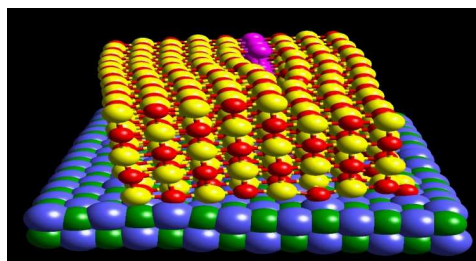


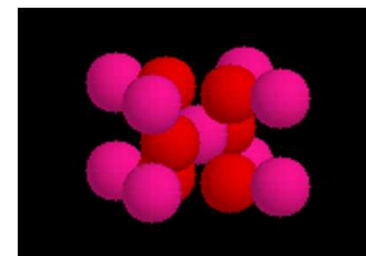
Molecular Simulations and Software Training
Antofagasta Chile 2019

Statistical Mechanics

Basic concepts, ensembles, distributions, partition functions,
phase space



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Books (lots of them!)



“Physical Chemistry”, P.W. Atkins.

“Molecular Driving Forces”, K.A. Dill and S. Bromberg, 2nd ed., Garland Science

“Statistical Mechanics: A Survival Guide”, M. Glazer and J. Wark, Oxford University Press.

“Statistical Mechanics”, D.A. McQuarrie.

“Statistical Mechanics: Principles and Selected Applications”, T.L. Hill, Dover.

“Introduction to Modern Statistical Mechanics”, David Chandler.

“Statistical Mechanics: Theory and Molecular Simulation”, Mark Tuckerman, Oxford Graduate Texts.

“Understanding Molecular Simulation”, Smit and Frenkel, 2nd edition

“Computer Simulation of Liquids”, 2nd edition, M.P. Allen and D.J. Tildesley, Oxford University Press.

Outline



- 1) Thermodynamics:
 - Systems and state variables.
 - Thermodynamic potentials.

- 2) Statistical Mechanics: an introduction to the statistical mechanics of interacting systems.
 - Overview of probability theory : Distributions.
 - Partition functions
 - Phase space
 - Time evolution

Thermodynamics

Thermodynamics: Phenomenological theory describing systems in equilibrium. Originating from macroscopic systems but of very wide generality.

Thermodynamic System: Macroscopic sample whose properties can be described by a small number of observables called **State Variables**.

Extensive variables: proportional to the amount of matter in the sample, *e.g.* energy, E , volume V , mass M .

Intensive variables: Independent of the sample size, *e.g.*

temperature, T , pressure p , chemical potential, μ $\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{p,T,N_{j \neq i}}$

The ratio of two extensive properties of the same system is an intensive property.

More Thermodynamics



The fundamental thermodynamics equations: $S=S(U,V,N)$ or $U=U(S,V,N)$. ($N = (N_1, N_2, N_3...N_r)$). Either completely specifies the state of a simple system. S and U are functions only of extensive variables.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum_{i=1}^r \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j \neq i}} dN_i$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \sum_{i=1}^r \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j \neq i}} dN_i$$

Define $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$; $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$; $\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j \neq i}}$

$$dU = TdS - pdV + \sum_{i=1}^r \mu_i dN_i \text{ (fundamental energy equation)}$$

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{p}{T}\right) dV - \sum_{i=1}^r \left(\frac{\mu_j}{T}\right) dN_i$$

More Thermodynamics (2)



The second law of thermodynamics: in an irreversible process, the entropy of the system and its surroundings (the universe) increases. In a reversible process the entropy of the universe remains constant.

An isolated system attains equilibrium when the entropy is maximised.

We often want to use other independent variables rather than entropy and volume, e.g., T and V , or T and p .

A **Legendre transform** of one thermodynamic state function $E(X_1, X_2)$ switches the functional dependence from X_1 to Y_1 ,

where $Y_1 = \left(\frac{\partial E}{\partial X_1} \right)_{X_2}$, generating a new extensive parameter $Z(Y_1, X_2)$

such that $Z(Y_1, X_2) = E(X_1, X_2) - X_1 Y_1$

Thermodynamic Functions (Potentials)



Function	Extremum at equilibrium	Fundamental Equation	Definition
$U(S,V,N)$ Internal Energy	Minimum	$dU = TdS - pdV + \sum_{i=1}^r \mu_i dN_i$	
$S(U,V,N)$	Maximum	$dS = \left(\frac{1}{T}\right) dU + \left(\frac{p}{T}\right) dV - \sum_{i=1}^r \left(\frac{\mu_j}{T}\right) dN_i$	
$H(S,p,N)$ Enthalpy	Minimum	$dH = TdS + VdP + \sum_{i=1} \mu_i dN_i$	$H = U + pV$
$A(T,V,N)$ Helmholtz energy	Minimum	$dA = -SdT - pdV + \sum_{i=1} \mu_i dN_i$	$A = U - TS$
$G(T,p,N)$ Gibbs energy	Minimum	$dG = -SdT + Vdp + \sum_{i=1} \mu_i dN_i$	$G = H - TS = A + pV$

Chemical potential

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j \neq i}} = \left(\frac{\partial H}{\partial N_i}\right)_{S,p,N_{j \neq i}} = \left(\frac{\partial A}{\partial N_i}\right)_{V,T,N_{j \neq i}} = \left(\frac{\partial G}{\partial N_i}\right)_{p,T,N_{j \neq i}}$$

Statistical Mechanics



So far we have dealt only with macroscopic quantities. Now we want to make quantitative connections between molecular, atomistic properties and macroscopic thermodynamic properties.

Statistical mechanics deals with more detailed information than classical thermodynamics and we can also find how real system fluctuate in time at equilibrium – such fluctuations can even dominate the behaviour of fluids near a critical point or that of small systems.

The statistical properties of collections or ensembles of molecules are examined to predict the average value of thermodynamic properties and the likelihood of observing deviations from this average.

Statistical Mechanics Postulates



Postulate: For a systems in equilibrium all **microstates** are equally probable. For an isolated system all microscopic states having the same volume, number of molecules and energy are equally likely to occur.

Toss a coin four times: HHTH, THHT, TTTT – 16 possible outcomes, each a microstate and all 16 equally probable. The most likely overall outcome is 2 heads and 2 tails (6/16): the number of heads and tails, regardless of the order in which they come. This is the **macrostate** – the macroscopic state of the system in which we're interested. For very large numbers of coins (molecules), the observed macrostate is the one with the most microstates. The width of the distribution of the number of microstates per macrostate narrows as the number of coins increases.



Toss the coin 10 times. Although 5 heads has the largest probability (number of ways 252), 4 heads is of comparable value (number of ways 210).

If we toss the coin 100 times the number of ways of obtaining 50 heads is 10^{29} , of obtaining 40 heads is 10^{28} .

As the number of throws of the coins increases the 50% heads configuration will not only be the most probable, but the number of ways of achieving 50% heads is so large relative to that of other outcomes that the probability of observing another outcome is minute. The **most probable configuration** evolves into the **dominant configuration** as the size of the system increases.

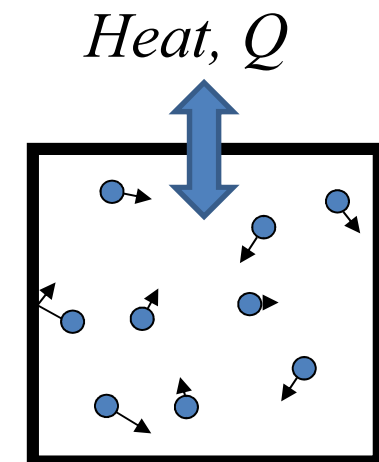
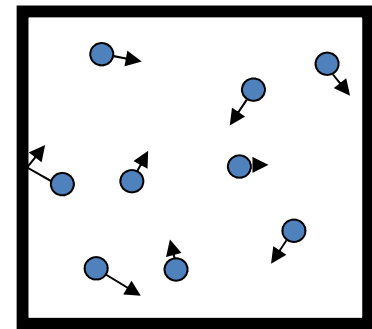
Ensembles

The term **ensemble** is used in two ways.

One way refers to which set of thermodynamic variables one is controlling e.g.,

(1) (N, V, U) N molecules, volume V , energy U (' E ' often used instead of ' U '). **Microcanonical** ensemble. No exchange of energy or matter with the surroundings. Isolated system.

(2) (N, V, T) **Canonical** ensemble: there is exchange of energy as heat but not matter with the surroundings. Closed system.

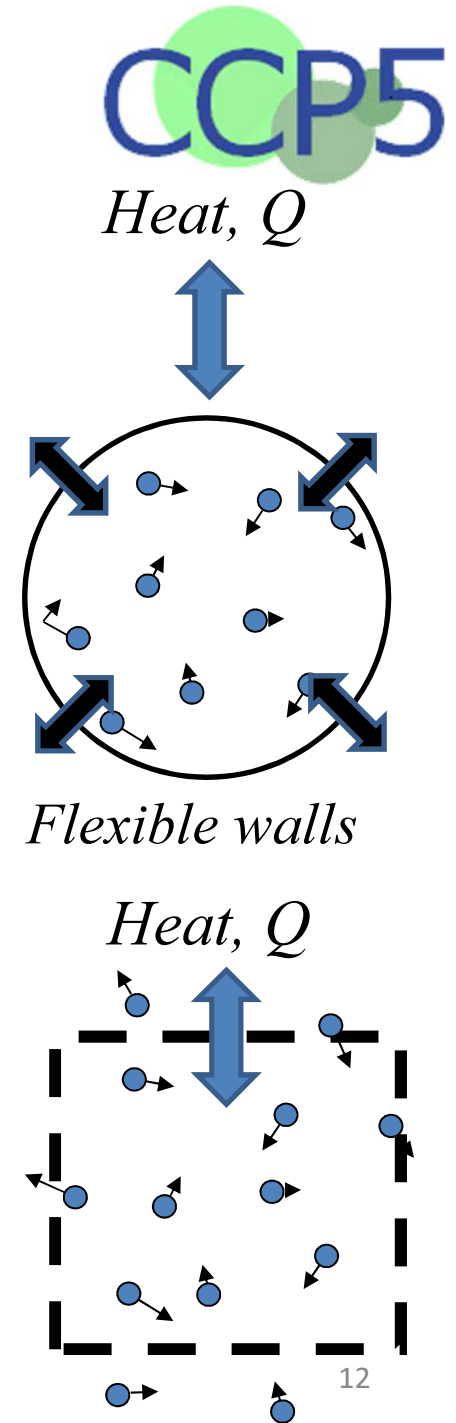


Ensembles (2)

(3) (N, p, T) **Isothermal-isobaric ensemble.**

Exchange of energy but not matter with the surroundings. System has flexible boundaries so can equalise pressure with the surroundings.

(4) (μ, V, T) **Grand Canonical ensemble:** there is exchange of energy and matter with the surroundings. Open system. Important for problems which involve e.g., ligand binding.



Ensembles (3)



Ensemble also refers to the collection of **all** the possible microstates of our system.

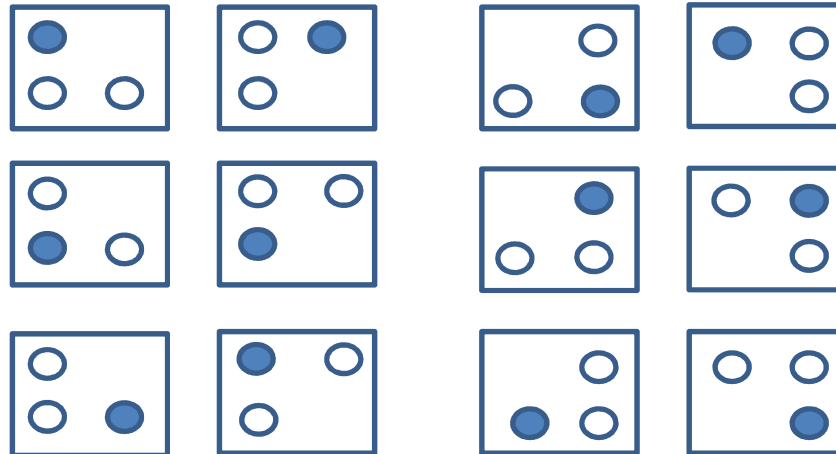
Consider first the microcanonical ensemble: Fix (N, V, U) so every microstate has exactly the same fixed energy and there are no fluctuations in energy. The probability p_i that the system is in a given microstate is the same,

$$p_i = \frac{1}{\Omega(N, V, U)}$$

where the number of microstates is $\Omega = \Omega(N, V, U)$. since the probability must be normalised to add up to unity.

$\Omega(N, V, U)$ is called the **microcanonical partition function**.

Ensembles (3)



Suppose we fix U , V and N as in this crude toy system, where there are 3 sodium atoms in a box with volume V and enough room for only 4 atoms. The total energy U is fixed, such that one (and only one atom) can be in an excited state.

There are 12 distinct ensemble states, 12 microstates.

Then other thermodynamic properties can be determined by **ensemble averaging** over these microstates. For example if each atom exerts pressure p_0 on the walls next to it, the average pressure against the top wall in the diagram is $3p_0/2$.

Statistical Mechanics Postulate



$$S(N, V, U) = k_B \ln \Omega(N, V, U)$$



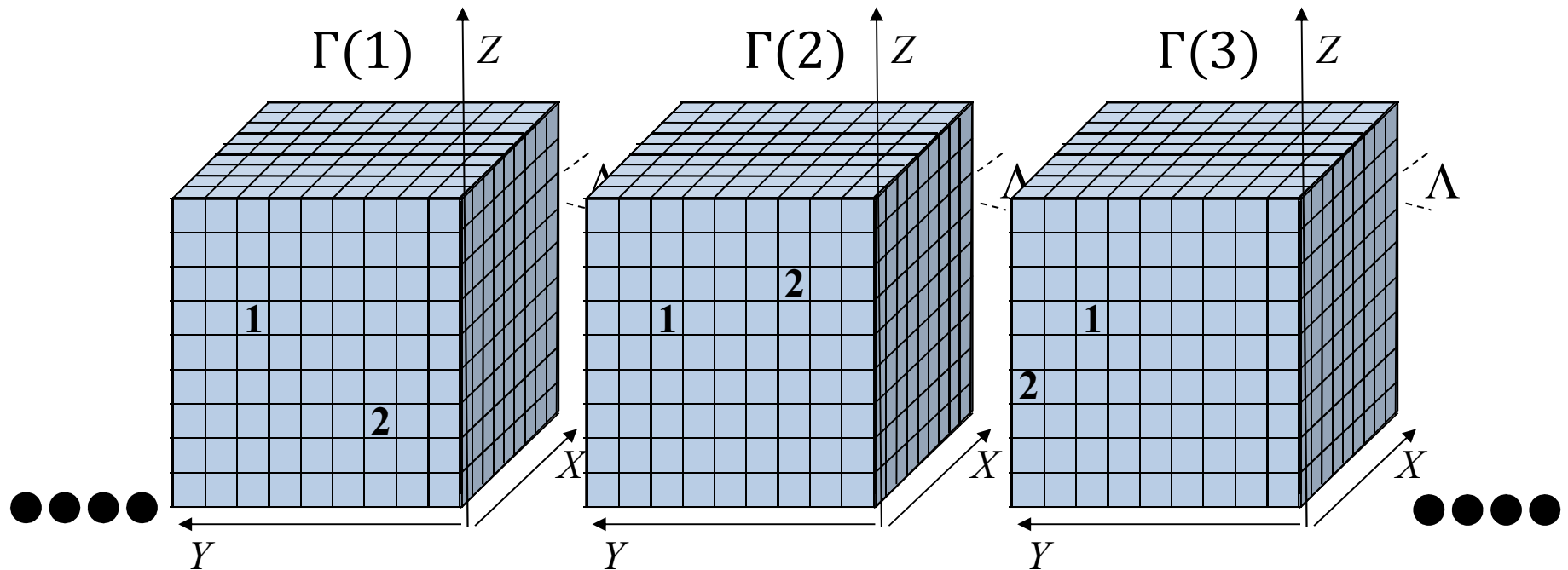
k_B is Boltzmann's constant $1.381 \times 10^{-23} \text{ J K}^{-1}$

Remember that the gas constant $R = N_A k_B$

Richard Feynman says in his Lectures on Physics "... entropy is just the logarithm of the number of ways of internally arranging a system while have it look the same from the outside"

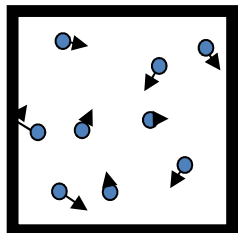
Ensemble Averaging

We recap: an **ensemble** is a set of systems that over which we average (thermodynamic averaging). This defines a phase space for the system.



Each member of the ensemble must be a microstate that conforms to the macroscopic constraints of the system, e.g. N , V , T , P , E , μ

Molecular dynamics



In molecular dynamics we use Newton's laws of motion to calculate a trajectory involving all particles in the system. Each particle has a position and a momentum:

$$r^N = x_1, y_1, z_1, x_2, y_2, z_2, \dots, z_N$$

$$p^N = m\dot{x}_1, m\dot{y}_1, m\dot{z}_1, m\dot{x}_2, m\dot{y}_2, m\dot{z}_2, \dots, m\dot{z}_N$$

Dot over variable implies time derivative.

The system has a **Hamiltonian**: $\mathcal{H}(r^N, p^N) = K(p^N) + V(r^N)$

The kinetic energy depends only on momentum and the potential energy only on position:

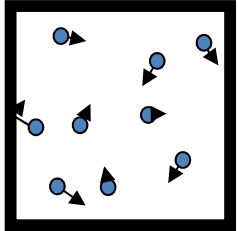
$$K(p^N) = \sum_{i=1}^N \frac{p_i^2}{2m} \quad V(r^N) = \sum_{i=1}^N \sum_{j>i}^N U(|r_i - r_j|)$$

The p_i and r_i are the three component vectors for the momentum and position respectively of atom i . U the inter-atomic potential

The trajectory is then evolved using the forces from Hamilton's equations.

$$\dot{r}_i = \frac{\partial \mathcal{H}(r^N, p^N)}{\partial p_i} \quad \dot{p}_i = -\frac{\partial \mathcal{H}(r^N, p^N)}{\partial r_i}$$

Molecular dynamics (2)



Consider a one-dimensional example – the simple harmonic oscillator

$$r = x$$

$$p = m\dot{x} \quad \text{Dot over variable implies time derivative.}$$

The system has a **Hamiltonian**: $\mathcal{H}(x, p) = K + V = \frac{p^2}{2m} + \frac{kx^2}{2}$

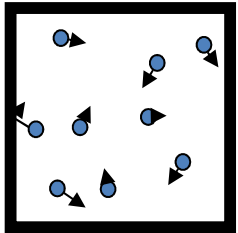
The trajectory is evolved using the forces from Hamilton's equations.

$$\dot{x} = \frac{\partial \mathcal{H}}{\partial p} = \frac{p}{m} \quad \dot{p} = -\frac{\partial \mathcal{H}}{\partial x} = -kx \quad \text{hence } m\ddot{x} = -kx$$



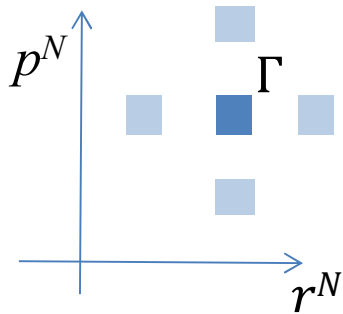
Important: since the equations of motion conserve the Hamiltonian (energy), a trajectory generated this way will generate microstates belonging to a microcanonical ensemble.

Phase space


 Γ

Molecular dynamics creates a trajectory each point of which has a set of particle positions, r^N , and momenta, p^N .

Each particle has 3 co-ordinates for its position and 3 components to its momentum so for N particles there are $6N$ degrees of freedom.



We can think of one particular set of co-ordinates and momenta as a point in this $6N$ dimensional **phase space**.

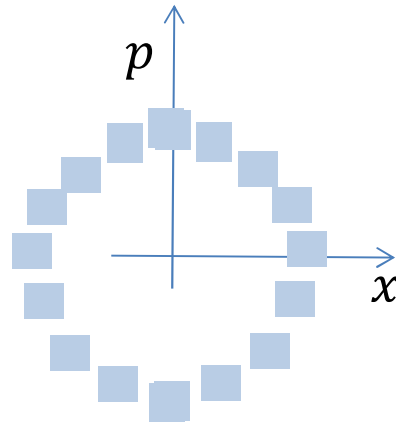
The goal of Statistical Mechanics is to take averages across all points in phase space with the correct weighting to obtain average properties.

$$A_{obs} = \langle A(\Gamma) \rangle = \int A(\Gamma) \rho(\Gamma) d\Gamma$$

The observed value will be the value for each point in phase space averaged across all points in phase space.

$\rho(\Gamma)$ = the probability density associated with the particular point in phase space, Γ .

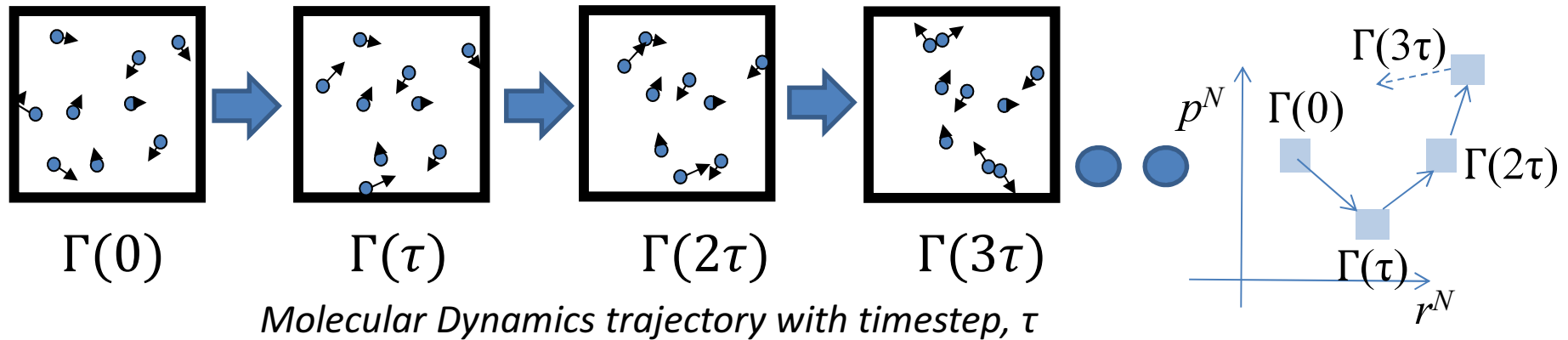
Phase space (2)



Region of phase space consistent with the motion of our single harmonic oscillator.

$$\mathcal{H} = \frac{p^2}{2m} + kx^2$$

Averages in Molecular Dynamics



We make the assumption that a **time average** is equivalent to the **ensemble average** required for statistical mechanics (the **ergodic hypothesis**).

$$A_{obs} = \langle A(\Gamma(t)) \rangle_t = \lim_{t_{obs} \rightarrow \infty} \frac{1}{t_{obs}} \int_0^{t_{obs}} A(\Gamma(t)) dt \quad \text{Continuous trajectory}$$

Discrete trajectory as in molecular dynamics

$$A_{obs} = \langle A(\Gamma(t)) \rangle_t = \frac{1}{(N_s + 1)} \sum_{n=0}^{n=N_s} A(\Gamma(n\tau))$$

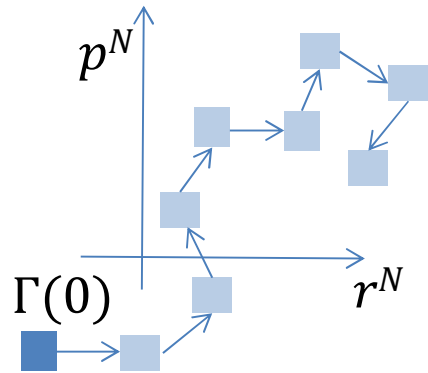
Here τ is the time between calculations of the value of A . N_s+1 is the total number of samples

If we do not sample phase space correctly, these averages will be subject to statistical problems.

The ensemble can be represented as a cluster of points in phase space and the trajectory of each point through phase space represents the time evolution of the ensemble. Furthermore, the density of points in phase space is a realisation of the probability density of the ensemble.

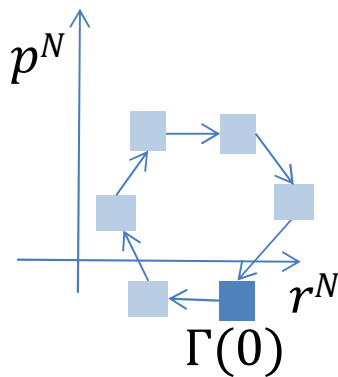
Advanced statistical mechanics discusses the collective motion of the ensemble as if it was a fluid flowing in phase space. This allows us to treat time dependent properties of the ensemble as a manifestation of flow of probability density rather than the result of the mechanics of individual molecules.

Ergodicity



When we start a simulation we hope that the results are independent of the initial set up of the atom co-ordinates and momenta.

This will be the case if all significant points in phase space are visited during the simulation; the system is said to be **ergodic**.



However, if the system is trapped in a small section of phase space the averages taken will be incomplete and results will depend on starting conditions.

Probabilities, partition functions and ensembles



We have already encountered the **microcanonical partition function** $\Omega = \Omega(N, V, U)$ and the probability p_i that the system is in a given microstate is the same for all microstates

$$p_i = \frac{1}{\Omega(N, V, U)}$$

But experiments (and simulations) are usually conducted under different conditions – e.g., constant T , V and N . So what is the **canonical-ensemble partition function**?

Imagine our system surrounded by a large heat bath or reservoir – the total energy remains constant but the energy of our system itself fluctuates through interactions with the bath.

$$p(U; U_{\text{Total}}) \propto \Omega(U)\Omega_{\text{Bath}}(U_{\text{Total}} - U) \propto \Omega(U)e^{\ln \Omega_{\text{Bath}}(U_{\text{Total}} - U)}$$

Since the heat bath is large $U \ll U_{\text{Total}}$, we can carry out a Taylor expansion of $\ln \Omega_{\text{Bath}}(U_{\text{Total}} - U)$ about U_{Total} .

$$\ln \Omega_{\text{Bath}}(U_{\text{Total}} - U) = \ln \Omega_{\text{Bath}}(U_{\text{Total}}) - U \frac{\partial(\ln \Omega_{\text{Bath}}(U_{\text{Total}}))}{\partial E} + \dots$$

$$\ln \Omega_{\text{Bath}}(U_{\text{Total}} - U) = \ln \Omega_{\text{Bath}}(U_{\text{Total}}) - U \frac{\partial(\ln \Omega_{\text{Bath}}(U_{\text{Total}}))}{\partial U} + \dots$$

$$\frac{\partial(\ln \Omega_{\text{Bath}}(U_{\text{Total}}))}{\partial U} = \frac{1}{k_B} \frac{\partial(S_{\text{Bath}}(U_{\text{Total}}))}{\partial U} = \frac{1}{k_B T} = \beta \quad \text{From slide 5} \quad \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$$

$$\text{Thus } p(U; U_{\text{Total}}) \propto e^{\ln \Omega_{\text{Bath}}(U_{\text{Total}})} \Omega(U) e^{-\beta U}$$

↑
constant

The sum over all possible configurations (microstates) must equal 1 so the probability of the system being in microstate i is

$$p_i = \frac{e^{-\beta U_i}}{Q} \quad Q(T, V, N) = \sum_i e^{-\beta U_i}$$

where Q is the canonical-ensemble partition function; its physical interpretation is simply how many states are thermally accessible to the system. Q is just a normalising factor, but it plays a central role in statistical mechanics. Most statistical mechanics involves trying to determine partition functions for real systems. Direct evaluation is almost always impractical since it requires a sum over all phase space.

Thermodynamic averaging



So we can summarise the basic equations that can be used in the canonical ensemble to calculate the thermodynamic properties of a closed, isothermal system – this is where the partition function Q comes into its own. For example the average energy $\langle U \rangle$ is given by

$$p_i = \frac{e^{-\beta U_i}}{Q} \quad Q(T, V, N) = \sum_i e^{-\beta U_i}$$

$$\text{So from simple probability theory } \langle U \rangle = \sum_i p_i U_i = \frac{\sum_i U_i e^{-\beta U_i}}{Q}$$

For the entropy we use Gibbs' entropy formula (which can be shown is equivalent to the multiplicity expression)

$$S = -k_B \sum_i p_i \ln p_i$$

$$\text{and so obtain } S = \frac{\langle U \rangle}{T} + k \ln Q$$

We can of course derive partition functions appropriate for other ensembles!

An aside: Molecular partition functions



For those who have taken Physical Chemistry course we regain the **molecular partition function q** for non-interacting (independent) molecules:

For N distinguishable independent molecules $Q = q^N$

For N indistinguishable independent molecules $Q = q^N/N!$

Textbooks such as *Physical Chemistry* (Atkins) discuss the translational, rotational, vibrational and electronic contributions to q . We now sum over the individual energy levels of the individual molecules rather than those of the system to obtain q .