

# Nanoscale simulation lectures 2008

## Statistical Mechanics

- **Lectures:** Thursdays 4 to 6 PM
- **Course contents:**
  - Thermodynamics and statistical mechanics
  - Structure and scattering
  - Mean-field approaches
  - Inhomogeneous systems
  - Monte Carlo methods
  - Non-equilibrium statistical mechanics
- **Assignments:** one per chapter. To be discussed with local tutor.

# Thermodynamics and Statistical Mechanics

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# Outline

- 1 Thermodynamics
  - The laws of thermodynamics
  - Thermodynamic potentials and equations of state
  - Response functions and thermodynamic stability
- 2 Statistical Mechanics
  - Time evolution
  - Ensemble theory and postulates
- 3 The most common ensembles
  - The microcanonical ensemble
  - The canonical ensemble
  - The grand canonical ensemble

# Thermodynamics

- **Thermodynamics:** Phenomenological universal theory that describes equilibrium states of macroscopic systems
- **Thermodynamic variables:** Macroscopic quantities describing the state of a system (energy  $E$ , volume  $V$ , temperature  $T$ , chemical potential,  $\mu$ , etc.)
  - Gibbs phase rule:  $F = K + 2 - P$ . For bulk homogeneous substance  $F = K + 1$
  - Extensive (additive) and intensive variables
- **Thermodynamic system:** Arbitrary amount of matter whose properties are uniquely and completely described by specifying certain macroscopic parameters
  - Isolated ( $N, V, E$ ), closed ( $N, V, T$ ) and open systems ( $\mu, V, T$ )
- **Equations of state:** empirically determined equations relating state variables. Example:  $PV = nRT$

# Work and heat

The thermodynamic state of a system can change by exchange of **mechanical work** ( $\delta W$ ), **heat** ( $\delta Q$ ) and **matter** with the surroundings:

- $\delta W = -PdV$  with  $P$  = hydrostatic pressure and  $V$  = volume
- $\delta W = \gamma dA$  with  $\gamma$  = surface tension and  $A$  = area
- $\delta W = \mathbf{H} \cdot d\mathbf{M}$  with  $\mathbf{H}$  = magnetic field and  $\mathbf{M}$  = magnetisation
- $\delta Q = dS/T$  for any reversible process.  $S$  = entropy and  $T$  = absolute temperature
- $\delta W' = \mu dN$  with  $\mu$  = chemical potential and  $N$  = number of moles

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# The laws of thermodynamics

## First law

In any transformation of a system, the variation of its internal energy  $U$  is the sum of heat and work exchange with the external world

$$dU = \delta Q + \delta W \quad (1)$$

**Note:** for hydrostatic systems,  $dU = \delta Q - PdV$

## Second law

For an infinitesimal transformation involving heat exchange  $\delta Q$  with a reservoir at temperature  $T$ , the entropy variation ( $dS$ ) of the system obeys:

$$dS \geq \delta Q/T \quad (2)$$

where the equality is valid only for a reversible transformation.

**Note:** the entropy of a thermally insulated system can only increase or be stationary,  $dS^{ins} \geq 0$

# Fundamental relation

Using the first and second laws we obtain:

$$dU = TdS - PdV + \mu dN \quad (\text{reversible transformation}) \quad (3)$$

- For an isolated system,  $U = U(S, V, N)$  is the **fundamental thermodynamic relation**
- $U(S, V, N)$  attains its global minimum at thermodynamic equilibrium
- Since  $dU$  is an exact differential, equation 3 leads to:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad -P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

- The equality of second derivatives (Maxwell relations ) gives:

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = - \left(\frac{\partial P}{\partial S}\right)_{V,N} \quad \text{etc.}$$

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# Thermodynamic potentials

Legendre transformations (change of independent state variables) of  $U(S, V, N)$  generate different **thermodynamic potentials**. For example:

- Scalar functions of the natural state variables that contain all the thermodynamic information for a given system
- Thermodynamic potentials satisfy extremum conditions at equilibrium
- Allow systematic derivation of all thermodynamic relations
- Note the difference between thermodynamic potentials and equations of state

# Thermodynamic potentials

Legendre transformations of  $U(S, V, N)$  generate different **thermodynamic potentials**

Transforming ,  $V \rightarrow P$

$$H(S, P, N) = U(S, V, N) - V \left( \frac{\partial U}{\partial V} \right)_{S, N} = U + PV \quad (\text{Enthalpy})$$

Similarly,

$$F(N, V, T) = U(S, V, N) - S \left( \frac{\partial U}{\partial S} \right)_{V, N} = U - ST \quad (\text{Helmholtz F.E.})$$

**Note:**  $F$  is minimum at equilibrium for  $(N, V, T)$  systems

Further transformation,  $N \rightarrow \mu$ , gives

$$\Omega(\mu, V, T) = F(N, V, T) - N \left( \frac{\partial F}{\partial N} \right)_{V, T} = F - N\mu = -PV \quad (\text{Grand Potential})$$

**Note:**  $\Omega$  is minimum at equilibrium for  $(\mu, V, T)$  systems

# Equations of state

- Relation between **generalised forces** and **conjugate extensive parameters** or their densities
- Obtained as derivatives of thermodynamic potentials. Example:

$$dF = -SdT - PdV + \mu dN \quad (4)$$

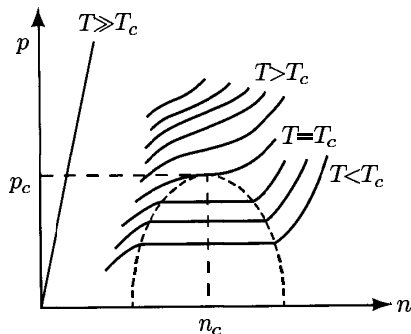
The corresponding equations of state are:

$$S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \quad -P = \left(\frac{\partial F}{\partial V}\right)_{T,N} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

- **Experimentally accessible**
- Thermodynamic potentials are constructed by measuring and combining mechanical, thermal and chemical equations of state

# Model phase diagram

- Phase diagram of a typical fluid. Pressure as a function of density at different temperatures
- For each value of  $\rho$  there is a unique value of  $P$  at each  $T$
- At low  $T$  there are two possible values of  $P$  at fixed  $T$ . Coexistence of liquid and gas at the same  $\mu$ ,  $T$  and  $P$
- At  $T_c$  the density of the two phases is the same



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# Thermodynamic stability

**Thermodynamic stability** : Response to small perturbations.  
Regression of spontaneous fluctuations.

- A **stable system** returns to equilibrium after the occurrence of a small fluctuation
- **Unstable systems** change macroscopically in response to the slightest perturbation or fluctuation

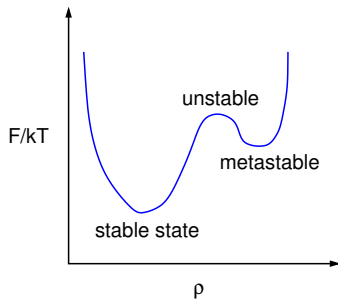


Figure: Free energy showing stable and metastable states

# Criteria of stability

If  $\Phi$  stands for the internal energy or a thermodynamic potential which is a function of the extensive variables  $X_1, X_2, \dots, X_r$  and the intensive variables  $l_{r+1}, \dots, l_n$ . Then

$$d\Phi = \sum_{i=1}^r l_i dX_i - \sum_{j=r+1}^n X_j dl_j \quad (5)$$

Stability criteria are:

$$0 \leq \left( \frac{\partial l_j}{\partial X_i} \right)_{\{A\}} = \left( \frac{\partial^2 \Phi}{\partial X_i^2} \right)_{\{A\}} \quad (6)$$

where  $\{A\} = \{X_1, \dots, X_{i-1}, X_{i+1}, \dots, X_r, l_{r+1}, \dots, l_n\}$

**Note:** Thermodynamic potentials are convex functions of the extensive parameters

# Physical consequences of stability

Local stability criteria impose limitations on the signs of (some) second derivatives of the internal or free energy (thermodynamic response functions). For example:

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{N,T} = -\left(\frac{\partial P}{\partial V}\right)_{N,T} = \frac{1}{V\kappa_T} \geq 0 \text{ or } \kappa_T \geq 0 \quad (7)$$

where  $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$  is the **isothermal compressibility**

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} = \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{C_V} \geq 0 \text{ or } C_V \geq 0 \quad (8)$$

where  $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$  is the **heat capacity** at constant volume

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# Classical many-particle systems

**Consider:** system composed of  $N$  classical particles interacting via pairwise potentials and in the presence of an external field.

$$\text{Hamiltonian} \rightarrow \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N) + \phi_N(\mathbf{r}^N) \quad (9)$$

$$K_N(\mathbf{p}^N) = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} \quad \text{Kinetic Energy} \quad (10)$$

$$V_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j \neq i} u^2(|\mathbf{r}_{ij}|) \quad \text{Potential Energy} \quad (11)$$

$$\phi(\mathbf{r}^N) \rightarrow \text{Spatially varying external field} \quad (12)$$

The dynamical state of the system is specified by the  $6N$ -dimensional **Phase vector:**  $\Gamma(t) = (\mathbf{r}_1(t), \dots, \mathbf{p}_N(t))$

# Some inter-atomic potentials

$$u(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{Coulomb potential} \quad (13)$$

$$u(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \quad \text{Lennard Jones potential} \quad (14)$$

$$u(1, 2) = -\mu_2 \cdot \mathbf{E}_1 = |r_{1,2}^{-3}| [\mu_1 \cdot \mu_2 - 3(\mu_2 \cdot \hat{\mathbf{r}}_{1,2})(\mu_1 \cdot \hat{\mathbf{r}}_{1,2})] \quad (15)$$

**Dipole-dipole potential**

# Time evolution of classical many-particle systems

Time evolution of  $\Gamma(t)$  determined by Hamilton's equations:

$$\dot{\mathbf{r}}_i = \left( \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \right) \quad \dot{\mathbf{p}}_i = - \left( \frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \right) \quad (16)$$

- 6N coupled non-linear differential equations
- Solved with initial conditions  $(\mathbf{r}^N(0), \mathbf{p}^N(0))$
- Unique solution
- In the absence of external forces  $\mathcal{H}$  is a conserved quantity

Consider all the trajectories with initial conditions on a given energy surface. The probability of observing the phase vector in the volume element  $d\mathbf{r}^N(t)d\mathbf{p}^N(t)$  a time  $t$  is give by:

## Phase-space probability density

$$f^{[N]}(\mathbf{r}^N, \mathbf{p}^N; t) \quad \text{with} \quad \int \int f^{[N]}(\mathbf{r}^N, \mathbf{p}^N; t) d\mathbf{r}^N d\mathbf{p}^N = 1 \quad (17)$$

# The Liouville equation

The time evolution of  $f^{[M]}(\mathbf{r}^N, \mathbf{p}^N; t)$  is governed by the Liouville equation:

$$\frac{df^{[M]}}{dt} = \frac{\partial f^{[M]}}{\partial t} + \sum_{i=1}^N \left( \frac{\partial f^{[M]}}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \frac{\partial f^{[M]}}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right) = 0 \quad (18)$$

which can be written as:

$$\frac{\partial f^{[M]}}{\partial t} = \{ \mathcal{H}, f^{[M]} \} \quad \rightarrow \text{Poisson bracket} \quad (19)$$

$$\{A, B\} \equiv \sum_{i=1}^N \left( \frac{\partial A}{\partial \mathbf{r}_i} \frac{\partial B}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \frac{\partial B}{\partial \mathbf{r}_i} \right) \quad (20)$$

Introducing the Liouville operator:

$$\mathcal{L} \equiv i \{ \mathcal{H}, \} \quad (21)$$

# The Liouville equation

## Liouville equation

$$\frac{\partial \mathbf{f}^{[N]}}{\partial \mathbf{t}} = -i\mathcal{L}\mathbf{f}^{[N]} \quad \text{with solution} \quad \mathbf{f}^{[N]}(\mathbf{t}) = \exp(-i\mathcal{L}\mathbf{t})\mathbf{f}^{[N]}(\mathbf{0}) \quad (22)$$

The **propagator**  $\exp(-i\mathcal{L}t)$  is a unitary operator  $\rightarrow$  volume of the phase space differential element is constant.

The time dependence of any function of phase-space variables,  $B(\mathbf{r}^N, \mathbf{p}^N)$ , can be represented in terms of the Hamiltonian as:

$$\frac{dB}{dt} = \sum_{i=1}^N \left( \frac{\partial B}{\partial \mathbf{r}_i} \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} - \frac{\partial B}{\partial \mathbf{p}_i} \frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \right) = i\mathcal{L}B \quad (23)$$

with solution:

$$B(t) = \exp(i\mathcal{L}t)B(0) \quad (24)$$

# Reduced distribution functions

The behavior of any subset on  $n$  particles is described by **reduced phase-space distribution functions**:

$$f^{(n)}(\mathbf{r}^n, \mathbf{p}^n; t) = \frac{N!}{(N-n)!} \int \int f^{[N]}(\mathbf{r}^N, \mathbf{p}^N; t) d\mathbf{r}^{(N-n)} d\mathbf{p}^{(N-n)} \quad (25)$$

Need equation of motion for  $f^{(n)}$ . Consider case when total force on particle  $i$  is the sum of external  $\mathbf{X}_i$  and internal  $\mathbf{F}_{ij}$  forces. Second Hamilton's equation is:

$$\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -\mathbf{X}_i - \sum_{j=1}^N \mathbf{F}_{ij} \quad (26)$$

and Liouville equation becomes:

$$\left( \frac{\partial}{\partial t} + \sum_{i=1}^N \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i=1}^N \mathbf{X}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) f^{[N]} = - \sum_i^N \sum_j^N \mathbf{F}_{i,j} \cdot \frac{\partial f^{[N]}}{\partial \mathbf{p}_i} \quad (27)$$

# Reduced distribution functions

- Multiplying by  $N!/(N - n)!$
- Integrating over  $3(N - n)$  coordinates and  $3(N - n)$  momenta
- Considering that the integrand vanishes at the limits of integration
- Considering that  $f^{[N]}$  is symmetric under exchange of particle labels

The previous equation leads to **BBGKY hierarchy**:

$$\left( \frac{\partial}{\partial t} + \sum_{i=1}^n \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i=1}^n \left( \mathbf{x}_i + \sum_{j=1}^n \mathbf{F}_{ij} \right) \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) f^{[n]} = \quad (28)$$

$$- \sum_{i=1}^n \int \int \mathbf{F}_{i,n+1} \cdot \frac{\partial f^{[n+1]}}{\partial \mathbf{p}_i} d\mathbf{r}_{(n+1)} d\mathbf{p}_{(n+1)} \quad (29)$$

# BBGKY hierarchy

- In the BBGKY system the unknown function  $f^{(n)}$  is expressed in terms of another unknown function,  $f^{(n+1)}$ .
- **Closure relation:** Approximation in which  $f^{(n+1)}$  is expressed in terms of  $f^{(n)}$ ,  $f^{(n-1)}$ , etc.

For example, the equation for  $n = 1$  is:

$$\left( \frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{X}_1 \cdot \frac{\partial}{\partial \mathbf{p}_1} \right) f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) = \quad (30)$$

$$- \int \int \mathbf{F}_{1,2} \cdot \frac{\partial}{\partial \mathbf{p}_1} f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) d\mathbf{r}_2 d\mathbf{p}_2 \quad (31)$$

The closure relation:

$$f^{(2)}(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t) \approx f^{(1)}(\mathbf{r}, \mathbf{p}, t) f^{(1)}(\mathbf{r}', \mathbf{p}', t) \quad (32)$$

is equivalent to ignoring all pair correlations.

# A simple kinetic equation

The resulting equation is the Vlasov equation (used in plasma physics)

$$\left( \frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial}{\partial \mathbf{r}} + [\mathbf{X}(\mathbf{r}, t) + \mathbf{F}(\mathbf{r}, t)] \cdot \frac{\partial}{\partial \mathbf{p}} \right) f^{(1)}(\mathbf{r}, \mathbf{p}, t) = 0 \quad (33)$$

where

$$\mathbf{F}(\mathbf{r}, t) = \int \int \mathbf{F}(\mathbf{r}, \mathbf{r}', t) f^{(1)}(\mathbf{r}', \mathbf{p}'; t) d\mathbf{r}' d\mathbf{p}' \quad (34)$$

is the average force exerted by particles situated at  $\mathbf{r}'$ , on a particle that at time  $t$  is at point  $\mathbf{r}'$ .

# Stationary distributions

At thermodynamic equilibrium  $f^{[M]}(\mathbf{r}^N, \mathbf{p}^N; t)$  does not explicitly depend on time ( $f^{[M]}(\mathbf{r}^N, \mathbf{p}^N; t) \rightarrow f_0^{[M]}(\mathbf{r}^N, \mathbf{p}^N)$ ) and :

$$\left( \frac{\partial f_0^{[M]}}{\partial t} \right) = 0 \quad (35)$$

which implies:

$$\sum_{i=1}^N \left( \frac{\partial f_0^{[M]}}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \frac{\partial f_0^{[M]}}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right) = 0 \quad (36)$$

This equality is satisfied if:

## Stationary distributions:

$$f_0^{[M]} = \text{constant} \quad \text{or} \quad f_0^{[M]} = f_0^{[M]}[\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)] \quad (37)$$

# Stationary distributions

One can define stationary reduced distributions. An important example is the Maxwell distribution of momenta:

$$f_0^{(1)}(\mathbf{p}) = \frac{\rho \exp(-\beta|\mathbf{p}|^2/2m)}{(2\pi mk_B T)^{3/2}} \equiv \rho f_M(\mathbf{p}) \quad (38)$$

normalised such that:

$$\int \rho f_M(\mathbf{p}) d\mathbf{p} = 1 \quad (39)$$

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## Time averages and ensemble averages

- **Mechanical properties** of classical systems can be obtained as averages of functions of coordinates  $\{\mathbf{r}^N\}$  and momenta  $\{\mathbf{p}^N\}$ .  
 Examples: E, P, etc.
- At equilibrium averages are independent of time
- The instantaneous value of  $B(\mathbf{r}^N, \mathbf{p}^N)$  fluctuates as  $\{\mathbf{r}^N(t), \mathbf{p}^N(t)\}$  evolves according to Hamilton's equations
- The observable  $\langle B \rangle_{obs}$  is a time average over the dynamical history of the system

$$\langle B \rangle_t = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau B[\mathbf{r}^N(t), \mathbf{p}^N(t)] dt \quad (40)$$

# Temperature as time average

**For example:**

The thermodynamic temperature is related to the time average of the total kinetic energy  $K_N(t)$

$$\mathcal{T}(t) = \frac{2}{3Nk_B} K_N(t) = \frac{1}{3Nk_B m} \sum_{i=1}^N |\mathbf{p}_i(t)|^2 \quad (41)$$

$$T \equiv \langle \mathcal{T} \rangle_t = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \mathcal{T}(t) dt \quad (42)$$

# Equation of state and *virial function*

The *virial function* is defined as:

$$\mathcal{V}(\mathbf{r}^N) = \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^N (\mathbf{r}_i \cdot \mathbf{F}_i^{int} + \mathbf{r}_i \cdot \mathbf{F}_i^{ext}) \quad (43)$$

Using previous formulae and integrating by parts:

$$\langle \mathcal{V}^{Tot} \rangle_t = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N \mathbf{r}_i(t) \cdot \mathbf{F}_i(t) dt \quad (44)$$

$$= \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N \mathbf{r}_i(t) \cdot m \ddot{\mathbf{r}}_i(t) dt \quad (45)$$

$$= - \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N m |\dot{\mathbf{r}}_i(t)|^2 dt \quad (46)$$

$$= -3Nk_B T \quad (47)$$

# Virial equation of state

$\mathcal{V}^{ext}$  arises from external forces and is related to the pressure:

$$\langle \mathcal{V}^{ext} \rangle = -P \int \mathbf{r} \cdot \mathbf{n} dS = -P \int \nabla \cdot \mathbf{r} dV = -3PV \quad (48)$$

Combining  $\mathcal{V}^{Tot}$ ,  $\mathcal{V}^{ext}$  and  $\mathcal{V}^{int}$  we obtain:

$$PV = Nk_B T + \frac{1}{3} \langle \mathcal{V}^{int} \rangle = Nk_B T - \frac{1}{3} \left\langle \sum_{i=1}^N m \mathbf{r}_i(t) \cdot \nabla V_N[\mathbf{r}^N(t)] \right\rangle \quad (49)$$

## Virial equation of state

$$\frac{\beta P}{\rho} = 1 - \frac{\beta}{3N} \left\langle \sum_{i=1}^N \mathbf{r}_i(t) \cdot \nabla V_N[\mathbf{r}^N(t)] \right\rangle_t \quad (50)$$

# Statistical ensembles

## Statistical ensemble

Large collection of "imaginary systems" each one is a replica of the system of interest and is characterised by the same macroscopic parameters

The equilibrium ensemble average of  $B(\mathbf{r}^N, \mathbf{p}^N)$  is given by

## Ensemble average

$$\langle B \rangle_e = \int \int B(\mathbf{r}^N, \mathbf{p}^N) f_0^{[M]}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \quad (51)$$

For example the thermodynamic internal energy is the ensemble average of the Hamiltonian

$$U \equiv \langle \mathcal{H} \rangle_e = \int \int \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) f_0^{[M]}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \quad (52)$$

The form of  $f_0^{[M]}$  depends on the macroscopic parameters defining the ensemble

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# The microcanonical ensemble

- Macroscopic parameters:  $(N, V, E)$ . **Isolated system**

## First postulate

All the microstates compatible with  $(N, V, E)$  are equally likely (equal a priori probabilities)

- Equilibrium probability density:

$$f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) = C \delta(\mathcal{H} - E) \quad \text{uniform distribution} \quad (53)$$

- **Partition function** (normalisation constant):

$$C = \frac{1}{\Omega(N, V, E)} \quad (54)$$

# The microcanonical ensemble

## Second postulate

Time averages and ensemble averages are identical if the system is *ergodic*, i.e. the phase trajectory passes equal number of times through every phase-space volume element.

$$\langle B \rangle_e = \langle B \rangle_t \quad \text{Ergodic dynamics} \quad (55)$$

- Connection with thermodynamics: **Entropy**

$$S = k_B \ln(\Omega(N, V, E)) \quad (56)$$

and the equations of states are obtained from:

$$\left( \frac{\partial S}{\partial E} \right)_{N, V} = \frac{1}{T} \quad \text{and} \quad \left( \frac{\partial S}{\partial V} \right)_U = \frac{P}{T} \quad (57)$$

- In general the entropy associated to  $f_0^{[M]}$ :

$$S = -k_B \int f_0^{[M]}(\mathbf{r}^N, \mathbf{p}^N) \ln f_0^{[M]}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \quad (58)$$

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# The canonical ensemble

- Independent thermodynamic variables:  $(N, V, T)$ . System in contact with heat bath at temperature  $T$
- Equilibrium probability density:

$$f_0^{[M]}(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{h^{3N} N!} \frac{\exp(-\beta\mathcal{H})}{Q_{N,V,T}} \quad (59)$$

$$\text{with} \quad (60)$$

$$Q_{N,V,T} = \frac{1}{h^{3N} N!} \int \int \exp(-\beta\mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N \quad (61)$$

- Thermodynamic potential:  $F = U - TS$ . Helmholtz free energy
  - From thermodynamics we know  $dF = -SdT - PdV + \mu dN$
  - Equations of state

$$S = - \left( \frac{\partial F}{\partial T} \right)_{N,V} \quad P = - \left( \frac{\partial F}{\partial V} \right)_{N,T} \quad (62)$$

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} \quad U = \left( \frac{\partial(F/T)}{\partial(1/T)} \right)_{V,N} \quad (63)$$

# The canonical ensemble

- Thermodynamic relations can be expressed in terms of  $Q_{N,V,T}$

$$U = \frac{1}{h^{3N} N! Q_{N,V,T}} \int \int \mathcal{H} \exp(-\beta \mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N = - \left( \frac{\partial \ln(Q_N)}{\partial \beta} \right)_V \quad (64)$$

and, similarly

$$P = -k_B T \left( \frac{\partial \ln(Q_N)}{\partial V} \right)_{T,N} \quad (65)$$

- $Q_{N,V,T}$  factorises into ideal and excess parts:

$$\text{If } \mathcal{H} = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N) + \Phi_N(\mathbf{r}^N) \rightarrow Q_{N,V,T} = Q_N^{id} Z_N / V^N \quad (66)$$

$$\text{with } Q_N^{id} = \frac{1}{N!} V^N / \Delta^{3N} \quad \text{with } \Delta = \left( \frac{2\pi\beta\hbar^2}{m} \right)^{1/2}$$

$$\text{and } Z_N = \int \exp(-\beta V_N) d\mathbf{r}^N \quad \text{Configurational integral}$$

# Canonical ensemble

- The previous relations imply:

$$F = F^{id} + F^{ex}$$

with  $F^{id}/N = k_B T [\ln(\Delta^3 \rho) - 1]$  Ideal gas free energy

and  $F^{ex} = -k_B T \ln(Z_N/V^N)$  Interactions and ext. potential

- Same factorisation applies to functions obtained by differentiation of  $F$  w.r.t  $V$  and  $T$ . For example:

$$U = U^{id} + U^{ex} = 3NK_B T/2 + \frac{1}{Z_N} \int V_N \exp(-\beta V_N) d\mathbf{r}^N$$

- Energy fluctuations:

$$\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = - \left( \frac{\partial U}{\partial \beta} \right)_{N,V} = kT^2 C_V \quad (67)$$

and

$$\sqrt{\langle (\Delta E)^2 \rangle} / \langle E \rangle = \sqrt{kT^2 C_V} / U = \mathcal{O}(N^{-1/2}) \quad (68)$$

# Outline

- 1 Thermodynamics
  - The laws of thermodynamics
  - Thermodynamic potentials and equations of state
  - Response functions and thermodynamic stability
- 2 Statistical Mechanics
  - Time evolution
  - Ensemble theory and postulates
- 3 **The most common ensembles**
  - The microcanonical ensemble
  - The canonical ensemble
  - **The grand canonical ensemble**

# The grand canonical ensemble

- Independent thermodynamic variables:  $(\mu, V, T)$ . **Open system**
- Thermodynamic potential. **Grand potential:**

$$\Omega = -PV = F - N\mu \quad \text{and} \quad d\Omega = -SdT - PdV - Nd\mu \quad (69)$$

- Equations of state:

$$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} \quad P = - \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu} \quad N = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, V} \quad (70)$$

- Distribution function:

$$f_0(\mathbf{r}^N, \mathbf{p}^N; N) = \frac{\exp(-\beta(\mathcal{H} - N\mu))}{\Xi_{\mu, V, T}}$$

with

$$\Xi_{\mu, V, T} = \sum_{N=0}^{\infty} \frac{\exp(N\beta\mu)}{h^{3N} N!} \int \int \exp(-\beta\mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N$$

# The grand canonical ensemble

- The partition function can be expressed in terms of the **activity**:

$$z = \frac{\exp(N\beta\mu)}{\Delta^3} \rightarrow \Xi_{\mu, V, T} = \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N \quad (71)$$

- The ensemble average of a microscopic variable  $B(\mathbf{r}^N, \mathbf{p}^N)$  is:

$$\langle B \rangle = \frac{1}{h^{3N} N!} \int \int B(\mathbf{r}^N, \mathbf{p}^N) f_0(\mathbf{r}^N, \mathbf{p}^N; N) d\mathbf{r}^N d\mathbf{p}^N \quad (72)$$

- The connection with thermodynamics is given by;

$$\Omega = -k_B T \ln(\Xi) \quad (73)$$

- Reduction.** Probability that system contains  $N$  particles independent of coordinates and momenta:

$$p(N) = \frac{1}{h^{3N} N!} \int \int f_0(\mathbf{r}^N, \mathbf{p}^N; N) d\mathbf{r}^N d\mathbf{p}^N = \frac{1}{\Xi} \frac{z^N}{N!} Z_N \quad (74)$$

# Fluctuations in the grand canonical ensemble

- Average number of particles is:

$$\langle N \rangle = \sum_{N=0}^{\infty} N p(N) = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N = \left( \frac{\partial \ln \Xi}{\partial \ln z} \right) \quad (75)$$

- Fluctuations in the number of particles:

$$\frac{\partial \langle N \rangle}{\partial \ln z} = z \frac{\partial}{\partial z} \left( \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N \right) \quad (76)$$

$$= \frac{1}{\Xi} \sum_{N=0}^{\infty} N^2 \frac{z^N}{N!} Z_N - \left( \frac{1}{\Xi} \sum_{N=0}^{\infty} N \frac{z^N}{N!} Z_N \right)^2 \quad (77)$$

$$= \langle N^2 \rangle - \langle N \rangle^2 \equiv \langle (\Delta N)^2 \rangle \quad (78)$$

# Fluctuations in the grand canonical ensemble

Using the previous equations:

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \frac{k_B T}{\langle N \rangle} \frac{\partial \langle N \rangle}{\partial \mu} \quad (79)$$

and  $\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} \rightarrow 0$  when  $N \rightarrow \infty$

The isothermal compressibility is defined as:

$$\chi_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (80)$$

and it is simple to show that:

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \rho k_B T \chi_T \quad (81)$$

Thus, compressibility can not be negative

# Bibliography

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