset{\sim}{X}(0) = \underset{\sim}{X}_1$) and the trajectory emanating from $\underset{\sim}{X}_2$ intersect at some point $\underset{\sim}{X}'$ for the first time. Point $\underset{\sim}{X}'$ is reached at time t_1 starting from $\underset{\sim}{X}_1$ and at time t_2 starting from $\underset{\sim}{X}_2$; let us assume that $t_1 > t_2$.

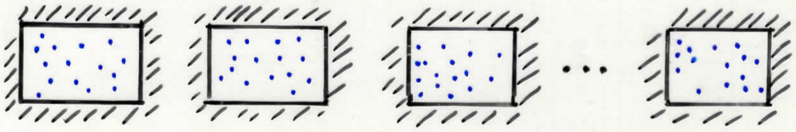
If we start at $\underset{\sim}{X}'$ and integrate the equations of motion backwards for time t_2, we will reach $\underset{\sim}{X}_2$. Again, if we start at $\underset{\sim}{X}'$ and integrate the equations of motion backwards for t_2, we will reach a point $\underset{\sim}{X}''$ on the the trajectory emanating from $\underset{\sim}{X}_1$, between $\underset{\sim}{X}'$ and $\underset{\sim}{X}_1$. We must therefore have $\underset{\sim}{X}'' \equiv \underset{\sim}{X}_2$, which means that $\underset{\sim}{X}_2$ lies on the trajectory emanating from $\underset{\sim}{X}_1$. This, however, is contrary to our hypothesis that $\underset{\sim}{X}'$ is the first point of intersection between the trajectories emanating from $\underset{\sim}{X}_1$ and from $\underset{\sim}{X}_2$. The two trajectories, therefore, cannot intersect.

Ensemble

A collection of representative points in phase space.



(Time t_1)



e.g., for N molecules of gas in a box with perfectly reflecting walls of volume V, there is an infinity of microstates corresponding to the macroscopic constraints of given N, V, and total energy E. We can think of a large set of such microstates (replicas of the system) at a given time as comprising an ensemble.

Ensemble probability density $\rho(\underset{\sim}{X}, t) \equiv \rho(\underset{\sim}{q}, \underset{\sim}{p}, t)$:

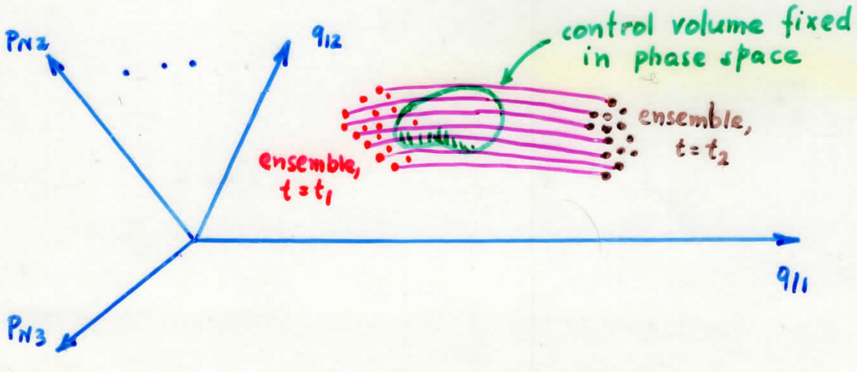
$\rho(\underset{\sim}{X}, t)\, d^{6N}X =$ probability that a representative point of the ensemble lies within the phase-space "volume" element $\underset{\sim}{X}$ to $\underset{\sim}{X} + d\underset{\sim}{X}$ at time t.

Normalization:

$$\int_\Gamma \rho(\underset{\sim}{X}, t)\, d^{6N}X \equiv \int_\Gamma \rho(\underset{\sim}{p}, \underset{\sim}{q}, t)\, d^{3N}p\, d^{3N}q = 1 \qquad (3.7)$$

all phase space

As time goes by, the collection of points constituting the ensemble moves through phase space, each point following its own trajectory. As a consequence, the probability density $\rho(\underset{\sim}{X}, t)$ evolves in time.



Conservation of representative points

$$\underbrace{\oint}_{\text{control surface}} dS\, \underbrace{\underset{\sim}{n}}_{\substack{\text{vector normal to}\\ \text{element of control}\\ \text{surface } dS}} \cdot\, \dot{\underset{\sim}{X}}\; \rho(\underset{\sim}{X}, t) = -\frac{\partial}{\partial t} \underbrace{\int}_{\text{control volume}} \rho(\underset{\sim}{X}, t)\, d^{6N}X$$

6N-dimensional gradient vector

Differential form of the balance: $-\frac{\partial \rho}{\partial t} = \underset{\sim}{\nabla}_{\underset{\sim}{x}} \cdot (\rho \dot{\underset{\sim}{x}})$ (3.9)

3-dimensional gradient vector wrt $\underset{\sim}{p}_i$

$$\text{or,}\quad -\frac{\partial \rho}{\partial t} = \sum_{i=1}^{N} \left(\frac{\partial \rho}{\partial \underset{\sim}{p}_i} \cdot \dot{\underset{\sim}{p}}_i + \frac{\partial \rho}{\partial \underset{\sim}{q}_i} \cdot \dot{\underset{\sim}{q}}_i \right) + \sum_{i=1}^{N} \rho \left(\frac{\partial}{\partial \underset{\sim}{p}_i} \cdot \dot{\underset{\sim}{p}}_i + \frac{\partial}{\partial \underset{\sim}{q}_i} \cdot \dot{\underset{\sim}{q}}_i \right)$$

[compare fluid mechanics: $-\frac{\partial \rho}{\partial t} = -\underset{\sim}{\nabla} \cdot (\rho \underset{\sim}{v})$ continuity equation]

From Hamilton's equations:

$$\frac{\partial}{\partial \underset{\sim}{p}_i} \cdot \dot{\underset{\sim}{p}}_i + \frac{\partial}{\partial \underset{\sim}{q}_i} \cdot \dot{\underset{\sim}{q}}_i = \frac{\partial}{\partial \underset{\sim}{p}_i} \cdot \frac{\partial \mathcal{H}}{\partial \underset{\sim}{q}_i} - \frac{\partial}{\partial \underset{\sim}{q}_i} \cdot \frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_i} = 0$$

In other words, $\boxed{\underset{\sim}{\nabla}_{\underset{\sim}{x}} \cdot \dot{\underset{\sim}{x}} = 0}$ (3.10)

[compare fluid mechanics: $\underset{\sim}{\nabla} \cdot \underset{\sim}{v} = 0$; true for an incompressible fluid]

Combine (3.9, 3.10)

$$\sum_{i=1}^{N} \left(\frac{\partial \rho}{\partial \underset{\sim}{p}_i} \cdot \dot{\underset{\sim}{p}}_i + \frac{\partial \rho}{\partial \underset{\sim}{q}_i} \cdot \dot{\underset{\sim}{q}}_i \right) + \frac{\partial \rho}{\partial t} = 0 \quad \text{, or} \quad \dot{\underset{\sim}{x}} \cdot \underset{\sim}{\nabla}_{\underset{\sim}{x}} \rho + \frac{\partial}{\partial t} \rho = 0 \qquad (3.11)$$

FLOW THROUGH PHASE SPACE IS INCOMPRESSIBLE!

"substantial time derivative".

or, defining $\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \dot{\underset{\sim}{x}} \cdot \underset{\sim}{\nabla}_{\underset{\sim}{x}}$, $\frac{D\rho}{Dt} = 0$ (3.12)

[compare fluid mechanics: incompressibility in a frame which moves with the representative points in the ensemble]

Eqs (3.11), (3.12) are forms of the *Liouville equation*:

$$\boxed{\frac{\partial \rho}{\partial t} + \overbrace{\sum_{i=1}^{N} \left(\frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_i} \cdot \frac{\partial}{\partial \underset{\sim}{q}_i} - \frac{\partial \mathcal{H}}{\partial \underset{\sim}{q}_i} \cdot \frac{\partial}{\partial \underset{\sim}{p}_i} \right)}^{\text{Poisson bracket operator, } \hat{\mathcal{H}}} \rho = 0}$$

, also written $i \frac{\partial \rho}{\partial t} = \overset{\text{Liouville operato}}{\hat{\mathcal{L}}} \rho$

$\hat{\mathcal{L}} = -i \hat{\mathcal{H}}$ (3.15)

The Liouville equation is an equation describing the evolution of the probability density of an ensemble with Hamiltonian $\mathcal{H}$ in phase space. It is time reversible.

An equation reminiscent of the Liouville equation can be written for the evolution of a function of the system microstate along a trajectory.

Let $\mathcal{A}(\underset{\sim}{p}, \underset{\sim}{q})$ a function of the microstate, with no explicit dependence on time.

As $\underset{\sim}{p}(t)$, $\underset{\sim}{q}(t)$ evolve along a dynamical trajectory, $\mathcal{A}$ changes.

Let $\mathcal{A}(t) = \mathcal{A}(\underset{\sim}{q}(t), \underset{\sim}{p}(t))$

Then,

$$\frac{d\mathcal{A}}{dt} = \sum_{i=1}^{N} \frac{\partial \mathcal{A}}{\partial \underset{\sim}{q}_i} \cdot \frac{\partial \underset{\sim}{q}_i}{\partial t} + \sum_{i=1}^{N} \frac{\partial \mathcal{A}}{\partial \underset{\sim}{p}_i} \cdot \frac{\partial \underset{\sim}{p}_i}{\partial t} \overset{\text{Hamilton's equations}}{=}$$

$$= \sum_{i=1}^{N} \frac{\partial \mathcal{A}}{\partial \underset{\sim}{q}_i} \cdot \frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_i} - \sum_{i=1}^{N} \frac{\partial \mathcal{A}}{\partial \underset{\sim}{p}_i} \cdot \frac{\partial \mathcal{H}}{\partial \underset{\sim}{q}_i} \Rightarrow$$

$$\Rightarrow \boxed{\frac{d\mathcal{A}}{dt} = \sum_{i=1}^{N} \left(\frac{\partial \mathcal{H}}{\partial \underset{\sim}{p}_i} \cdot \frac{\partial}{\partial \underset{\sim}{q}_i} - \frac{\partial \mathcal{H}}{\partial \underset{\sim}{q}_i} \cdot \frac{\partial}{\partial \underset{\sim}{p}_i} \right) \mathcal{A} = \hat{\mathcal{H}} \mathcal{A}} \qquad (3.16)$$

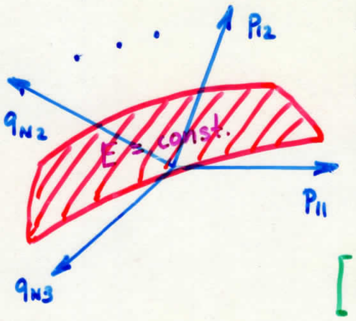
or

$$-i \frac{d\mathcal{A}}{dt} = \hat{\mathcal{L}} \mathcal{A} \qquad (3.17)$$

- If we know $\rho(\underset{\sim}{X}, 0)$ and $\mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p})$, we can determine $\rho(\underset{\sim}{X}, t)$ at any time.
- If we know $\mathcal{A}(0)$ and $\mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p})$, we can determine $\mathcal{A}(t)$ at any time.

Simple dynamical description involving all degrees of freedom

Ergodicity and Mixing in Phase Space



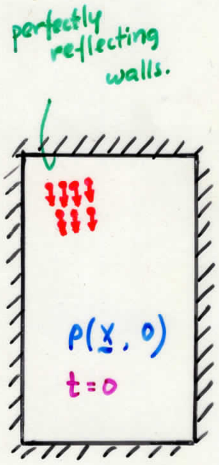
FOCUS: Ensemble of representative points of a conservative system of N particles with Hamiltonian $\mathcal{H}(\underset{\sim}{p}, \underset{\sim}{q})$. All points in ensemble have the same total energy E

Ensemble lies on constant energy hypersurface E. (A (6N-1)-dimensional surface, defined by the constraint $\mathcal{H}(\underset{\sim}{X}) = E$)

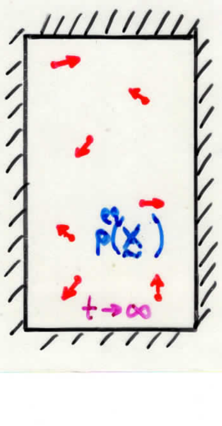
[Ensemble is not necessarily an equilibrium ensemble!]

"Area" of E-hypersurface: $$\Sigma(E) = \int_{E\text{-hypersurface}} d^{6N-1}X \qquad (3.18)$$

EMPIRICAL OBSERVATION: An isolated system, prepared under arbitrary initial conditions, evolves to a state of equilibrium, wherein macroscopic properties are time-independent.



MICROSCOPIC INTERPRETATION: An ensemble of state points, representing the system under its conditions of preparation, will evolve in time in such a way that the probability density $\rho(\underset{\sim}{X}, t)$ will tend towards an equilibrium probability density $\rho^{eq}(\underset{\sim}{X})$. The function $\rho^{eq}(\underset{\sim}{X})$ will be a stationary solution of the Liouville equation, characteristic of an equilibrium ensemble.



QUESTIONS What causes this decay to equilibrium, given that evolution equations (Hamilton's equations, Liouville equation) are time reversible?

What are the conditions for decay to equilibrium $(\rho(\underset{\sim}{X}, t) \longrightarrow \rho^{eq}(\underset{\sim}{X}))$ to occur?

Ergodic Flow: The flow of state points on the energy hypersurface is defined to be ergodic, if almost all points $\underset{\sim}{X} \equiv (\underset{\sim}{p}, \underset{\sim}{q})$ on the hypersurface move in such a way that they pass through every small finite neighborhood on the energy surface. (Each representative point, excluding a set of points of measure zero, follows a trajectory that, given sufficient time, will pass arbitrarily close to any other point on the energy hypersurface.)

Ergodic Theorem (Birkhoff, 1931)

$f(\underset{\sim}{X})$ = an integrable function of the state point $\underset{\sim}{X}$ on E-hypersurface.

Define:

Phase average
$$\langle f \rangle_\Sigma \equiv \frac{\int_{E\text{-hypersurf.}} f(\underset{\sim}{X})\, d^{6N-1}X}{\int_{E\text{-hypersurf.}} d^{6N-1}X} = \frac{1}{\Sigma(E)} \int_{E\text{-hypersurf.}} f(\underset{\sim}{X})\, d^{6N-1}X \qquad (3.20$$

[average over all pts on E-hypersurfac

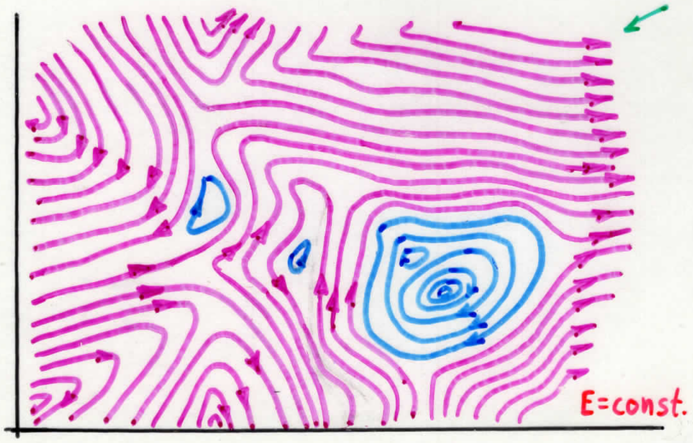
Time average
$$\langle f \rangle_t \equiv \lim_{t\to\infty} \frac{1}{t} \int_{t_0}^{t_0+t} f(\underset{\sim}{X}(t))\, dt \qquad (3.21)$$

[average along a trajectory]

A system is ergodic, if

(i) Time average exists for almost all $\underset{\sim}{X}(t_0)$

(ii) when it exists, $\langle f \rangle_t = \langle f \rangle_\Sigma$

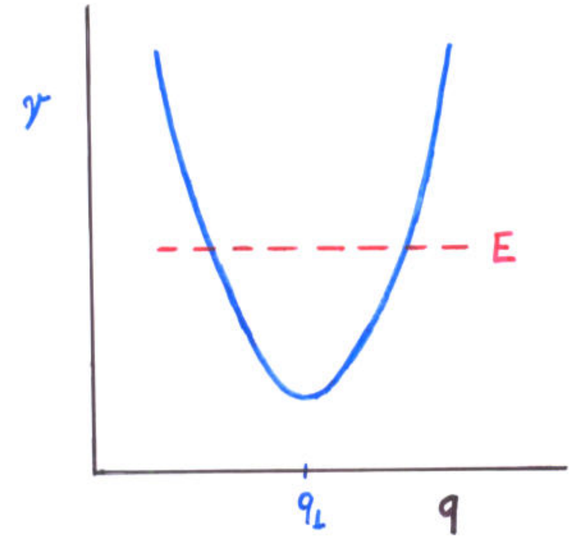


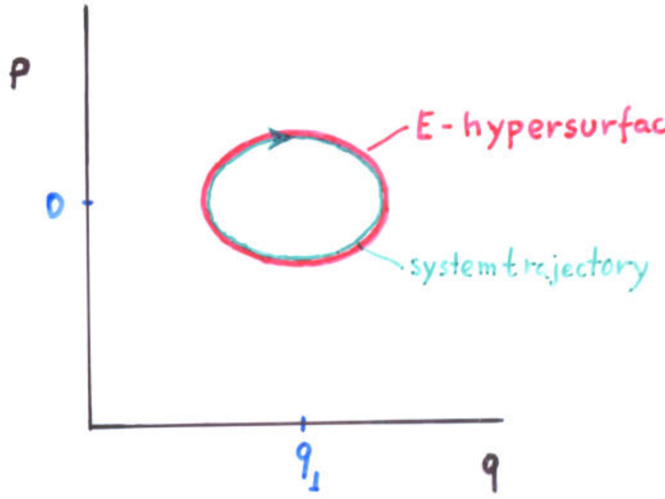
The flow on this energy hypersurface is not ergodic.

For an ergodic system, all lines would ultimately be sections of a single, long closed-loop trajectory. The time required to traverse this immensely long loop and return to exactly the same point in phase space (Poincaré cycle) is on the order e^N ($e^{10^{23}}$, incomprehensibly large!)

Simple Examples (One configurational degree of freedom).

1. Single - well potential

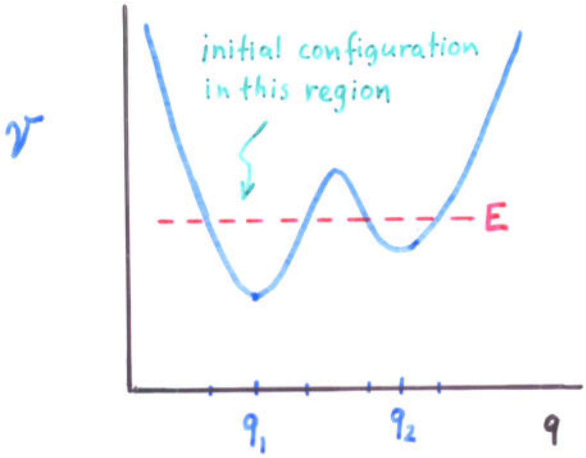


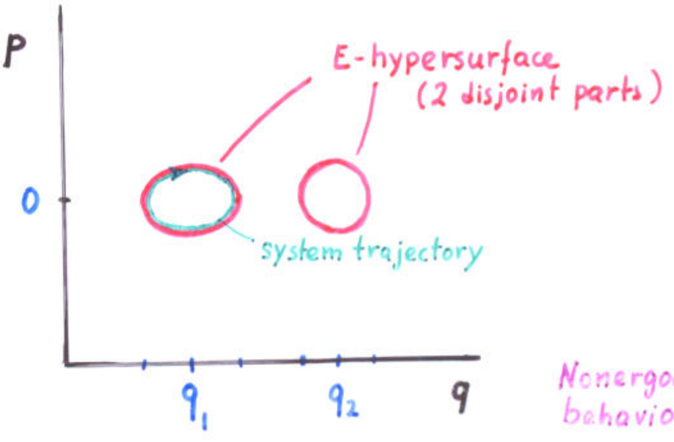


Harmonic oscillator: $\mathcal{H}(p,q) = \frac{1}{2}\frac{p^2}{m} + \mathcal{V}(q) = \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}k\,(q-q_1)^2$

System trajectory traces the entire E-hypersurface. Ergodic behavior.

2. Double-well potential



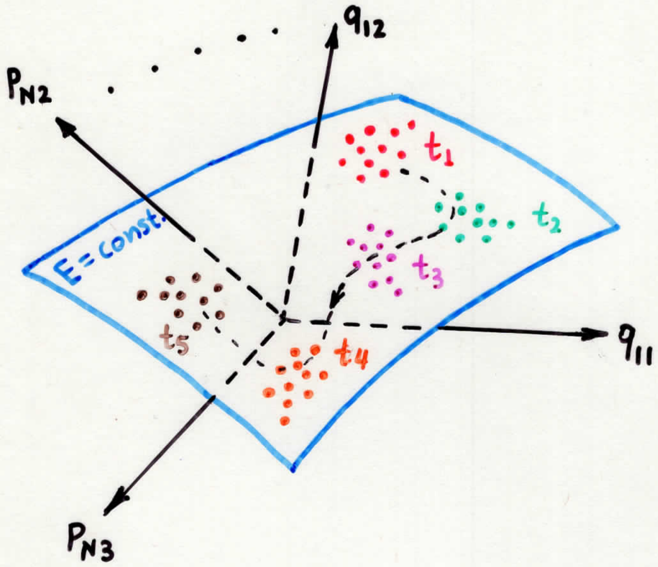


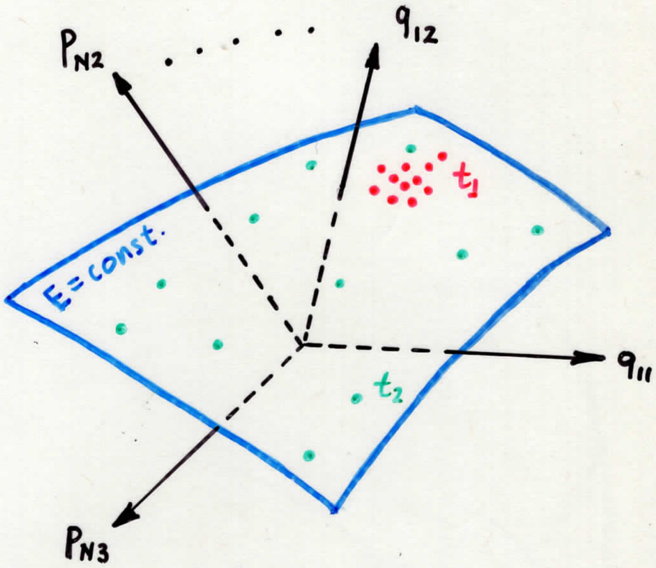
Nonergodi behavior

System will oscillate in the vicinity of the minimum where it was originally placed.

Q: Is ergodic flow a sufficient requirement for $\rho(\underset{\sim}{X}, t)$ to decay to equilibrium $\rho^{eq}(\underset{\sim}{X})$?

A: No. The stronger requirement of <u>mixing flow</u> is required for this.





Ergodic, but not mixing flow

Swarm of ensemble points moves over the entire hypersurface, ultimately visiting all of it, but does not disperse itself. (points move "in formation"). $\rho(\underset{\sim}{X}, t)$ does not decay to an equilibrium density $\rho^{eq}(\underset{\sim}{X})$

Mixing flow

Swarm of ensemble points quickly disperses itself over the entire E-hypersurface. Representative points that initially neighbor one another move apart exponentially with time, and soon arrive at entirely different parts of the E-hypersurface.

Mixing flow characterizes systems with chaotic dynamics.

An example of transition to chaotic dynamics:

Henon-Heiles model system: $\mathcal{H}(p_1, p_2, q_1, q_2) = \frac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2) + q_1 q_2^2 - \frac{1}{3} q_1^3$

Astr. J. 1964, 69, 73-79

2-dimensional configuration space

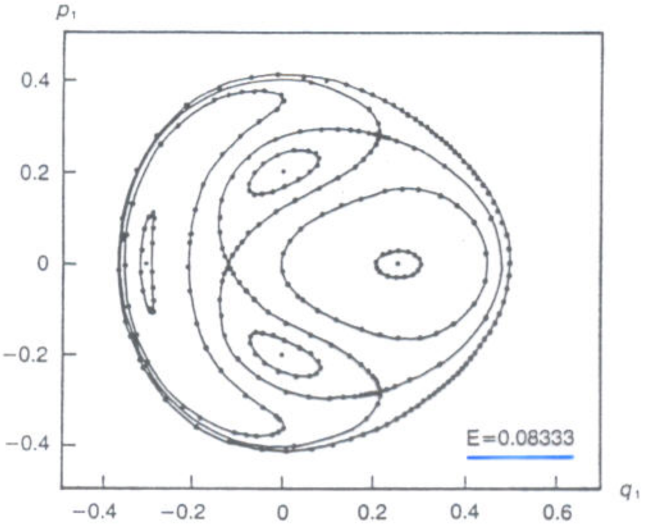
4-dimensional phase space

3-dimensional const. E-hypersurfaces.

Consider 2-d intersections of E-hypersurface with plane $q_2 = 0$. Record points at which these intersections are intersected by trajectories with $p_2 > 0$.

Low E:

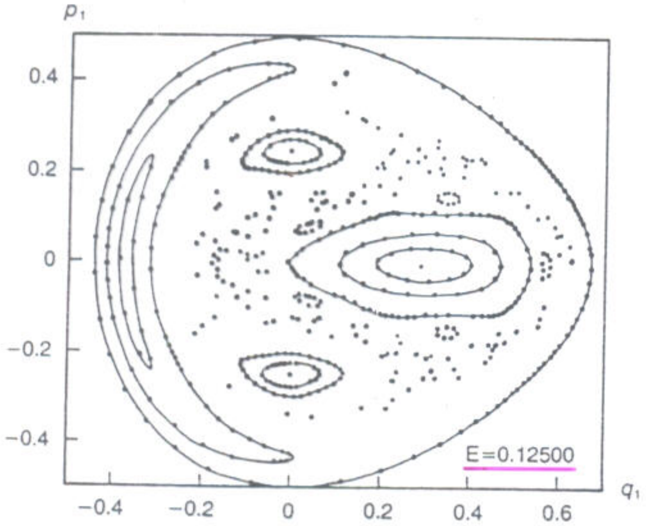
Each closed curve comes from one trajectory.

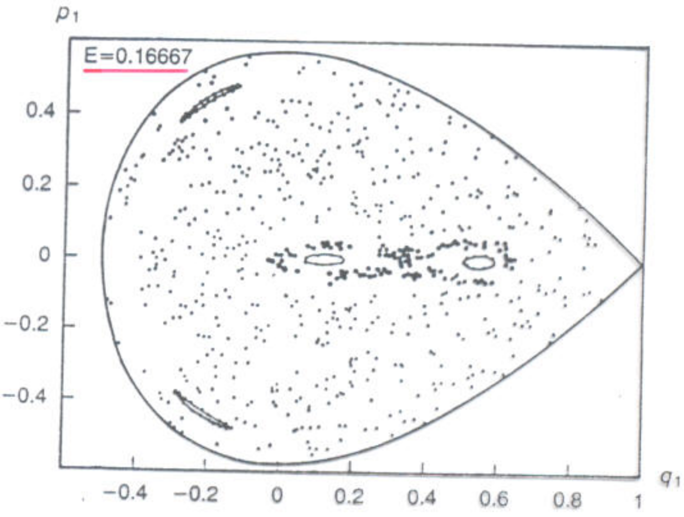


Stable dynamics

not intersecting trajectories - [illegible]

NONERGODIC BEHAVIOR





Higher E:

Breakdown of stable dynamics.

A chaotic trajectory appears (random points)

High E

Almost completely chaotic behavior.

MIXING FLOW on E-hypersurface

Ensemble average of a quantity $f(\underset{\sim}{p},\underset{\sim}{q})$

$$\langle f(t)\rangle_{\rho(\underset{\sim}{X},t)} \equiv \int\limits_{E\text{-hypersurface}} f(\underset{\sim}{X})\;\rho(\underset{\sim}{X},t)\;d^{6N-1}X \qquad (3.22)$$

or

$$\langle f(t)\rangle_{\rho(\underset{\sim}{X},t)} = \int\limits_{\Gamma} f(\underset{\sim}{X})\;\rho(\underset{\sim}{X},t)\;d^{6N}X$$

[ρ assumed to be normalized on E-hypersurface and zero outside the E-hypersurface].

For a system exhibiting mixing flow,

$$\langle f(t)\rangle_{\rho(\underset{\sim}{X},t)} \equiv \int\limits_{E\text{-hypersurface}} f(\underset{\sim}{X})\,\rho(\underset{\sim}{X},t)\;d^{6N-1}X \xrightarrow{t\to\pm\infty} \frac{1}{\Sigma(E)}\int\limits_{E\text{-hypersurface}} f(\underset{\sim}{X})\;d^{6N-1}X \equiv \langle f\rangle_{\Sigma} \qquad (3.24)$$

Ensemble average for t → ±∞ becomes indistinguishable from phase average.

This suggests that $\rho(\underset{\sim}{X},t)$ spreads out with time, and ultimately evolves into the stationary, equilibrium ensemble distribution

$$\rho^{eq}_{NVE}(\underset{\sim}{X}) = \begin{cases} \dfrac{1}{\Sigma(E)} = \dfrac{1}{\int\limits_{E\text{-hypersurface}} d^{6N-1}X}, & \text{if } \mathcal{H}(\underset{\sim}{X}) = E \\ 0, & \text{otherwise} \end{cases}$$

NOTE: This equilibrium distribution is uniform on the E-hypersurface!

Ergodicity and mixing flow in phase space have been proved mathematically for some simple model systems (e.g., hard sphere fluids). under certain conditions.

Most of the molecular systems we deal with in nature are characterized by complex, strongly nonlinear potential energy functions, such that Hamiltonian dynamics leads to chaos and mixing flow in phase space.

Our everyday experience that, for an isolated system, $\rho(\underset{\sim}{X}, t) \xrightarrow{t\to\infty} \rho^{eq}(\underset{\sim}{X})$, i.e. that thermodynamic equilibrium will be established, is a consequence of the chaotic nature of phase-space trajectories. It does not contradict the time-reversible nature of Hamiltonian dynamics and the Liouville equation.

Considerations of ergodic and mixing flow on constant energy hypersurfaces form a basis for the postulates of equilibrium statistical mechanics.

4. THE EQUILIBRIUM ENSEMBLES

4.2. Microcanonical Ensemble: N, V, E constant (isolated system)

Fundamental Postulates:

1. Postulate of Equal a Priori Probabilities.

   For an isolated system at fixed E, V, N [or $(N_1, N_2, \dots, N_m)$] all possible microstates are equally likely in thermodynamic equilibrium.

2. Ergodic Hypothesis

   Given enough time, an isolated system will sample all microstates consistent with the macroscopic constraints imposed on it. Time averages [measured properties] can be substituted by equilibrium ensemble averages.

Probability Density

Quantum Mechanical Formulation: Microstates = discrete quantum states.

Probability of microstate ν

$$P_\nu^{NVE} = \begin{cases} \dfrac{1}{\Omega(N,V,E)} & \text{if } E-\delta E < E_\nu < E \\ 0 & \text{otherwise} \end{cases} \qquad (4.1)$$

$\Omega(N,V,E)$ ← total number of microstates with energy $E-\delta E < E_\nu < E$

Note: ν labels quantum states, not energy levels

Classical Formulation: Microstates form a continuum in phase space

Probability density

$$p^{NVE}(\underset{\sim}{p},\underset{\sim}{q}) = \begin{cases} \dfrac{1}{\Sigma(N,V,E)} & ,\text{if } E-\delta E < \mathcal{H}(\underline{p},\underline{q}) < E \\ 0 & \text{otherwise} \end{cases} \qquad (4.2)$$

where $\Sigma(N,V,E) = \displaystyle\int\limits_{\substack{\text{region of phase space} \\ \text{where } E-\delta E < \mathcal{H}(\underline{p},\underline{q}) < E}} d^{3N}p \; d^{3N}q$

"Number of microstates" $\Omega(N,V,E) = \dfrac{1}{h^{3N} N!} \Sigma(N,V,E)$

There is a limit to the resolution with which we can define microstates in continuous phase space

In a quantum mechanical description, particles are indistinguishable (interchange may at most change sign of ψ, but does not change state) "correct Boltzmann counting".

Connection with Thermodynamics $S(N,V,E) = k_B \ln \Omega(N,V,E)$

entropy.

Boltzmann constant, R/N_A

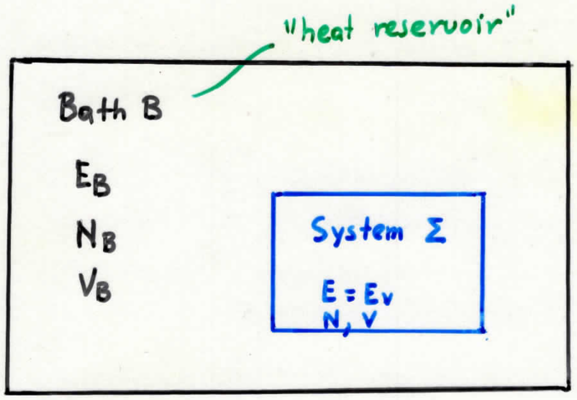
A fundamental equation, in the entropy representation.

CONSEQUENCES

- Entropy is extensive.
- For an isolated system, the imposition of any internal constraint decreases the entropy (2nd Law).
- At $T=0$, for a perfect crystalline substance, there is only one quantum state (ground state), so $S \to 0$. (3rd law)

Temperature: $\beta \equiv \dfrac{1}{k_B T} = \dfrac{\partial \ln\Omega}{\partial E} = \dfrac{1}{k_B} \left.\dfrac{\partial S}{\partial E}\right)_{N,V}$ (compare $T = \left.\dfrac{\partial U}{\partial S}\right)_{N,V}$

4.5. Canonical Ensemble: N, V, T constant.



$B >> \Sigma$

Total system

$\Sigma' = \Sigma + B$

isolated, at constant N, V, E.

$N_{\Sigma'} = N + N_B = \text{const.}$ $\quad$ $N = \text{const.}$

$V_{\Sigma'} = V + V_B = \text{const.}$ $\quad$ $V = \text{const.}$

$E_{\Sigma'} = E + E_B = \text{const.}$ $\quad$ E fluctuates

Assume that Σ is in a given microstate ν, of energy E_ν.
Number of microstates accessible to total system is $\underbrace{\Omega_B(N_B, V_B, E_{\Sigma'} - E_\nu)}_{\text{for brevity, call } \Omega_B(E_{\Sigma'} - E_\nu)}$

Total system Σ' is isolated, therefore described by the microcanonical ensembl
All the microstates of Σ' are equiprobable, each with probability $\dfrac{1}{\Omega_{\Sigma'}(E_{\Sigma'})}$

Then: Probability that Σ will be in state ν will be:

$$P_\nu = \frac{\Omega_B(E_{\Sigma'} - E_\nu)}{\Omega_{\Sigma'}(E_{\Sigma'})} = \text{Const.} \exp\left[\ln \Omega_B(E_{\Sigma'} - E_\nu)\right] \qquad (4.8)$$

Since $E_\nu << E_{\Sigma'}$, to an excellent approximation,

$$\ln \Omega_B(E_{\Sigma'} - E_\nu) = \underbrace{\ln \Omega_B(E_{\Sigma'})}_{\text{Const.}} - E_\nu \underbrace{\left.\frac{\partial \ln \Omega_B}{\partial E_B}\right)_{N_B, V_B}}_{\text{const.}} \qquad (4.9)$$

By definition (microcanonical ensemble for bath): $\left.\dfrac{\partial \ln \Omega_B}{\partial E_B}\right)_{N_B, V_B} = \dfrac{1}{k_B T_B}$ (4.10

bath temperature, equal to system temperat

Combining (4.8) to (4.10), $P_\nu^{NVT} = \text{Const.} \exp\left(-\frac{E_\nu}{k_B T_B}\right) = \text{Const.} \exp(-\beta E_\nu)$. (4.12)

Conclusion: The equilibrium distribution of system Σ in its phase space is given by the Boltzmann distribution

Probability $\underline{P_\nu^{NVT} = \frac{1}{Q} \exp(-\beta E_\nu)}$ (4.13)

where $\underline{Q(N,V,T) \equiv Q(N,V,\beta) = \sum_\nu \exp(-\beta E_\nu)}$ CANONICAL PARTITION FUNCTION. (4.14)

Classical Formulation:

Probability density $\underline{\rho^{NVT}(\underset{\sim}{q}, \underset{\sim}{p}) = \frac{1}{Q(N,V,T)} \frac{1}{h^{3N} N!} \exp\left[-\beta \mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p})\right]}$ (4.15)

$$\underline{Q(N,V,T) = \int_{\substack{\text{all phase}\\ \text{space}, \Gamma}} \frac{e^{-\beta \mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p})}}{N!\, h^{3N}} \, d^{3N}q \, d^{3N}p} \qquad (4.16)$$

Connection with Thermodynamics

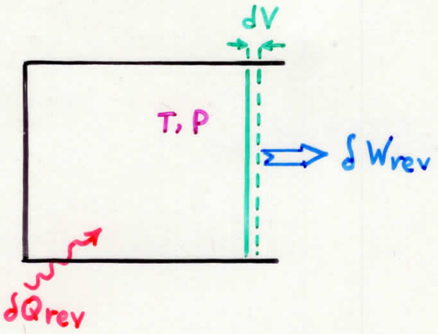
$$\underline{A(N,V,T) = -k_B T \ln Q(N,V,T) = -\frac{1}{\beta} \ln Q(N,V,T)} \qquad (4.18)$$

A fundamental equation, in the Helmholtz energy representation

Makes sense:

$$\underset{\substack{\uparrow\\ \text{internal}\\ \text{energy}}}{U}(N,V,T) = \left.\frac{\partial(A/T)}{\partial(1/T)}\right|_{N,V} = -\left.\frac{\partial \ln Q}{\partial \beta}\right|_{N,V} = \sum_\nu E_\nu P_\nu^{NVT} = \langle E \rangle_{NVT}$$

Work, Heat, and Entropy in the Canonical Ensemble



Consider reversible thermodynamic process that entails change in volume of a closed system.
System is at equilibrium all along the proces

$$\delta W_{rev} = P\,dV$$

V-dependent

But $P = -\frac{\partial A}{\partial V}\Big)_{T,N} = k_BT\frac{\partial \ln Q}{\partial V}\Big)_{T,N} = \frac{k_BT}{Q}\Big[\frac{\partial}{\partial V}\Big(\sum_\nu e^{-\beta E_\nu}\Big)\Big]_{T,N} =$

$$= \frac{k_BT}{Q}\Big(-\frac{1}{k_BT}\Big)\sum_\nu\Big[e^{-\beta E_\nu}\frac{\partial E_\nu}{\partial V}\Big)_N\Big] = -\sum_\nu \frac{e^{-\beta E_\nu}}{Q}\frac{\partial E_\nu}{\partial V}\Big)_N = -\sum_\nu P_\nu^{NVT}\frac{\partial E_\nu}{\partial V}\Big)$$

So, $$\boxed{\delta W_{rev} = -\sum_\nu P_\nu^{NVT}\,dE_\nu} \qquad (4.23)$$

(Doing work on the system reversibly amounts to changing the energy levels of microstates, while keeping their probability distribution constant

Change in system internal energy:

$$dU = d\Big[\sum_\nu P_\nu^{NVT}E_\nu\Big] = \sum_\nu P_\nu^{NVT}\,dE_\nu + \sum_\nu E_\nu\,dP_\nu^{NVT} \qquad (4.24)$$

By 1st law, $dU = \delta Q_{rev} - \delta W_{rev}$, so $$\boxed{\delta Q_{rev} = \sum_\nu E_\nu\,dP_\nu^{NVT}} \qquad (4.25)$$

(Exchanging heat with the system reversibly amounts to changing the probability distribution of microstates, while keeping the energy levels constant).

δQ_{rev} can be written in terms of $\{P_\nu^{NVT}\}$ only:

$$P_\nu^{NVT} = \frac{e^{-\beta E_\nu}}{Q} \Rightarrow E_\nu = -k_B T \left(\ln P_\nu^{NVT} + \ln Q \right)$$

$$\delta Q_{rev} = -k_B T \sum_\nu \left(\ln P_\nu^{NVT} + \ln Q \right) d P_\nu^{NVT} = -k_B T \sum_\nu \ln P_\nu^{NVT} d P_\nu^{NVT} - k_B T \ln Q \cancelto{0}{\sum_\nu d P_\nu^{NV}}$$

or $$\boxed{\delta Q_{rev} = -k_B T \sum_\nu \ln P_\nu^{NVT} \, d P_\nu^{NVT}} \qquad (4.26)$$

Entropy $$S \equiv \frac{U-A}{T} = \frac{1}{T} \left[\sum_\nu E_\nu P_\nu^{NVT} + k_B T \ln \left(\sum_\nu e^{-\beta E_\nu} \right) \right] =$$

$$\frac{1}{T} \left[\sum_\nu \left\{ -k_B T \left(\ln P_\nu^{NVT} + \ln Q \right) P_\nu^{NVT} \right\} + k_B T \ln Q \right] = -k_B \sum_\nu P_\nu^{NVT} \ln P_\nu^{NVT} - k_B \ln Q \cancelto{1}{\sum_\nu P_\nu^{NVT}}$$

$$-k_B \ln Q, \text{ or } \boxed{S = -k_B \sum_\nu P_\nu^{NVT} \ln P_\nu^{NVT}} \qquad (4.27)$$

(Gibbs entropy formula)

Then, $dS = -k_B \sum_\nu \ln P_\nu^{NVT} d P_\nu^{NVT} - k_B \cancelto{0}{\sum_\nu} d P_\nu^{NVT}$, or $dS = -k_B \sum_\nu \ln P_\nu^{NVT} d P_\nu^{NV}$

(4.28)

Combining (4.26, 4.28) $$\boxed{\delta Q_{rev} = T \, dS} \qquad (4.29)$$

(Macroscopic thermodynamic definition of entropy is consistent with equilibrium ensemble formalism).

Energy fluctuations in the canonical ensemble

Variance of the energy:

$$\langle (\delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \sum_\nu P_\nu^{NVT} E_\nu^2 - \left(\sum_\nu P_\nu^{NVT} E_\nu \right)^2 =$$

$$= \frac{1}{Q} \sum_\nu \{\exp(-\beta E_\nu)\} E_\nu^2 - \left\{ \frac{1}{Q} \sum_\nu [\exp(-\beta E_\nu)] E_\nu \right\}^2 =$$

$$= \frac{1}{Q} \frac{\partial^2}{\partial \beta^2} \left[\sum_\nu \exp(-\beta E_\nu) \right] - \left\{ \frac{1}{Q} \frac{\partial}{\partial \beta} \left[\sum_\nu \exp(-\beta E_\nu) \right] \right\}^2 =$$

$$= \frac{Q \frac{\partial}{\partial \beta}\left(\frac{\partial Q}{\partial \beta}\right) - \left(\frac{\partial Q}{\partial \beta}\right) \cdot \left(\frac{\partial Q}{\partial \beta}\right)}{Q^2} = \frac{\partial}{\partial \beta} \left(\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right) = \frac{\partial^2 \ln Q}{\partial \beta^2} =$$

$$= -\frac{\partial}{\partial \beta} \left(-\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right) = -\frac{\partial}{\partial \beta} \left\{ -\frac{1}{Q} \frac{\partial}{\partial \beta} \left[\sum_\nu \exp(-\beta E_\nu) \right] \right\} =$$

$$= -\frac{\partial}{\partial \beta} \left\{ +\frac{1}{Q} \sum_\nu [\exp(-\beta E_\nu)] E_\nu \right\} = -\frac{\partial \langle E \rangle}{\partial \beta} = k_B T^2 \left.\frac{\partial U}{\partial T}\right)_{N,V}$$

or
$$\langle (\delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = k_B T^2 \underset{\nwarrow \text{system heat capacity}}{C_V} \qquad (4.20)$$

The magnitude of spontaneous fluctuations in energy at equilibrium under isothermal conditions is a measure of the system heat capacity.

Magnitude of energy fluctuations relative to mean value of energy:

$$\frac{\langle (\delta E)^2 \rangle^{1/2}}{\langle E \rangle} = \frac{(k_B T^2 C_V)^{1/2}}{\langle E \rangle} = \frac{\left(\frac{R}{N_A} T^2 \frac{N}{N_A} \overset{\text{molar heat capacity} \swarrow}{c_v} \right)^{1/2}}{\frac{N}{N_A} \underset{\nwarrow \text{molar internal energy}}{u}} = \underset{\text{intensive}}{\boxed{\left(\frac{R T^2 c_v}{u^2} \right)^{1/2}}} \frac{1}{N^{1/2}} \qquad (4.22)$$

Energy fluctuations become insignificantly small relative to average energy for $N = \mathcal{O}(10^{23})$. (Equivalence of canonical and microcanonical ensembles in the thermodynamic limit $N \to \infty$, all intensive properties constant)

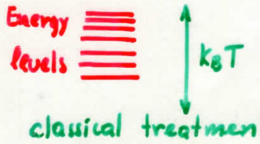
4.6. Elementary Statistical Mechanics of Fluids.

Configurational Integral.

Q: When is it legitimate to treat the contribution of a degree of freedom to the Hamiltonian with classical Statistical mechanics?

A: When the separation of successive energy levels (E-eigenvalues) associated with this degree of freedom is small compared to the thermal energy $k_B T$.

$$k_B T = 4.1 \times 10^{-21} \frac{\text{J}}{\text{d.o.f.}} = 2.5 \frac{\text{kJ}}{\text{mol}} = 0.6 \frac{\text{kcal}}{\text{mol}} \text{ at room temperature}$$



classical treatment permissible.

Nuclear spin contributions: $\Delta E \simeq 10^{-11}$ J/d.o.f.
electronic contributions: $\Delta E \simeq 10^{-17}$ J/d.o.f.
Vibrational contributions: $\Delta E \simeq 10^{-20}$ J/d.o.f

} must be treated quantum mechanically.

Classical treatment satisfactory in most cases for translational, torsional, and overall rotational contributions.

For this discussion, assume monatomic fluid (Each molecule contributes 3 translational degrees of freedom).

Hamiltonian

$$\mathcal{H}(\underset{\sim}{p}, \underset{\sim}{r}) = \mathcal{K}(\underset{\sim}{p}) + \mathcal{V}(\underset{\sim}{r}) = \sum_{i=1}^{N} \frac{p_i^2}{\underbrace{2m_i}_{\text{assume} = m\ \forall i}} + \mathcal{V}(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \dots, \underset{\sim}{r}_N) \qquad (4.31)$$

Canonical partition function (N molecules in volume V at temperature T):

$$Q(N,V,T) = \frac{1}{h^{3N} N!} \underbrace{\int \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] d\underset{\sim}{p}^{3N}}_{\text{Kinetic energy contribution}} \underbrace{\int \exp\left[-\beta \mathcal{V}(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_N)\right] d\underset{\sim}{r}^{3N}}_{\text{Potential energy contribution}} \qquad (4.3$$

SEPARABILITY

Momentum integral is a product of 3N Gaussian integrals:

$$\int \exp\left[-\beta \sum_{i=1}^{N} \frac{\underline{p}_i^{\,2}}{2m}\right] d^{3N}\underline{p} = \prod_{i=1}^{N} \int \exp\left(-\beta \frac{\underline{p}_i^{\,2}}{2m}\right) d^3\underline{p}_i = \prod_{i=1}^{N} \int_{-\infty}^{+\infty} \exp\left(-\beta \frac{p_x^2}{2m}\right) dp_x \int_{-\infty}^{+\infty} \exp\left(-\beta \frac{p_y^2}{2m}\right) dp_y \int_{-\infty}^{+\infty} \exp\left(-\beta \frac{p_z^2}{2m}\right.$$

But $\int_{-\infty}^{+\infty} \exp\left(-\frac{\beta p_x^2}{2m}\right) dp_x = (2m k_B T)^{1/2} \int_{-\infty}^{+\infty} e^{-x^2} dx = (2\pi m k_B T)^{1/2}$

$$\int_{-\infty}^{+\infty} \exp\left[-\beta \sum_{i=1}^{N} \frac{\underline{p}_i^{\,2}}{2m}\right] d^{3N}\underline{p} = (2\pi m k_B T)^{3N/2}$$

Realization: At equilibrium, the distribution of molecular momentum vectors follows the Maxwell-Boltzmann law:

$$P_1(\underline{p}_1) = \frac{\int \rho^{NVT}(\underline{p}, \underline{r})\, d^3p_2\, d^3p_3 \ldots d^3p_N\, d^3r_1\, d^3r_2 \ldots d^3r_N}{\int \rho^{NVT}(\underline{p}, \underline{r})\, d^3p_1\, d^3p_2 \ldots d^3p_N\, d^3r_1\, d^3r_2 \ldots d^3r_N} = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left(-\frac{\underline{p}_1^{\,2}}{2m k_B T}\right) \tag{4.34}$$

Partition function becomes:

$$Q(N,V,T) = \frac{1}{h^{3N} N!} (2\pi m k_B T)^{3N/2} \int \exp\left[-\beta \mathcal{V}(\underline{r}_1, \ldots, \underline{r}_N)\right] d^3r_1 \ldots d^3r_N$$

$$Q(N,V,T) = \frac{1}{N!\, \Lambda^{3N}} \int \exp\left[-\beta \mathcal{V}(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N)\right] d^3r_1 \ldots d^3r_N \tag{4.35}$$

where

$$\Lambda = \Lambda(T) = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} = \text{thermal wavelength} \tag{4.36}$$

$\Lambda \sim$ de Broglie wavelength of a molecule with mass m and energy $k_B T$. A classical treatment is not satisfactory when $\Lambda \sim$ intermolecular separation. In practice, quantum effects in translational motion are important only for He, H_2, Ne.

Can write $$Q(N,V,T) = \frac{1}{N!\;\Lambda^{3N}}\, Z(N,V,T) \qquad (4.37)$$

where $$\underline{Z(N,V,T) = \int \exp\left[-\beta \mathcal{V}(\underline{r}_1,\dots,\underline{r}_N)\right] d^3r_1 \dots d^3r_N} \quad : \text{configurational integral} \qquad (4.38)$$

integration limits: each $\underline{r}_i$ spans the volume V accessible to the system.

All dependence of the partition function on the spatial extent (density) of the system is incorporated in the configurational integral.

e.g., pressure $$P = -\left.\frac{\partial A}{\partial V}\right)_{T,N} = \frac{1}{\beta}\left.\frac{\partial \ln Q}{\partial V}\right)_{T,N} = k_B T \left.\frac{\partial \ln Z}{\partial V}\right)_{T,N} \qquad (4.39).$$

obtainable from configurational part of the partition function only.

4.8. Ideal Monatomic Gas: Canonical Ensemble Treatment

Definition of the Ideal gas: No intermolecular interactions.

$$\mathcal{V}(\underline{r}_1,\dots,\underline{r}_N) = 0 \qquad (4.40).$$

Consequences:

$$Z^{ig}(N,V,T) = \int d^3r_1 \dots d^3r_N = V^N \qquad (4.41)$$

$$Q^{ig}(N,V,T) = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \qquad (4.42)$$

Equation of state: $$P^{ig} = k_B T \left.\frac{\partial \ln(V^N)}{\partial V}\right)_{T,N} = \frac{N k_B T}{V} \qquad (4.43)$$

Helmholtz energy $$A^{ig}(N,V,T) = -\frac{1}{\beta}\ln\left\{\frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N\right\} =$$

Stirling approximation: $\ln N! \simeq N\ln N - N$

$$= N k_B T\left\{-1 + \ln\left(\frac{N\Lambda^3}{V}\right)\right\} = N k_B T\left\{-1 + \ln(\rho\Lambda^3)\right\}$$

molecular density

Chemical potential $$\underline{\mu^{ig}(\rho,T) = \frac{A^{ig} + P^{ig}V}{N} = k_B T \ln(\rho\Lambda^3)} \qquad (4.45)$$

Internal energy $u^{ig} = \left.\frac{\partial(\beta A)}{\partial \beta}\right)_{N,V} = \frac{3}{2} N k_B T$ ($\frac{1}{2} k_B T$ per translational degree of freedom) EQUIPARTITION

Heat capacity $c_v^{ig} = \left.\frac{\partial u^{ig}}{\partial T}\right)_v = \frac{3}{2} R$

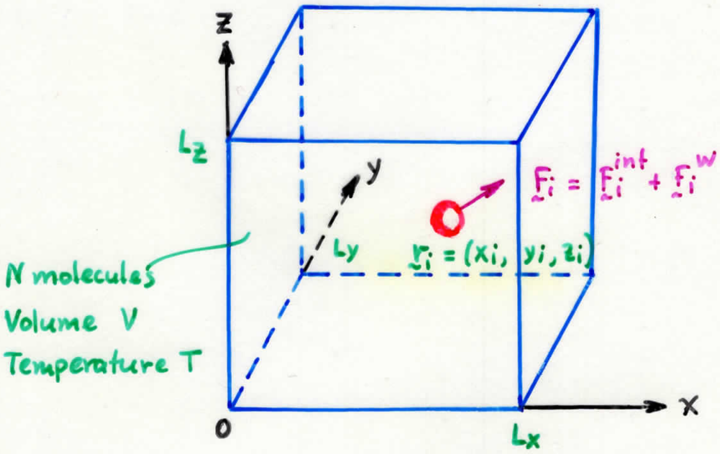
Entropy $s^{ig} = \frac{u^{ig} - a^{ig}}{T} = R\left[\frac{5}{2} - \ln(\rho \Lambda^3)\right]$ (Sackur- Tetrode equation)

Expressions of thermodynamic properties as canonical ensemble averages are particularly convenient for molecular simulation work. Molecular simulations are designed to compute such averages in phase space (MD) or configuration space (MC).

We will briefly derive expressions for pressure and chemical potential in a monatomic substance that have the form of ensemble averages.

4.8. Pressure as an Equilibrium Ensemble Average:

THE VIRIAL THEOREM OF CLAUSIUS



Isotropic fluid:
N molecules
in box of volume $V = L_x L_y L_z$
at temperature T.

(Assume fluid of structureless molecules, subject to central forces)

Newton's second law of motion, applied to molecule i:

$$m_i \frac{d^2 x_i}{dt^2} = \overset{\text{total force on molecule } i \text{ in direction } x}{F_{x_i}} \quad \text{, and similarly for } y \text{ and } z. \qquad (4.50)$$

Multiply by x_i:

$$x_i F_{x_i} = m_i x_i \frac{d^2 x_i}{dt^2} = \frac{d}{dt}\overbrace{\left(m_i x_i \frac{dx_i}{dt}\right)}^{x_i p_{i,x}} - \overbrace{m_i \left(\frac{dx_i}{dt}\right)^2}^{p_{i,x}^2/m_i}$$

Sum over all molecules, and take time average:

$$\left\langle \sum_{i=1}^{N} x_i F_{x_i} \right\rangle_t = \underbrace{\left\langle \sum_{i=1}^{N} \frac{d}{dt}(x_i p_{i,x}) \right\rangle_t} - \left\langle \sum_{i=1}^{N} \frac{p_{i,x}^2}{m_i} \right\rangle_t \qquad (4.51)$$

$$\lim_{\tau\to\infty} \frac{1}{\tau} \int_0^{\tau} \left[\sum_{i=1}^{N} \frac{d}{dt}(x_i p_{i,x})\right] dt = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^{\tau} \frac{d}{dt}\left[\sum_{i=1}^{N}(x_i p_{i,x})\right] dt =$$

$$= \lim_{\tau\to\infty} \underset{\text{going to infinity.}}{\frac{1}{\tau}} \left\{ \left[\sum_{i=1}^{N} \underset{\substack{\text{bounded} \\ \in[0,L_x]}}{x_i}\, \underset{\text{bounded}}{p_{i,x}}\right]_{\tau} - \underbrace{\left[\sum_{i=1}^{N} x_i p_{i,x}\right]_0}_{\text{bounded}} \right\} = 0 \qquad (4.52)$$

Isotropy: $\langle \underset{\sim}{p}_i^2 \rangle = \langle p_{i,x}^2 \rangle + \langle p_{i,y}^2 \rangle + \langle p_{i,z}^2 \rangle = 3 \langle p_{i,x}^2 \rangle$

ergodic theorem + equipartition

$$\text{Also,}\quad \left\langle \sum_{i=1}^{N} \frac{p_{i,x}^2}{m_i} \right\rangle_t = \frac{1}{3} \left\langle \sum_i \frac{\underset{\sim}{p}_i^2}{m_i} \right\rangle_t = \frac{2}{3} \langle \mathcal{K} \rangle_t = \frac{2}{3} \cdot \frac{3N}{2} k_B T = N k_B T \qquad (4.54)$$

kinetic energy

Combining:

$$\left\langle \sum_{i=1}^{N} x_i F_{x_i} \right\rangle_t = - N k_B T \quad , \text{ or } \quad \left\langle \sum_{i=1}^{N} x_i F_{x_i} \right\rangle = - N k_B T \qquad (4.55)$$

time average

ensemble average

(in any ensemble with constant N)

Using y- and z- analogues of (4.55), and combining,

$$\left\langle \frac{1}{3} \sum_{i=1}^{N} \underset{\sim}{r}_i \cdot \underset{\sim}{F}_i \right\rangle = - N k_B T \qquad (4.56)$$

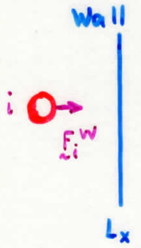
Separate force on molecule i into internal and external contributions:

$$\underset{\sim}{F}_i = \underset{\sim}{F}_i^{\text{int}} + \underset{\sim}{F}_i^{W} \qquad (4.57)$$

total force from other molecules

force from walls

$$\underbrace{\left\langle \sum_{i=1}^{N} x_i F_{x_i}^{W} \right\rangle}_{\text{"wall virial" contribution}} + \underbrace{\left\langle \sum_{i} x_i F_i^{\text{int}} \right\rangle}_{\text{"internal virial" contribution}} = - N k_B T \qquad (4.58)$$



Wall forces are short-ranged (range = $\mathcal{O}$(molecular diameter))
Hence: For all molecule-wall collisions contributing to the term $\left\langle \sum_{i=1}^{N} x_i F_{x_i}^{W} \right\rangle$, the coordinate x_i is practically either 0 or L_x

no contribution.

$$\left\langle \sum_{i=1}^{N} x_i F_{x_i}^{W} \right\rangle = L_x \underbrace{\left\langle \sum_{i=1}^{N} F_{x_i}^{W} \right\rangle_{x = L_x}}_{\text{average total force from wall at } L_x \text{ on molecules}} = L_x \left[- P L_y L_z \right] = - P V \qquad (4.60)$$

Combine (4.58), (4.60):

$$PY = N k_B T + \left\langle \sum_{i=1}^{N} x_i F_i^{int} \right\rangle$$

or, using isotropy,

$$PV = N k_B T + \left\langle \frac{1}{3} \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i^{int} \right\rangle \equiv N k_B T + \langle \underbrace{W^{int}}_{\text{internal virial}} \rangle$$

total force on molecule i from other molecules

$$\mathbf{F}_i^{int} = - \nabla_{\mathbf{r}_i} \mathcal{V}(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

where $\mathcal{V}$ = intermolecular potential energy function

Result is valid for any intermolecular force law, in any ensemble with constant N.

For <u>pairwise additive forces</u>:

$$\mathcal{V}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \mathcal{V}^{pair}(|\mathbf{r}_i - \mathbf{r}_j|) \equiv \sum_{i<j}\sum \mathcal{V}^{pair}(r_{ij}) \Rightarrow$$

$$\Rightarrow \mathbf{F}_i^{int} = \sum_{j=1}^{N} \mathbf{F}_{ij} \longleftarrow \text{force on } i \text{ due to } j \,;\; \mathbf{F}_{ij} = -\mathbf{F}_{ji}$$

the virial theorem assumes the form:

$$PV = N k_B T + \frac{1}{3} \left\langle \sum_{i=1}^{N} \sum_{j=i+1}^{N} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} \right\rangle \tag{4.64}$$

Analogous expressions can be derived for the entire <u>stress tensor</u> at equilibrium.

4.9 Chemical Potential as a Canonical Ensemble Average:

WIDOM'S TEST PARTICLE INSERTION THEOREM

Basic Idea:

Estimate μ as

from partition functions

$$\mu = \left.\frac{\partial A}{\partial N}\right)_{V,T} = \lim_{\substack{N\to\infty\\ V\to\infty\\ N/V=\rho}} \frac{A(N+1,V,T) - A(N,V,T)}{(N+1)-N} = \lim_{\substack{N\to\infty\\ V\to\infty\\ N/V=\rho}} \left\{A(N+1,V,T) - A(N,V,T)\right\} \qquad (4.72)$$

chemical potential per molecule

thermodynamic limit

From canonical ensemble formalism:

$$\left.\begin{aligned} A(N,V,T) &= -\frac{1}{\beta}\ln Q(N,V,T) \\ A(N+1,V,T) &= -\frac{1}{\beta}\ln Q(N+1,V,T) \end{aligned}\right\} \Rightarrow A(N+1,V,T) - A(N,V,T) = -\frac{1}{\beta}\ln\frac{Q(N+1,V,T)}{Q(N,V,T)} =$$

$$= -k_BT\ln\left\{\frac{N!\,\Lambda^{3N}}{(N+1)!\,\Lambda^{3(N+1)}}\;\frac{Z(N+1,V,T)}{Z(N,V,T)}\right\} = k_BT\ln\left[\frac{(N+1)\Lambda^3}{V}\right] - \frac{1}{\beta}\ln\left\{\frac{Z(N+1,V,T)}{V\,Z(N,V,T)}\right. \qquad (4.67)$$

Take thermodynamic limit:

$$\underbrace{\lim_{\substack{N\to\infty\\ V\to\infty\\ N/V=\rho}} \left\{A(N+1,V,T) - A(N,V,T)\right\}}_{\mu(\rho,T)} = \underbrace{\lim_{\substack{N\to\infty\\ V\to\infty\\ N/V=\rho}} k_BT\ln\left[\frac{(N+1)\Lambda^3}{V}\right]}_{k_BT\ln(\rho\Lambda^3)\equiv\mu^{ig}(\rho,T)} - \lim_{\substack{N\to\infty\\ V\to\infty\\ N/V=\rho}} \frac{1}{\beta}\ln\left\{\frac{Z(N+1,V,T)}{V\,Z(N,V,T)}\right.$$

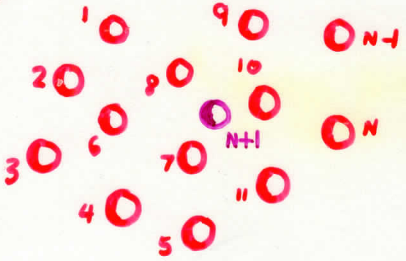
$$\underbrace{\mu(\rho,T) - \mu^{ig}(\rho,T)}_{\text{"Excess chemical potential" @ }\rho,T} = -k_BT \lim_{\substack{N\to\infty\\ V\to\infty\\ N/V=\rho}} \ln\left\{\frac{Z(N+1,V,T)}{V\,Z(N,V,T)}\right\}$$

can one express right hand side as an NVT-ensemble average?

$$\frac{Z(N+1,V,T)}{V\,Z(N,V,T)} = \frac{\int \exp[-\beta \mathcal{V}_{N+1}(\mathbf{r}_1,\cdots,\mathbf{r}_N,\mathbf{r}_{N+1})]\, d^3r_1\, d^3r_2 \cdots d^3r_N\, d^3r_{N+1}}{V \int \exp[-\beta \mathcal{V}_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)]\, d^3r_1\, d^3r_2 \cdots d^3r_N} \qquad (4.68)$$

Now, $\mathcal{V}_{N+1}(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N,\mathbf{r}_{N+1}) = \mathcal{V}_N(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N) + \mathcal{V}_{test}(\mathbf{r}_{N+1};\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)$

total energy of N molecules in configuration $(\mathbf{r}_1,\cdots,\mathbf{r}_N)$, due to their interactions with each other



energy felt by molecule (N+1) due to its interaction with molecules 1, 2, .., N in configuration $(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)$

Thus, taking also into account the fact that $V = \int d^3r_{N+1}$,

$$\frac{Z(N+1,V,T)}{V\,Z(N,V,T)} = \frac{\int d^3r_{N+1} \overbrace{\int d^3r_1\, d^3r_2 \cdots d^3r_N\, \exp[-\beta \mathcal{V}_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)]\, \exp[-\beta \mathcal{V}_{test}(\mathbf{r}_{N+1};\mathbf{r}_1,\cdots,\mathbf{r}_N}^{\text{a function of } \mathbf{r}_{N+1}}}{\int d^3r_{N+1} \int d^3r_1\, d^3r_2 \cdots d^3r_N\, \exp[-\beta \mathcal{V}_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)]}$$

all possible positions of molecule (N+1) considered.

configurational probability density of NVT-ensemble

(4.70)

an ensemble average!

- Take all Boltzmann-weighted configurations of molecules 1, 2, ..., N.
- In each configuration, insert molecule (N+1) at a position $\mathbf{r}_{N+1}$. Inserted molecule "feels" the N molecules, experiencing a total energy of interaction $\mathcal{V}_{test}$, but is not "felt" by them.
- Average over all configurations of "real" molecules 1, 2, ..., N feeling each other, and over all positions of the "test" molecule, the quantity $\exp[-\beta \mathcal{V}_{test}(\mathbf{r}_{N+1};\mathbf{r}_1,\cdots,\mathbf{r}_N)]$

Abbreviated symbolism: $$\frac{Z(N+1,V,T)}{V\,Z(N,V,T)} = \left\langle \exp\left(-\beta\,\mathcal{V}_{test}\right)\right\rangle \qquad (4.71)$$

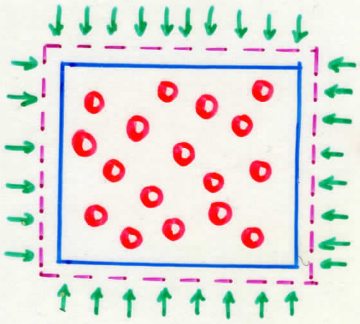
canonical ensemble average for N molecules in volume V at temperature T, and average over all positions of test particle.

Final result (Test particle theorem)

$$\underline{\exp[-(\mu(\rho,T) - \mu^{ig}(\rho,T))= \langle \exp(-\beta\,\mathcal{V}_{test})\rangle}$$

energy felt by particle inserted in system of density ρ at temperature T.

4.10 Isothermal - Isobaric (NPT) Ensemble



N, P, T fixed

Configurational degrees of freedom:

$q_1, q_2, \cdots, q_N, V$ ← volume fluctuates!

Probability density has to be defined in the augmented phase space $\underset{\sim}{q}, \underset{\sim}{p}, V$

Probability density $$\rho^{NPT}(\underset{\sim}{q}, \underset{\sim}{p}; V) = \frac{\exp\{-\beta[\mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p}; V) + PV]\}}{Q_{NPT}(N,P,T)} \qquad (4.75)$$

Q_{NPT} is the isothermal-isobaric partition function:

$$Q_{NPT} = \frac{1}{N!\,h^{3N}} \frac{1}{V_0} \int dV \int d\underset{\sim}{q}\, d\underset{\sim}{p}\, \exp\{-\beta[\mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p}; V) + PV]\} \qquad (4.76)$$

↑ a unit of volume, introduced to make Q_{NPT} dimensionless. (Its exact value is immaterial).

Note: $$Q_{NPT} = \frac{1}{V_0} \int dV \exp(-\beta PV)\, Q(\underset{\sim}{q}, \underset{\sim}{p}; V) \qquad (4.77)$$

isothermal-isobaric partition function

↑ canonical partition function

[Passing from the NVT to the NPT ensemble is the microscopic analogue of doing a Legendre transformation wrt volume]

Connection with Thermodynamics

$$\beta G(N,P,T) = -\ln Q_{NPT}(N,P,T) \qquad (4.78)$$

↑ Gibbs energy.

(A fundamental equation in the Gibbs energy representation)