

Fundamentals of Condensed Matter (lecture 2)



Summary lecture 1

- Equations of state
- Laws of Thermodynamics
- Fundamental equations
 - dU, dH, dA, dG
 - Total differentials
 - Maxwell relations
- Phase diagrams and condensation (Van der Waals)

$$p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots) \quad \rho = \frac{N}{V}$$

$$dU = \bar{d}q + \bar{d}w \quad dS \geq \frac{dq}{T}$$

$$dU = TdS - pdV + \mu dn \quad (n, V, S)$$

$$dH = TdS + Vdp + \mu dn \quad (n, p, S)$$

$$dA = -SdT - pdV + \mu dn \quad (n, V, T)$$

$$dG = -SdT + Vdp + \mu dn \quad (n, p, T)$$

$$p = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

Content of the Liquids part (lectures 1-6)

- Recap thermodynamics and phase diagrams
- **Recap statistical mechanics and classical statistical mechanics** → Today, lecture (2)
- Second virial coefficient and model liquids
- Structure of liquids and compressibility relation
- Ornstein-Zernike relation and link to (scattering) experiments
- Complex and biological fluids

Today's lecture (2)

- Recap of Statistical Mechanics
 - Partition function
 - Ensembles
 - Ideal gas partition functions
 - Harmonic oscillators: solids
- Classical statistical mechanics
 - Phase space
 - Classical partition function
 - Configuration integral

Macroscopic properties of 10^{23} molecules?

Thermodynamics

- Description of macroscopic systems (10^{23} molecules) in equilibrium
- Variables like volume, pressure, temperature,

$$p = \rho k_B T$$

$$\rho = \frac{N}{V}$$

$$p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots)$$

- No interpretation or explanation at the molecular level

Macroscopic properties of 10^{23} molecules?

Quantum/Classical mechanics

- Description on a microscopic, i.e. molecular, level

$$\hat{H}\psi_i = \epsilon_i\psi_i$$

- How to calculate macroscopic properties from molecular properties?

each (pointlike) molecule is described by 3 position and 3 momentum coordinates: $6N$ variables required ... hmmm...

We need a statistical approach to tackle this

Statistical Mechanics

Goal: to calculate thermodynamic properties in terms of molecular properties

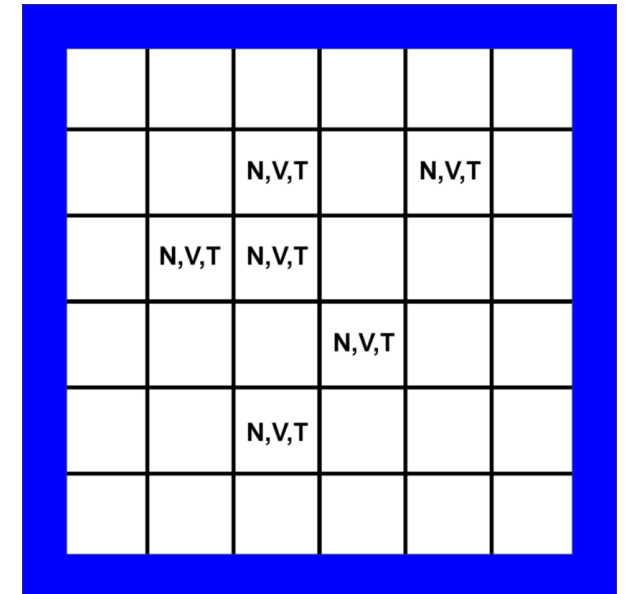
Single molecule ($N = 1$)		Bulk matter ($N \sim 10^{23}$)
Quantum Mechanics	Stat.TD $1 \rightarrow 10^{23}$	Classical Thermodynamics

- Equilibrium statistical mechanics: ***statistical thermodynamics***
 - Non-interacting systems (e.g. perfect gas, Einstein solid, ...)
 - Interacting systems (e.g. imperfect gases, liquids, ...)
- Non-equilibrium statistical mechanics

Ensembles in statistical thermodynamics

Goal: to calculate thermodynamic properties in terms of molecular properties

- Ensemble: collection of all possible microstates* corresponding to a well-defined macroscopic state (defined by quantities like N , V , T , p , E , ...)
- Microcanonical ensemble (N , V , E)
- Canonical ensemble (N , V , T)
- Isobaric-isothermal (Gibbs) ensemble (N , p , T)
- Grand-canonical ensemble (μ , V , T)



* Obeying the principle of equal a-priori probabilities

Ensembles in statistical thermodynamics

Goal: to calculate thermodynamic properties in terms of molecular properties

- Ensemble: collection of all possible microstates* corresponding to a well-defined macroscopic state (defined by quantities like N, V, T, p, E, \dots)
- The time-average of a macroscopic quantity is equal to the instantaneous average over an infinitely large number of systems (the ensemble) (Ergodic hypothesis)
- Calculating averages (expectation values):
$$\langle A \rangle = \sum_i A_i P_i$$

* Obeying the principle of equal a-priori probabilities

The Boltzmann distribution and canonical partition function

Boltzmann distribution

$$P_i = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} = \frac{e^{-\beta E_i}}{Q}$$

Canonical partition function

$$Q = \sum_i e^{-E_i/k_B T} \quad \left(\beta = \frac{1}{k_B T} \right)$$

- P_i : probability of the system being in microstate i with associated energy E_i
- Q : *central quantity in statistical thermodynamics*
 - Measure of distribution across all available energy levels (at given T)
 - Contains all thermodynamic information about a system

The canonical partition function Q and thermodynamics

- Average energy $U = \langle E \rangle = \sum_i E_i P_i = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$
- Helmholtz free energy $A = -k_B T \ln Q$
- Entropy $S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$
- Pressure $p = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T}$

... just need know the canonical partition function Q ...

Note: different relations exist for different ensembles

The molecular partition function q

Factorising Q for independent (i.e. non-interacting) particles

$$E_i = \epsilon_{1,j} + \epsilon_{2,k} + \dots + \epsilon_{N,z}$$

$$Q = q_1 q_2 \cdots q_N$$

molecular partition function:

$$q = \sum_i e^{-\beta \epsilon_i}$$

N independent &
distinguishable particles

$$Q = q^N$$

N independent &
indistinguishable particles

$$Q = \frac{q^N}{N!}$$

The molecular partition function q

$$q = \sum_i e^{-\beta \epsilon_i}$$

$$\epsilon_i = \epsilon_{tr,i} + \epsilon_{rot,i} + \epsilon_{vib,i} + \epsilon_{elec,i}$$

↓

→

$$q = q_{tr} \cdot q_{rot} \cdot q_{vib} \cdot q_{elec}$$

For example:

translational (1D)

$$\epsilon_{tr,x} = \frac{n^2 h^2}{8mL^2}$$



$$q_{tr,x} = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} L$$

vibrational (1D)

$$\epsilon_{vib} = \left(v + \frac{1}{2} \right) h\nu$$



(problem set)

$$q_{vib} = \frac{e^{-\frac{1}{2}h\nu/k_B T}}{1 - e^{-h\nu/k_B T}}$$

Example 1: internal energy and pressure of perfect gas

Molecular partition function for a particle of mass m in 3D:

$$q_{tr} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

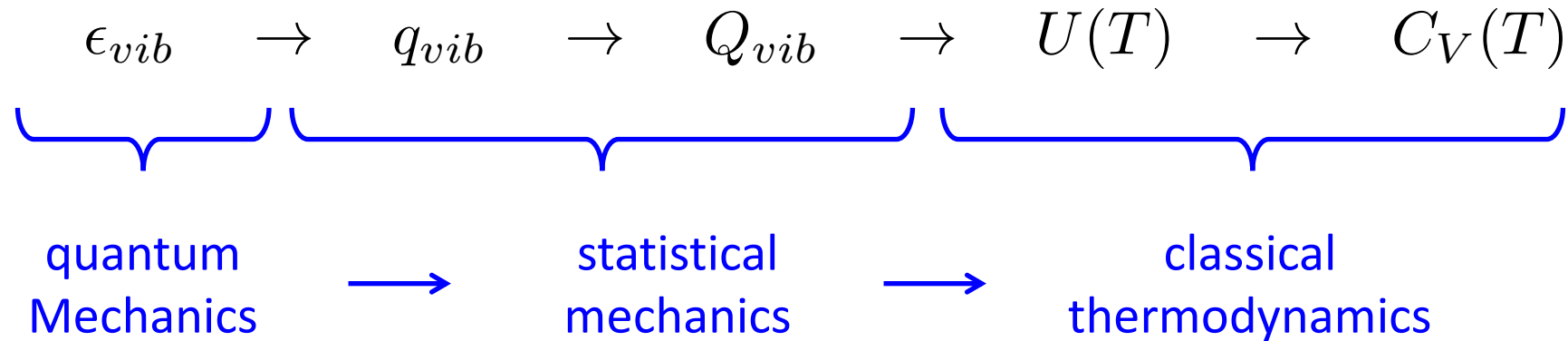
N independent & indistinguishable particles: $Q = \frac{q^N}{N!}$

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

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

Example 2: Einstein crystal (see problem set)

N harmonic oscillators on a lattice all independently vibrating with the Einstein frequency



Canonical Ensemble: interacting systems

$$Q \neq q^N$$

The trouble is finding the canonical partition function for interacting systems*

* Like liquids, which is of course the point of these lectures

Example of canonical partition function for an interacting system

$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} (V - Nb)^N \exp \left[\frac{aN^2}{V k_B T} \right]$$

Van der Waals gas

$$p = \frac{Nk_B T}{V - Nb} - a \left(\frac{N}{V} \right)^2$$

Later on: expressions for a and b (see also problem set)

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- **Classical statistical mechanics**
 - Phase space
 - Classical partition function
 - Configuration integral

Classical Statistical Mechanics

So far: classical stat mech = limiting case of QM

Example: partition function for a particle of mass m (1st hour)

$$q = \sum_n \exp\left(-\frac{\beta n^2 h^2}{8mL^2}\right) \approx \int \exp\left(-\frac{\beta n^2 h^2}{8mL^2}\right) dn$$

High temperature limit:
energy levels close of $k_B T$

Seek approach that uses classical mechanics throughout

Phase space

- Classical mechanical state is completely defined by specifying the positions (τ) and momenta (p) of all the particles simultaneously

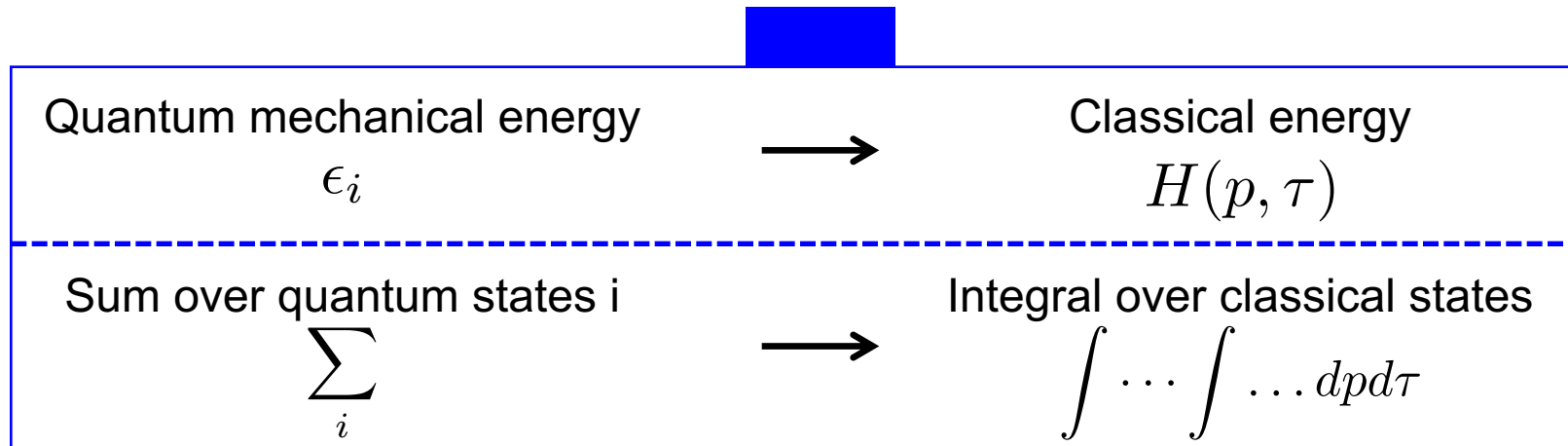
- In 3D this means that 6 coordinates must be specified for each particle

$$(p_x, p_y, p_z, x, y, z) = (p, \tau)$$

- The $6N$ dimensional space spanned by the coordinates required for a system of N particles is called phase space

Classical molecular partition function

$$q = \sum_i e^{-\beta \epsilon_i}$$



natural assumption

$$q_{class} \sim \int \dots \int e^{-\beta H(p, \tau)} dp d\tau$$

q_{class} for monatomic perfect gas

$$q_{class} \sim \int \dots \int e^{-\beta H(p, \tau)} dp d\tau$$

$$H(p, \tau) = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

$$q_{class} \sim (2\pi m k_B T)^{3/2} V$$

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

Where's Planck's constant?!?

factor $1/h^3$ missing

q_{class} for monatomic perfect gas

partition functions are dimensionless

$$(2\pi mk_B T)^{3/2} V \quad \rightarrow \quad \left(\frac{kg \cdot m^2}{s} \right)^3$$

$$h = 6.626 \times 10^{-34} \text{ Js} \quad \rightarrow \quad \frac{kg \cdot m^2}{s}$$

$$q = \sum_i e^{-\beta \epsilon_i} \quad \rightarrow \quad q_{class} = \frac{1}{h^3} \int \cdots \int e^{-\beta H(p, \tau)} dp d\tau$$

Classical canonical partition function for monatomic perfect gas

$$Q_{class} = \frac{q_{class}^N}{N!}$$

$$Q_{class} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta H_N(p, \tau)} dp d\tau$$

$H_N(p, \tau)$: Hamiltonian of the N -body system

Q_{class} for interacting particles

Conjecture:

$$Q_{\text{class}} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta H_N(p, \tau)} dp d\tau$$

$H_N(p, \tau)$: Classical N-body Hamiltonian for interacting particles

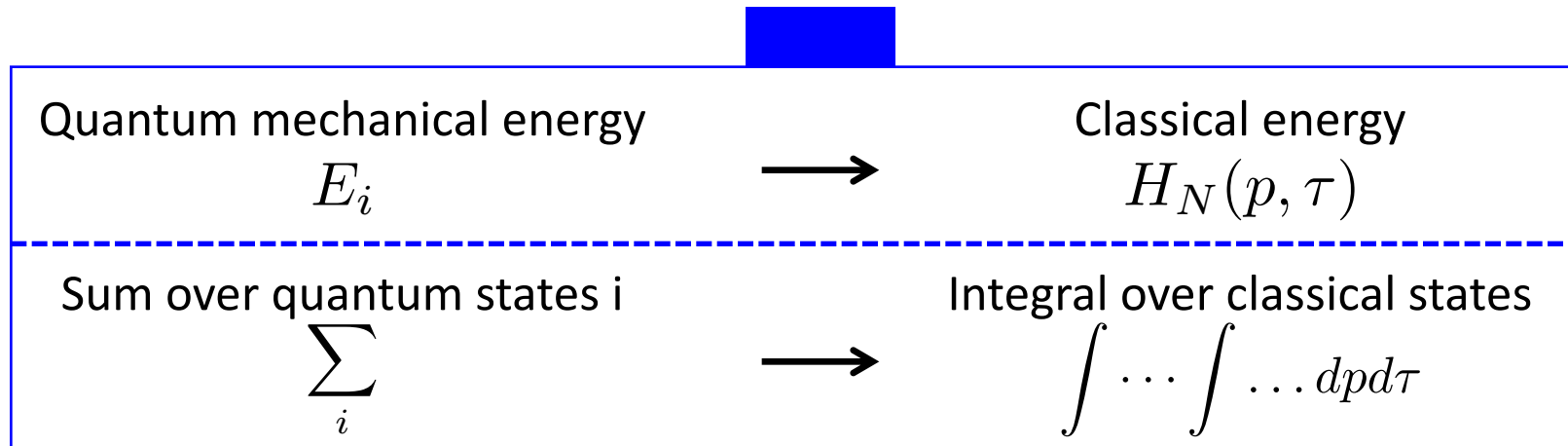
$H_N(p, t)$ for monatomic *interacting* gas

$$H_N(p, \tau) = \frac{1}{2m} \sum_{i=1}^N (p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2) + U(x_1, y_1, z_1, \dots, x_N, y_N, z_N)$$

Interactions!!

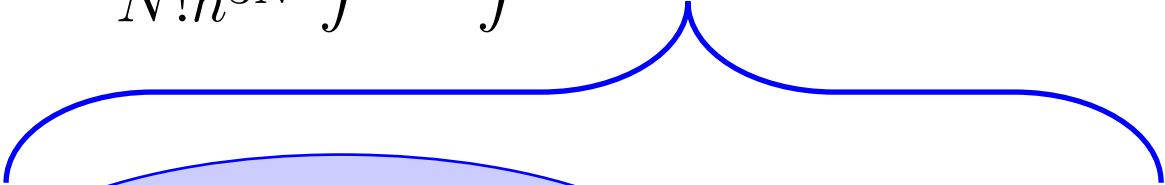
Classical Canonical partition function

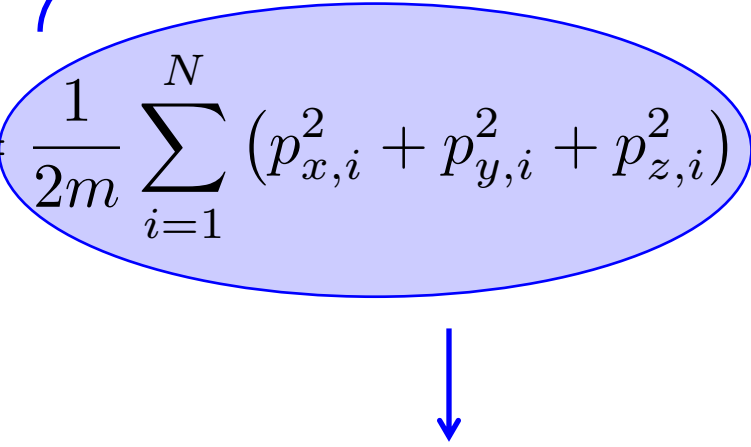
$$Q = \sum_i e^{-\beta E_i}$$



$$Q_{class} = \frac{1}{N!h^{3N}} \int \dots \int e^{-\beta H_N(p, \tau)} dpd\tau$$

Integrating out the momenta ...

$$Q_{class} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta H_N(p,\tau)} dp d\tau$$


$$H_N(p, \tau) = \frac{1}{2m} \sum_{i=1}^N (p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2) + U(x_1, \dots, z_N)$$


$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \int \cdots \int e^{-\beta U(x_1, \dots, z_N)} dx_1 \cdots dz_N$$

Q_{class} for monatomic *interacting* gas

Interactions!!

$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \int \cdots \int e^{-\beta U(x_1, \dots, z_N)} dx_1 \cdots dz_N$$



Classical Configuration Integral Z_N

- depends on relative distances between molecules
- in general, extremely difficult
- central equation in statistical thermodynamics

Classical Configuration Integral Z_N

$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} Z_N$$

$$Z_N = \int \cdots \int e^{-\beta U(x_1, \dots, z_N)} d\tau_1 \cdots d\tau_N$$

**Fundamental equations in the study of monatomic,
classical imperfect gases and liquids**

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Next lecture (3)