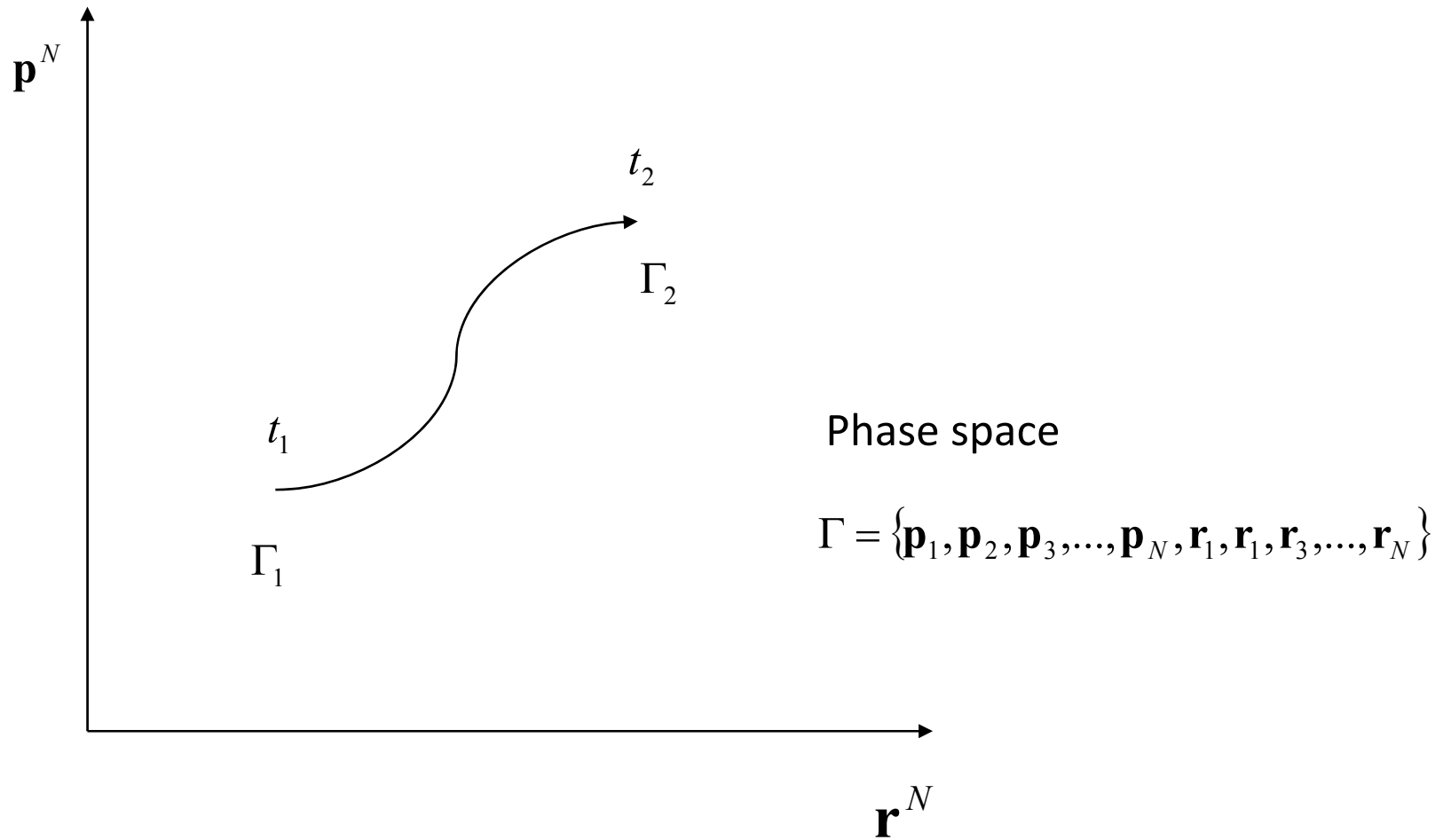


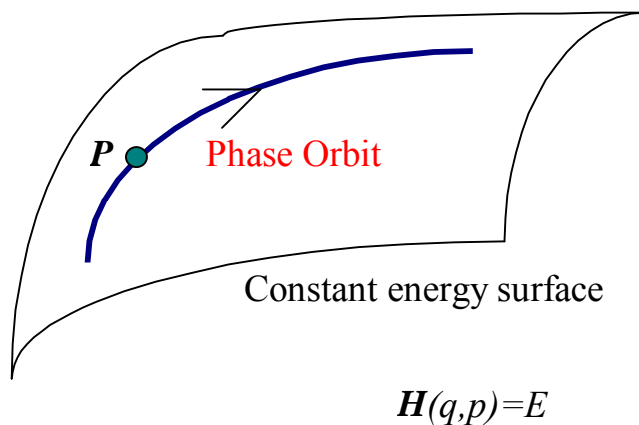
Phase Space



Phase Orbit

If the Hamiltonian of the system is denoted by $H(q,p)$, the motion of phase point can be along the *phase orbit* and is determined by the canonical equation of motion

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dot{q}_i = \frac{\partial H}{\partial p_i} \quad (i=1,2,\dots,s) \quad (1.1)$$



$$H(q, p) = E \quad (1.2)$$

Therefore the phase orbit must lie on a surface of constant energy (*ergodic surface*).

μ - space and Γ -space

Let us define μ - *space* as phase space of one particle (atom or molecule). The macrosystem phase space (Γ -*space*) is equal to the sum of μ - *spaces*.

The set of possible microstates can be presented by continuous set of phase points. Every point can move by itself along its own phase orbit. The overall picture of this movement possesses certain interesting features, which are best appreciated in terms of what we call a *density function* $\rho(q,p;t)$.

This function is defined in such a way that at any time t , the number of representative points in the '*volume element*' ($d^{3N}q d^{3N}p$) around the point (q,p) of the phase space is given by the product $\rho(q,p;t) d^{3N}q d^{3N}p$.

Clearly, the *density function* $\rho(q,p;t)$ symbolizes the manner in which the members of the ensemble are distributed over various possible microstates at various instants of time.

Function of Statistical Distribution

Let us suppose that the probability of system detection in the volume $d\Gamma \equiv dp dq \equiv dp_1, \dots, dp_s dq_1, \dots, dq_s$ near point (p, q) equal $dw(p, q) = \rho(q, p) d\Gamma$. The *function of statistical distribution* ρ (density function) of the system over microstates in the case of nonequilibrium systems is also depends on time. The statistical average of a given dynamical physical quantity $f(p, q)$ is equal:

$$\langle f \rangle = \frac{\int f(p, q) \rho(q, p; t) d^{3N} q d^{3N} p}{\int \rho(q, p; t) d^{3N} q d^{3N} p} \quad (1.3)$$

The right *"phase portrait"* of the system can be described by the set of points distributed in phase space with the density ρ . This number can be considered as the description of great (number of points) number of systems each of which has the same structure as the system under observation copies of such system at particular time, which are by themselves existing in admissible microstates

Statistical Ensemble

*The number of macroscopically identical systems distributed along admissible microstates with density ρ defined as **statistical ensemble**. A statistical ensembles are defined and named by the distribution function which characterizes it. The **statistical average value** have the same meaning as the **ensemble average value**.*

An ensemble is said to be stationary if ρ does not depend explicitly on time, i.e. at all times

$$\frac{\partial \rho}{\partial t} = 0 \quad (1.4)$$

*Clearly, for such an ensemble the **average value $\langle f \rangle$** of any physical quantity **$f(p,q)$** will be **independent of time**. Naturally, then, a stationary ensemble qualifies to represent a system in equilibrium. To determine the circumstances under which Eq. (1.4) can hold, we have to make a rather study of the movement of the representative points in the phase space.*

Liouville's theorem and its consequences

Consider an arbitrary "volume" ω in the relevant region of the phase space and let the "surface" enclosing this volume increases with time is given by

$$\frac{\partial}{\partial t} \int_{\omega} \rho d\omega \quad (1.5)$$

where $d\omega \equiv (d^{3N}q d^{3N}p)$. On the other hand, the net rate at which the representative points "flow" out of the volume ω (across the bounding surface σ) is given by

$$\int_{\sigma} \rho (\mathbf{v} \cdot \hat{\mathbf{n}}) d\sigma \quad (1.6)$$

here \mathbf{v} is the vector of the representative points in the region of the surface element $d\sigma$, while $\hat{\mathbf{n}}$ is the (outward) unit vector normal to this element. By the **divergence theorem**, (1.6) can be written as

Statistics of Multiparticle Systems in Thermodynamic Equilibrium

The macroscopic thermodynamic parameters, $X = (V, P, T, \dots)$, are macroscopically observable quantities that are, in principle, functions of the canonical variables, i.e.

$$f_i = f_i(p_1, p_2, \dots, p_s, q_1, q_2, \dots, q_s), \quad i = 1, 2, \dots, n, \quad n \leq s$$

$$(f_1, f_2, \dots, f_n) \equiv (V, P, T, \dots) = X$$

$$\Downarrow$$

$$X = X(p_1, p_2, \dots, p_s, q_1, q_2, \dots, q_s)$$

However, the specification of all the macroparameters X does not determine a unique microstate,

$$p_i \neq p_i(X), \quad q_i \neq q_i(X)$$

- Consequently, **on the basis of macroscopic measurements, one can make only statistical statements about the values of the microscopic variables.**

Statistical Description of Mechanical Systems

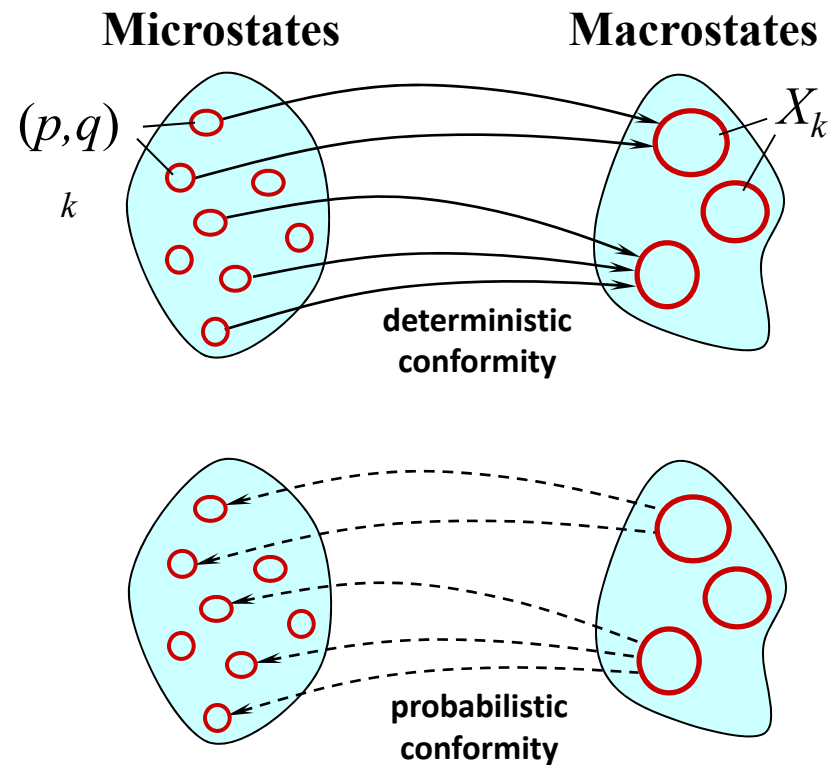
Statistical description of mechanical systems is utilized for multi-particle problems, where individual solutions for all the constitutive atoms are not affordable, or necessary. Statistical description can be used to reproduce averaged macroscopic parameters and properties of the system.

Comparison of objectives of the deterministic and statistical approaches:

Deterministic particle dynamics	Statistical mechanics
Provides the phase vector , as a function of time $Q(t)$, based on the vector of initial conditions $Q(0)$	Provides the time-dependent probability density to observe the phase vector Q , $w(Q,t)$, based on the initial value $w(Q,0)$

Statistical Description of Mechanical Systems

From the contemporary point of view, statistical mechanics can be regarded as a hierarchical *multiscale method*, which eliminates the atomistic degrees of freedom, while establishing a *deterministic* mapping from the atomic to macroscale variables, and a *probabilistic* mapping from the macroscale to the atomic variables:



Distribution Function

Though the specification of a macrostate X_i cannot determine the microstate $(p, q)_i = (p_1, p_2, \dots, p_s; q_1, q_2, \dots, q_s)_i$, a *probability density* w of all the microstates can be found,

$$w(p_1, p_2, \dots, p_s; q_1, q_2, \dots, q_s; t)$$

or abbreviated:

$$w(p, q, t)$$

The *probability* of finding the system in a given phase volume G :

$$W(G, t) = \int_G w(p, q, t) dp dq$$

The *normalization condition*:

$$\int_{(p, q)} w(p, q, t) dp dq = 1$$

Statistical Ensemble

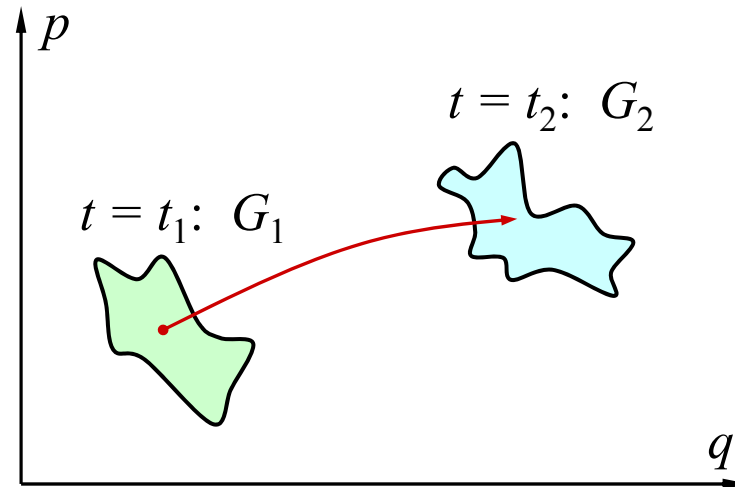
Within the statistical description, the motion of one single system with given initial conditions is not considered; thus, $p(t)$, $q(t)$ are not sought.

Instead, the motion of a *whole set of phase points*, representing the collection of possible states of the given system.

Such a set of phase points is called a **phase space ensemble**.

If each point in the phase space is considered as a random quantity with a particular probability ascribed to every possible state (i.e. a probability density $w(p, q, t)$ is introduced in the phase space), the relevant phase space ensemble is called a **statistical ensemble**.

G – volume in the phase space, occupied by the statistical ensemble.



Statistical Averaging

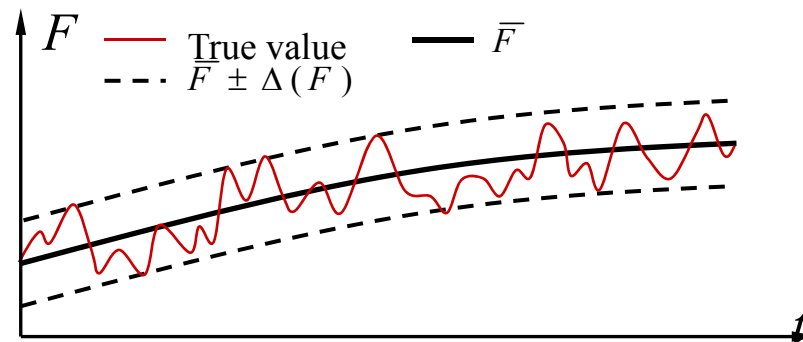
Statistical average (expectation) of an arbitrary physical quantity $F(p,q)$, is given most generally by the **ensemble average**,

$$\langle F(t) \rangle = \int_{(p,q)} F(p,q) w(p,q,t) dp dq$$

The root-mean-square fluctuation (standard deviation):

$$\Delta(F) = \sqrt{\langle F - \langle F \rangle \rangle^2}$$

The curve representing the real motion (the experimental curve) will mostly proceed within the band of width $2\Delta(F)$



For some standard equilibrium systems, thermodynamic parameters can be obtained, using a single phase space integral. This approach is discussed below.

Ergodic Hypothesis and the Time Average

Evaluation of the ensemble average (previous slide) requires the knowledge of the distribution function w for a system of interest.

Alternatively, the statistical average can be obtained by utilizing the **ergodic hypothesis** in the form,

$$\langle F \rangle = \bar{F}$$

Here, the right-hand side is the **time average** (in practice, time t is chosen finite, though as large as possible)

$$\bar{F} = \frac{1}{t} \int_0^t F(p(\tau), q(\tau)) d\tau, \quad t \rightarrow \infty$$

This approach requires F as a function of the generalized coordinates.

Some examples

Internal energy: $U = \overline{H(p, q)}$

Temperature: $T = \frac{2\overline{E_k}}{k_B}$

Change of entropy: $\Delta S = \int_{U_1}^{U_2} \frac{dU}{T} = \int_{T_1}^{T_2} \frac{C_V}{T} dT$

Gas diffusion constant: $D = \frac{\bar{v}l}{3}$

Here,

$\overline{E_k}$ – mean kinetic energy per degree of freedom

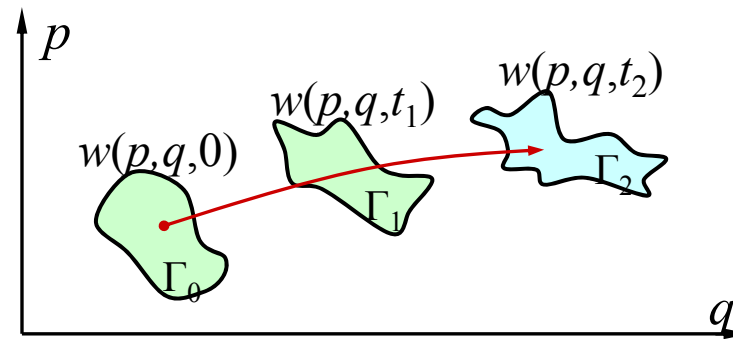
\bar{v} – mean velocity of molecules

l – mean free path of gas particles

Law of Motion of a Statistical Ensemble

A statistical ensemble is described by the probability density in phase space, $w(p, q, t)$. It is important to know how to find $w(p, q, t)$ at an arbitrary time t , when the initial function $w(p, q, 0)$ at the time $t = 0$ is given.

In other words, the equation of motion satisfied by the function $w(p, q, t)$ is needed.



The motion of an ensemble in phase space may be considered as the motion of a *phase space fluid* in analogy to the motion of an ordinary fluid in a 3D space.

Liouville's theorem claims that

$$\Gamma_0 = \Gamma_1 = \Gamma_2 = \dots$$

Due to Liouville's theorem, the following **equation of motion** holds

$$\frac{\partial w}{\partial t} = [H, w], \quad [H, w] = \sum_{i=1}^{2s} \left(\frac{\partial H}{\partial q_i} \frac{\partial w}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial w}{\partial q_i} \right) \quad (\text{Poisson bracket})$$

Equilibrium Statistical Ensemble: Ergodic Hypothesis

For a system in a state of thermodynamic equilibrium the probability density in phase space must not depend explicitly on time,

$$\frac{\partial w}{\partial t} = 0$$

Thus, the equation of motion for an equilibrium statistical ensemble reads

$$[H, w] = 0$$

A direct solution of this equation is not tractable.

Therefore, the **ergodic hypothesis** (in a more general form) is utilized: **the probability density in phase space at equilibrium depends only on the total energy:**

$$w(p, q) = \varphi(H(p, q, a))$$

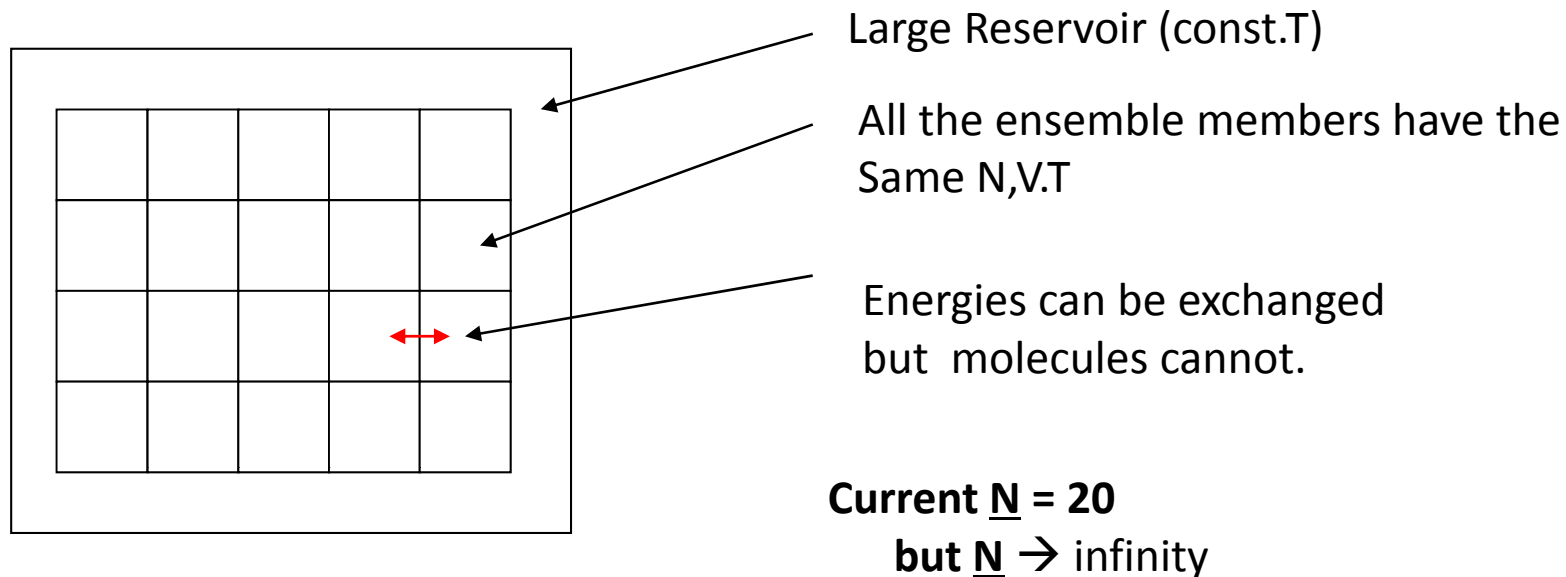
Notes: the Hamiltonian gives the total energy required; the Hamiltonian may depend on the values of external parameters $a = (a_1, a_2, \dots)$, besides the phase vector X .

This distribution function satisfies the equilibrium equation of motion, because

$$[H, \varphi(H)] = 0$$

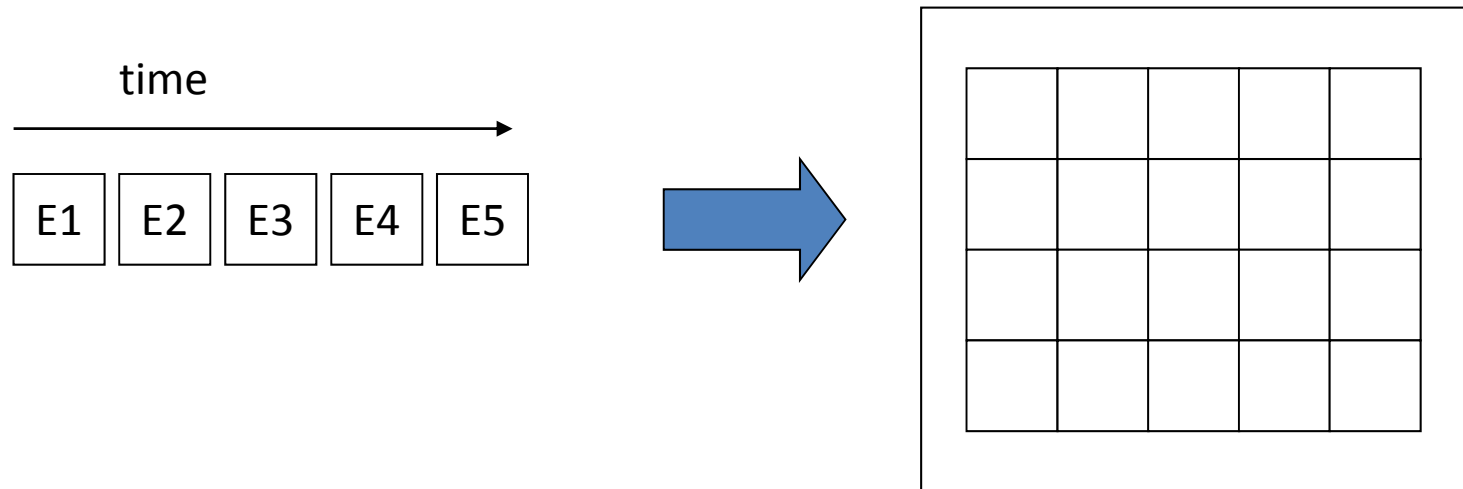
Exercise: Check the above equality.

- Ensemble Method
- Ensemble ? : Infinite number of mental replica of the system of interest



Two postulates

- Long time average = Ensemble average at $N \rightarrow \text{infinity}$



- In an ensemble, the systems of ensembles are distributed uniformly (equal probability or frequency)
 - Ergodic Hypothesis
 - Principle of equal a priori probability

Averaging Method

- **Probability of observing particular quantum state i**

$$P_i = \frac{n_i}{\sum_i n_i}$$

- **Ensemble average of a dynamic property**

$$\langle E \rangle = \sum_i E_i P_i$$

- **Time average and ensemble average**

$$U = \lim_{\tau \rightarrow \infty} \sum E_i \Delta t_i = \lim_{n \rightarrow \infty} \sum_i E_i P_i$$

Calculation of Probability in Ensemble

- Several methods are available
 - Method of Undetermined multiplier
 - :
 - :

Maximization of Weight

- Most probable distribution

- Weight

$$W = \frac{N!}{n_1!n_2!n_3!\dots} = \frac{N!}{\prod_i n_i!}$$

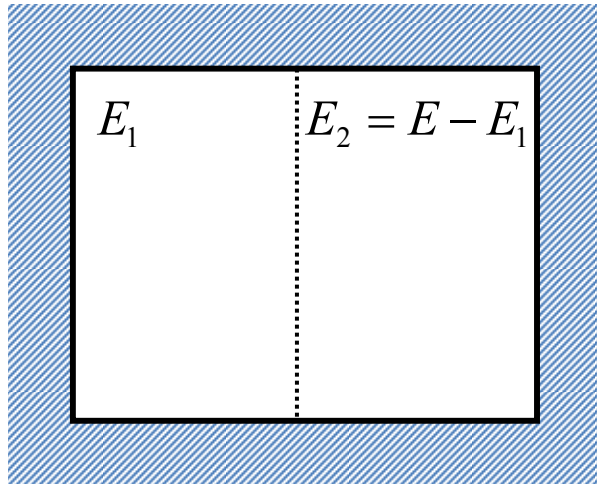
Ensembles

- Micro-canonical ensemble: E, V, N
- Canonical ensemble: T, V, N
- Constant pressure ensemble: T, P, N
- Grand-canonical ensemble: T, V, μ

Canonical Ensemble:

The canonical ensemble occurs when a system with fixed V and N and the system is at constant temperature (connected to an infinite heat bath).

In the canonical ensemble, the probability of each microstate is proportional to $\exp(-\beta E_m)$.



Systems 1 and 2 are weakly coupled such that they can exchange energy.

What will be E_1 ?

$$\Omega(E_1, E - E_1) = \Omega_1(E_1) \times \Omega_2(E - E_1)$$

BA: each configuration is equally probable; but the number of states that give an energy E_1 is not known.

$$\Omega(E_1, E - E_1) = \Omega_1(E_1) \times \Omega_2(E - E_1)$$

$$\ln \Omega(E_1, E - E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E - E_1)$$

$$\left(\frac{\partial \ln \Omega(E_1, E - E_1)}{\partial E_1} \right)_{N_1, V_1} = 0$$

Energy is conserved!
 $dE_1 = -dE_2$

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right)_{N_1, V_1} + \left(\frac{\partial \ln \Omega_2(E - E_1)}{\partial E_1} \right)_{N_2, V_2} = 0$$

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right)_{N_1, V_1} = \left(\frac{\partial \ln \Omega_2(E - E_1)}{\partial E_2} \right)_{N_2, V_2}$$

This can be seen as
 an equilibrium
 condition

$$\beta \equiv \left(\frac{\partial \ln \Omega(E)}{\partial E} \right)_{N, V}$$

$$\beta_1 = \beta_2$$

Entropy and number of configurations

Conjecture: $S = \ln \Omega$

$$S = k_B \ln \Omega(E)$$

With $k_B = 1.380662 \cdot 10^{-23} \text{ J/K}$

In thermodynamics, the absolute (Kelvin) temperature scale was defined such that

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T}$$

$$dE = TdS - pdV + \sum_{i=1}^n \mu_i dN_i$$

But we define:

$$\beta \equiv \left(\frac{\partial \ln \Omega(E)}{\partial E} \right)_{N,V}$$

And this gives the “statistical” definition of temperature:

$$\frac{1}{T} \equiv k_B \left(\frac{\partial \ln \Omega(E)}{\partial E} \right)_{N,V}$$

In short:

Entropy and temperature are both related to the fact that we can COUNT states.

Basic assumption:

1. leads to an equilibrium condition: equal temperatures
2. leads to a maximum of entropy
3. leads to the third law of thermodynamics

Number of configurations

How large is Ω ?

- For macroscopic systems, super-astronomically large.
- For instance, for a glass of water at room temperature:

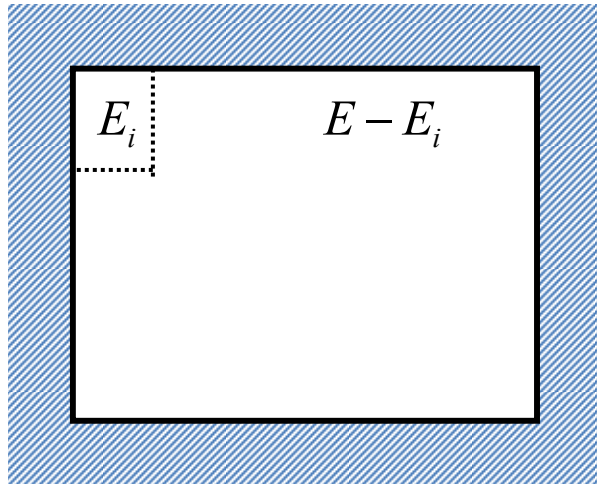
$$\Omega \approx 10^{2 \times 10^{25}}$$

- Macroscopic deviations from the second law of thermodynamics are not forbidden, but they are extremely unlikely.

Canonical ensemble

$$1/k_B T$$

Consider a small system that can exchange heat with a big reservoir



$$\ln \Omega(E - E_i) = \ln \Omega(E) - \frac{\partial \ln \Omega}{\partial E} E_i + \dots$$

$$\ln \frac{\Omega(E - E_i)}{\Omega(E)} = -\frac{E_i}{k_B T}$$

Hence, the probability to find E_i :

$$P(E_i) = \frac{\Omega(E - E_i)}{\sum_j \Omega(E - E_j)} = \frac{\exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)}$$

$$P(E_i) \propto \exp(-E_i/k_B T)$$

Boltzmann distribution

Averaging Method

- **Probability of observing particular quantum state i**

$$P_i = \frac{n_i}{\sum_i n_i}$$

- **Ensemble average of a dynamic property**

$$\langle E \rangle = \sum_i E_i P_i$$

- **Time average and ensemble average**

$$U = \lim_{\tau \rightarrow \infty} \sum E_i \Delta t_i = \lim_{n \rightarrow \infty} \sum_i E_i P_i$$

Thermodynamics

What is the average energy of the system?

$$\begin{aligned}\langle E \rangle &\equiv \sum_i E_i P(E_i) = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)} \\ &= - \frac{\partial \ln \sum_i \exp(-\beta E_i)}{\partial \beta} \\ &= - \frac{\partial \ln Q_{N,V,T}}{\partial \beta}\end{aligned}$$

Compare:

$$\left(\frac{\partial F/T}{\partial 1/T} \right) = E$$

Hence: $\frac{F}{k_B T} = -\ln Q_{N,V,T}$

➤ Canonical Partition Function

$$Q = \sum_j e^{-\beta E_j}$$

The Boltzmann Distribution

- Task : Find the dominating configuration for given N and total energy E .
- → Find Max. W which satisfies ;

$$\begin{array}{ccc} N = \sum_i n_i & \longrightarrow & \sum_i dn_i = 0 \\ E_t = \sum_i E_i n_i & & \sum_i E_i dn_i = 0 \end{array}$$

Method of Undetermined Multipliers

➤ Maximum weight , W

→ Recall the method to find min, max of a function...

$$d \ln W = 0$$

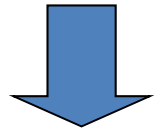
$$\left(\frac{\partial \ln W}{\partial n_i} \right) = 0$$

➤ Method of undetermined multiplier :

- Constraints should be multiplied by a constant and added to the main variation equation.

Method of undetermined multipliers

$$\begin{aligned} d \ln W &= \sum_i \left(\frac{\partial \ln W}{\partial n_i} \right) dn_i + \alpha \sum_i dn_i - \beta \sum_i E_i dn_i \\ &= \sum_i \left\{ \left(\frac{\partial \ln W}{\partial n_i} \right) + \alpha - \beta E_i \right\} dn_i = 0 \end{aligned}$$



$$\left(\frac{\partial \ln W}{\partial n_i} \right) + \alpha - \beta E_i = 0$$

$$\ln W = N \ln N - \sum n_i \ln n_i$$

$$\left(\frac{\partial \ln W}{\partial n_i} \right) = \frac{\partial N \ln N}{\partial n_i} - \sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i}$$

$$\frac{\partial N \ln N}{\partial n_i} = \left(\frac{\partial N}{\partial n_i} \right) \ln N + N \times \frac{1}{N} \left(\frac{\partial N}{\partial n_i} \right) = \ln N + 1$$

$$\sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i} = \sum_j \left\{ \left(\frac{\partial n_j}{\partial n_i} \right) \ln n_j + n_j \times \frac{1}{n_j} \left(\frac{\partial n_j}{\partial n_i} \right) \right\} = \ln n_i + 1$$



$$\frac{\partial \ln W}{\partial n_i} = -(\ln n_i + 1) + (\ln N + 1) = -\ln \frac{n_i}{N}$$

$$-\ln \frac{n_i}{N} + \alpha + \beta E_i = 0$$

$$\frac{n_i}{N} = e^{\alpha - \beta E_i}$$

$$N = \sum_j n_j = N e^{\alpha} \sum_j e^{-\beta E_j}$$

$$e^{\alpha} = \frac{1}{\sum_j e^{-\beta E_j}}$$

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$$



Boltzmann Distribution

**(Probability function for
energy distribution)**

Canonical Partition Function

- Boltzmann Distribution

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Q}$$

- Canonical Partition Function

$$Q = \sum_j e^{-\beta E_j}$$

Canonical Distribution: Preliminary Issues

One important preliminary issue related to the use of Gibbs' canonical distribution is the **additivity of the Hamiltonian** of a mechanical system.

Structure of the Hamiltonian of an atomic system:

$$\begin{aligned} H &= E^{\text{kin}}(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \\ &= \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_i W_1(\mathbf{r}_i) + \sum_{i,j>i} W_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,j>i,k>j} W_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \end{aligned}$$

Here, kinetic energy and the one-body potential are **additive**, i.e. they can be expanded into the components, each corresponding to one particle in the system:

$$\begin{aligned} E^{\text{kin}}(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) &= E^{\text{kin}}(\mathbf{p}_1) + E^{\text{kin}}(\mathbf{p}_2) + \dots \\ \sum_i W_1(\mathbf{r}_i) &= W_1(\mathbf{r}_1) + W_1(\mathbf{r}_2) + \dots \end{aligned}$$

Two-body and higher order potentials are **non-additive** (function Q_2 does not exist),

$$W_2(r_{ij}) = W(|\mathbf{r}_i - \mathbf{r}_j|) \Rightarrow \sum_{i,j>i} W_2(\mathbf{r}_i, \mathbf{r}_j) \neq \dots + Q_2(\mathbf{r}_i) + \dots + Q_2(\mathbf{r}_j) + \dots,$$

Canonical Distribution: Preliminary Issues

Thus, if the inter-particle interaction is negligible,

$$W_2 + W_3 + \dots \ll E^{\text{kin}} + W_1$$

the system is described by an **additive Hamiltonian**,

$$H = \sum_i h_i, \quad h_i = \frac{\mathbf{p}_i^2}{2m_i} + W_1(\mathbf{r}_i)$$

Here, H is the *total Hamiltonian*, and h_i is the *one-particle Hamiltonian*.

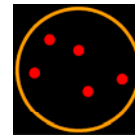
- For the statistical description, it is sufficient that this requirement holds for the *averaged* quantities only.
- The multi-body components, $W_{>1}$, cannot be completely excluded from the physical consideration, as they are responsible for heat transfer and establishing the thermodynamic equilibrium between constitutive parts of the total system.
- A micromodel with small averaged contributions to the total energy due to particle-particle interactions is called the **ideal gas**.

Example: particles in a circular cavity. Statistically averaged value W_2 is small:



3 particles:

$$\bar{W}_2 \approx 0.049E^{\text{tot}}$$



5 particles:

$$\bar{W}_2 \approx 0.026E^{\text{tot}}$$

Canonical Distribution

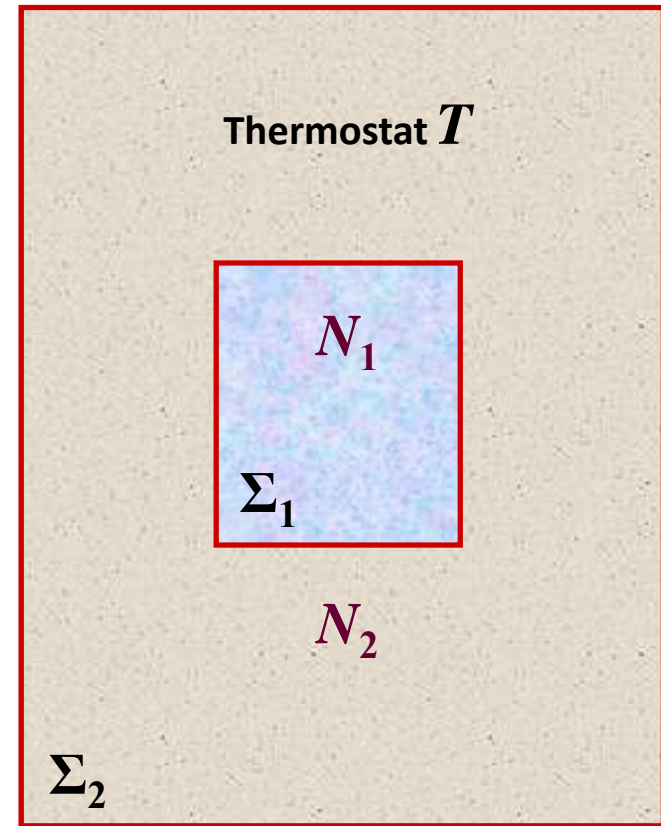
Suppose that system under investigation Σ_1 is in thermal contact and thermal equilibrium with a much larger system Σ_2 that serve as the *thermostat*, or “*heat bath*” at the temperature T . From the microscopic point of view, both Σ_1 and Σ_2 are mechanical systems whose states are described by the phase vectors (sets of canonical variables X_1 and X_2). The entire system $\Sigma_1 + \Sigma_2$ is adiabatically isolated, and therefore the microcanonical distribution is applicable to $\Sigma_1 + \Sigma_2$,

$$w(p_1, q_1; p_2, q_2) = \frac{1}{\Omega(E)} \delta(E - H(p_1, q_1; p_2, q_2))$$

Assume N_1 and N_2 are number of particles in Σ_1 and Σ_2 respectively. Provided that $N_1 \ll N_2$, the **Gibbs’ canonical distribution** applies to Σ_1 :

$$w(p, q) = \frac{1}{Z} e^{-\frac{H(p, q)}{kT}}$$

$$(p, q) \equiv (p_1, q_1)$$

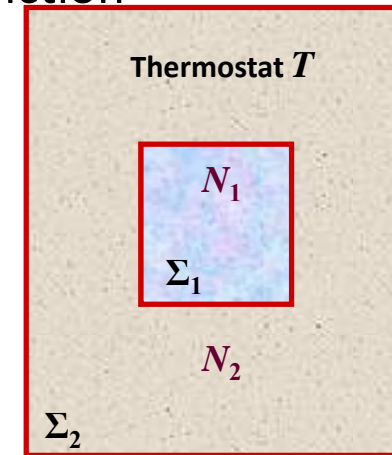


Canonical Distribution: Partition Function

The normalization factor Z for the canonical distribution called the **integral over states** or **partition function** is computed as

$$Z = \frac{1}{(2\pi\hbar)^{3N} N!} \int_{(p,q)} e^{-\frac{H(p,q,a)}{kT}} dp dq$$

$$= \frac{1}{(2\pi\hbar)^{3N} N!} \int_{(\mathbf{p},\mathbf{r})} e^{-\frac{H(\mathbf{p},\mathbf{r})}{kT}} d\mathbf{p}_1 \dots d\mathbf{p}_N d\mathbf{r}_1 \dots d\mathbf{r}_N$$



Before the normalization, *this integral represents the statistically averaged phase volume occupied by the canonical ensemble.*

The total energy for the canonical ensemble is not fixed, and, in principle, it may occur arbitrary in the range from $-\infty$ to ∞ (for the infinitely large thermostat, $N_2 \rightarrow \infty$).

Partition Function and Thermodynamic Properties

The partition function Z is the major *computational characteristic* of the canonical ensemble. The knowledge of Z allows computing thermodynamic parameters of the closed isothermal system ($a \square V$, external parameter):

Free energy:

(relates to mechanical work)

Entropy

(variety of microstates)

Pressure

Internal energy

$$F(T, V) = -kT \ln Z$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k \left(\ln Z + T \frac{\partial}{\partial T} \ln Z \right)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = kT \frac{\partial}{\partial V} \ln Z$$

$$U = F + TS = kT^2 \frac{\partial}{\partial T} \ln Z$$

These are the **major results** in terms of practical calculations over canonical ensembles.

Class exercise: check the last three above formulas with the the method of thermodynamic potentials, using the first formula for the free energy.

Thermodynamic Properties and Canonical Ensemble

Internal Energy

$$U = \langle E \rangle = \sum_i E_i P_i = \frac{1}{Q} \sum_{i(qs)} E_i e^{-\beta E_i}$$

$$\left(\frac{\partial Q}{\partial \beta} \right)_{N,V} = - \sum_{i(qs)} E_i e^{-\beta E_i}$$

$$U = - \frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{N,V} = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V}$$

Thermodynamic Properties and Canonical Ensemble

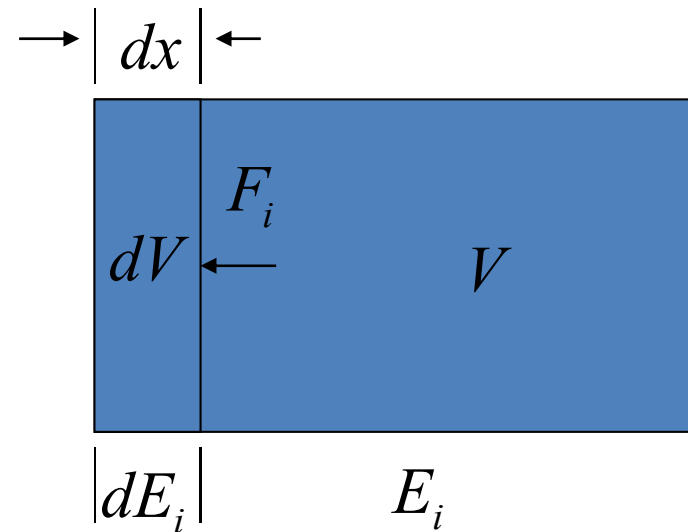
Pressure at i state

$$(\delta w_i)_N = P_i dV = F_i dx$$

$$(dE_i)_N = -F_i dx = -P_i dV = -\delta w_i$$

$$P_i = -\left(\frac{\partial E_i}{\partial V}\right)_N$$

Small Adiabatic expansion of system



Thermo recall (2)

First law of thermodynamics

$$dE = TdS - pdV$$

Helmholtz Free energy:

$$F \equiv E - TS$$

$$dF = -SdT - pdV$$

$$\begin{aligned}\left(\frac{\partial F/T}{\partial 1/T}\right) &= F + \frac{1}{T} \frac{\partial F}{\partial 1/T} = F - T \frac{\partial F}{\partial T} \\ &= F + TS = E\end{aligned}$$

We have assume quantum mechanics (discrete states) but we are interested in the classical limit

$$\sum_i \exp(-\beta E_i) \rightarrow \frac{1}{h^3 N!} \iint d\mathbf{p}^N d\mathbf{r}^N \exp \left\{ -\beta \left[\sum_i \frac{p_i^2}{2m_i} + U(r^N) \right] \right\}$$

$\frac{1}{h^3} \rightarrow$ Volume of phase space (particle in a box)

$\frac{1}{N!} \rightarrow$ Particles are indistinguishable

Integration over the momenta can be carried out for most system

$$\int d\mathbf{p}^N \exp \left\{ -\beta \left[\sum_i \frac{p_i^2}{2m_i} \right] \right\} = \left[\int dp \exp \left\{ -\beta \frac{p^2}{2m} \right\} \right]^{3N} = \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}N}$$

Define *de Broglie* wave length:

$$\Lambda \equiv \left(\frac{h^2 \beta}{2\pi m} \right)^{1/2}$$

Partition function:

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp \left[-\beta U(\mathbf{r}^N) \right]$$

Example: ideal gas

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]$$
$$= \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N 1 = \frac{V^N}{\Lambda^{3N} N!}$$

Free energy:

$$\beta F = -\ln\left(\frac{V^N}{\Lambda^{3N} N!}\right)$$
$$\approx N \ln \Lambda^3 + N \ln\left(\frac{N}{V}\right) = N \ln \Lambda^3 + N \ln \rho$$

Pressure:

e:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{N}{\beta V}$$

Energy:

$$E = \left(\frac{\partial \beta F}{\partial \beta}\right) = \frac{3N}{\Lambda} \frac{\partial \Lambda}{\partial \beta} = \frac{3}{2} N k_B T$$

Ideal gas (2)

Chemical potential:

$$\mu_i = \left(\frac{\partial F}{\partial N_i} \right)_{T, V, N_j}$$

$$\beta F = N \ln \Lambda^3 + N \ln \left(\frac{N}{V} \right)$$

$$\beta \mu = \ln \Lambda^3 + \ln \rho + 1$$

$$\beta \mu^{IG} = \beta \mu^0 + \ln \rho$$

Ensembles

- Micro-canonical ensemble: E, V, N
- Canonical ensemble: T, V, N
- Constant pressure ensemble: T, P, N
- Grand-canonical ensemble: T, V, μ

Summary:

Canonical ensemble (N, V, T)

Partition function:

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]$$

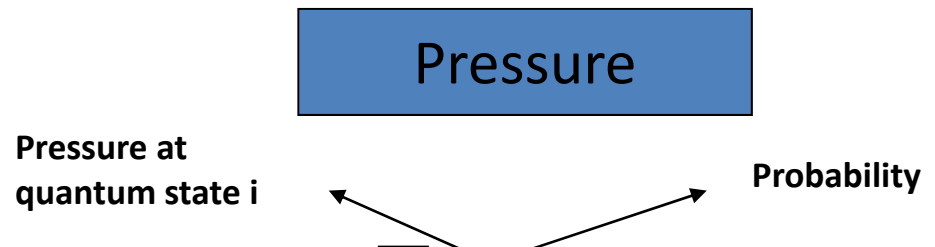
Probability to find a particular configuration

$$P(\Gamma) \propto \exp[-\beta U(\Gamma)]$$

Free energy

$$\beta F = -\ln Q_{N, V, T}$$

Thermodynamic Properties and Canonical Ensemble



$$P = \langle P \rangle = \sum_i P_i P_i$$

$$P = \frac{1}{Q} \sum_i P_i e^{-\beta E_i} = \frac{1}{Q} \sum_i \left(\frac{\partial E_i}{\partial V} \right)_N e^{-\beta E_i}$$

$$\left(\frac{\partial \ln Q}{\partial V} \right)_{\beta, N} = \frac{\beta}{Q} \sum_i \left(\frac{\partial E_i}{\partial V} \right)_N e^{-\beta E_i}$$

$$P = \frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial V} \right)$$

—————→ ***Equation of State in Statistical Mechanics***

Thermodynamic Properties and Canonical Ensemble

Entropy

$$dU = \delta q_{rev} - \delta w_{rev}$$

$$dU = d\left(\sum_i E_i P_i\right) = \sum_i E_i dP_i + \sum_i P_i dE_i$$

$$\sum_i P_i dE_i = \sum_i P_i \left(\frac{\partial E_i}{\partial V} \right)_N dV = -P dV = -\delta w_{rev}$$

$$\sum_i E_i dP_i = -\frac{1}{\beta} \left(\sum_i \ln P_i dP_i + \ln Q \sum_i dP_i \right)$$

$$= -\frac{1}{\beta} \sum_i \ln P_i dP_i$$

Thermodynamic Properties and Canonical Ensemble

Entropy

$$\begin{aligned}\sum_i P_i dE_i &= -\frac{1}{\beta} \sum_i \ln P_i dP_i = \delta q_{rev} & S &= k \ln Q + U/T + \cancel{S_0} \nearrow \\ \beta \delta q_{rev} &= -d\left(\sum_i P_i \ln P_i\right) = \beta T dS & S &= k \ln Q + U/T \\ \beta \delta q_{rev} &= d(U + \ln Q) = \beta T dS & S &= -k \sum_i P_i \ln P_i = -k \langle \ln P \rangle\end{aligned}$$

The only function that links heat (path integral) and state property is TEMPERATURE.

$$\beta = 1/kT$$

Summary of Thermodynamic Properties in Canonical Ensemble

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

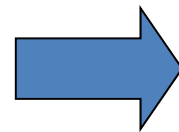
$$S = k \left(\ln Q + \left(\frac{\partial \ln Q}{\partial \ln T} \right)_{V,N} \right)$$

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

$$A = -kT \ln Q$$

$$G = -kT \left(\ln Q - \left(\frac{\partial \ln Q}{\partial \ln V} \right)_{T,N} \right)$$

$$\mu_i = -kT \left(\frac{\partial \ln Q}{\partial N_i} \right)_{T,V,N_{j \neq i}}$$



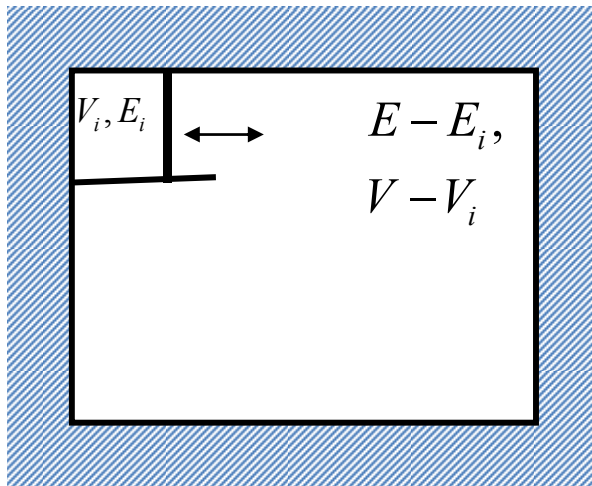
**All thermodynamic properties
Can be obtained from
“PARTITION FUNCTION”**

Ensembles

- Micro-canonical ensemble: E, V, N
- Canonical ensemble: T, V, N
- Constant pressure ensemble: T, P, N
- Grand-canonical ensemble: T, V, μ

Constant pressure simulations:

N, P, T ensemble



$$1/k_B T$$

Consider a small system that can exchange volume and energy with a big reservoir

$$p/k_B T$$

$$\ln \Omega(V - V_i, E - E_i) = \ln \Omega(V, E) - \left(\frac{\partial \ln \Omega}{\partial E} \right)_V E_i - \left(\frac{\partial \ln \Omega}{\partial V} \right)_E V_i + \dots$$

$$\ln \frac{\Omega(E - E_i, V - V_i)}{\Omega(E, V)} = -\frac{E_i}{k_B T} - \frac{p V_i}{k_B T}$$

Hence, the probability to find E_i, V_i :

$$P(E_i, V_i) = \frac{\Omega(E - E_i, V - V_i)}{\sum_{j,k} \Omega(E - E_j, V - V_k)} = \frac{\exp[-\beta(E_i + pV_i)]}{\sum_{j,k} \exp[-\beta(E_j + pV_k)]}$$

$$\propto \exp[-\beta(E_i + pV_i)]$$

Thermo recall (4)

First law of thermodynamics

$$dE = TdS - pdV + \sum_i \mu_i dN_i$$

Hence

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

and

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

N, P, T ensemble (2)

In the classical limit, the partition function becomes

$$Q(N, P, T) = \frac{1}{\Lambda^{3N} N!} \int dV \exp(-\beta P V) \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]$$

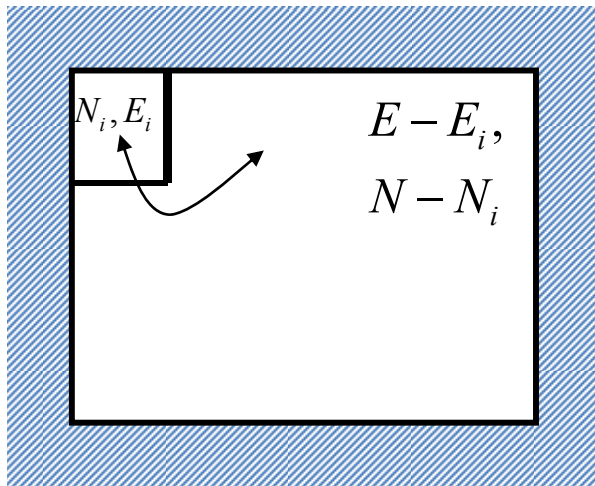
The probability to find a particular configuration:

\mathbf{r}^N, V

$$P(\mathbf{r}^N, V) \propto \exp[-\beta(PV + U(\mathbf{r}^N))]$$

Grand-canonical simulations:

μ, V, T ensemble



$1/k_B T$

Consider a small system that can exchange *particles* and energy with a big reservoir

$-\mu/k_B T$

$$\ln \Omega(N - N_i, E - E_i) = \ln \Omega(N, E) - \left(\frac{\partial \ln \Omega}{\partial E} \right)_N E_i - \left(\frac{\partial \ln \Omega}{\partial N} \right)_E N_i + \dots$$

$$\ln \frac{\Omega(E - E_i, N - N_i)}{\Omega(E, N)} = -\frac{E_i}{k_B T} + \frac{\mu_i N_i}{k_B T}$$

Hence, the probability to find E_i, N_i :

$$P(E_i, N_i) = \frac{\Omega(E - E_i, N - N_i)}{\sum_{j,k} \Omega(E - E_j, N - N_k)} = \frac{\exp[-\beta(E_i - \mu_i N_i)]}{\sum_{j,k} \exp[-\beta(E_j - \mu_k N_k)]}$$

$$\propto \exp[-\beta(E_i - \mu_i N_i)]$$

Thermo recall (5)

First law of thermodynamics

$$dE = TdS - pdV + \sum_i \mu_i dN_i$$

Hence

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

and

$$\left(\frac{\partial S}{\partial N_i} \right)_{T,V} = -\frac{\mu_i}{T}$$

μ, V, T ensemble (2)

In the classical limit, the partition function becomes

$$Q(\mu, V, T) = \sum_{N=1}^{\infty} \frac{\exp(\beta\mu N)}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp[-\beta U(r^N)]$$

The probability to find a particular configuration:

$$N, \mathbf{r}^N$$

$$P(N, \mathbf{r}^N) \propto \exp[\beta\mu N - \beta U(r^N)]$$

Classical Statistical Mechanics

- It is not easy to derive all the partition functions using quantum mechanics
- Classical mechanics can be used with negligible error when energy difference between energy levels (E_i) are smaller than kT .
- However, vibration and electronic states cannot be treated with classical mechanics. (The energy spacings are order of kT)

Phase Space

- Recall Hamiltonian of Newtonian Mechanics

$$H(\mathbf{r}^N, \mathbf{p}^N) = \text{KE}(\text{kinetic energy}) + \text{PE}(\text{potential energy})$$

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

$$\left[\frac{\partial H}{\partial \mathbf{r}_i} \right] = -\dot{\mathbf{p}}_i$$

$$\left[\frac{\partial H}{\partial \mathbf{p}_i} \right] = \dot{\mathbf{r}}_i$$

- Instead of taking replica of systems (ensemble members), use abstract 'phase space' composed of momentum space and position space (6N)
- Average of infinite phase space

Ensemble Average

$$U = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau E(\Gamma) d\tau = \lim_{n \rightarrow \infty} \int \mathcal{P}_N(\Gamma) E(\Gamma) d\Gamma$$

$$\mathcal{P}_N(\Gamma) d\Gamma \longrightarrow \text{Fraction of Ensemble members in this range } (\Gamma \text{ to } \Gamma + d\Gamma)$$

\downarrow
Using similar technique used for Boltzmann distribution

$$\mathcal{P}_N(\Gamma) d\Gamma = \frac{\exp(-H / kT) d\Gamma}{\int \dots \int \exp(-H / kT) d\Gamma}$$

Canonical Partition Function

Phase Integral

$$\mathcal{T} = \int \dots \int \exp(-H / kT) d\Gamma$$

Canonical Partition Function

$$Q = c \int \dots \int \exp(-H / kT) d\Gamma$$

Match between Quantum and Classical Mechanics

$$c = \lim_{T \rightarrow \infty} \frac{\sum_i \exp(-E_i / kT)}{\int \dots \int \exp(-H / kT) d\Gamma} \longrightarrow c = \frac{1}{N! h^{NF}}$$

For rigorous derivation see Hill, Chap.6

Canonical Partition Function in Classical Mechanics

$$Q = \frac{1}{N!h^{NF}} \int \dots \int \exp(-\mathbf{H} / kT) d\Gamma$$

Example :

Translational Partition Function for an Ideal Gas

$$H(\mathbf{r}^N, \mathbf{p}^N) = \text{KE}(\text{kinetic energy}) + \text{PE}(\text{potential energy})$$

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

No potential energy, 3 dimensional space.

$$H = \sum_i^{3N} \frac{p_i^2}{2m_i}$$



$$Q = \frac{1}{N! h^{3N}} \int \dots \int \exp\left(-\sum_i \frac{p_i^2}{2m_i}\right) dp_1 \dots dp_N dr_1 \dots dr_N$$

$$= \frac{1}{N! h^{3N}} \left[\int_{-\infty}^{\infty} \exp\left(-\frac{p}{2m_i}\right) dp \right]^{3N} \left[\int_0^V dr_1 dr_2 dr_3 \right]^N$$

$$= \frac{1}{N!} \left[\frac{2\pi m k T}{h^2} \right]^{3N/2} V^N$$

Semi-Classical Partition Function

The energy of a molecule is distributed in different modes

- Vibration, Rotation (Internal : depends only on T)
- Translation (External : depends on T and V)

Assumption 1

Hamiltonian operator can be separated into two parts
(internal + center of mass motion)

$$H_{op} = H_{op}^{CM} + H_{op}^{int}$$

$$Q = \sum \exp\left(-\frac{E_i^{CM} + E_i^{int}}{kT}\right) = \sum \exp\left(-\frac{E_i^{CM}}{kT}\right) \sum \exp\left(-\frac{E_i^{int}}{kT}\right)$$

$$Q = Q_{CM}(N, V, T) Q_{int}(N, T)$$

Semi-Classical Partition Function

- Internal parts are density independent and most of the components have the same value with ideal gases.

$$Q_{\text{int}}(N, \rho, T) = Q_{\text{int}}(N, 0, T)$$

- For solids and polymeric molecules, this assumption is not valid any more.

Semi-Classical Partition Function

Assumption 2

**For $T > 50\text{K}$, classical approximation
can be used for translational part.**

$$H_{CM} = \sum_i \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m} + U(r_1, r_2, \dots, r_{3N})$$

$$Q = \frac{1}{N! h^{3N}} \int \dots \int \exp\left(-\sum_i \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2mkT}\right) dp^{3N} \int \dots \int (-U / kT) dr^{3N}$$

$$= \frac{\Lambda^{-3N}}{N!} Z$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{1/2}$$

$$Z = \int \dots \int (-U / kT) dr_1 dr_2 \dots dr_{3N}$$



**Configuration
Integral**

$$Q = \frac{1}{N!} Q_{\text{int}} \Lambda^{-3N} Z$$

**For non-central forces
(orientation effect)**

$$Z = \left(\frac{1}{\Omega} \right)^N \int \dots \int (-U / kT) dr_1 dr_2 \dots dr_{3N} d\omega_1 \dots d\omega_N$$

$$\Omega = \int d\omega$$

Canonical Ensembles

After adoption of the ergodic hypothesis, it then remains to determine the actual form of the function $\varphi(H)$. This function depends on the type of the thermodynamic system under consideration, i.e. on the character of the interaction between the system and the external bodies.

We will consider canonical ensembles of **two types of systems**:

1) **Adiabatically isolated systems** that have no contact with the surroundings and have a specified energy E .

- The corresponding statistical ensemble is referred to as the *microcanonical ensemble*, and the distribution function – *microcanonical distribution*.

2) **Closed isothermal systems** that are in contact and thermal equilibrium with an external thermostat of a given temperature T .

- The corresponding statistical ensemble is referred to as the *canonical ensemble*, and the distribution function – *Gibbs' canonical distribution*.

Both systems do not exchange particles with the environment.

Microcanonical Distribution

For an adiabatically isolated system with constant external parameters, a , the total energy cannot vary. Therefore, only such microstates X can occur, for which

$$H(p, q, a) = E = \text{constant}$$

This implies (δ – Dirac's delta function)

$$w(p, q) \propto \delta(E - H(p, q, a))$$

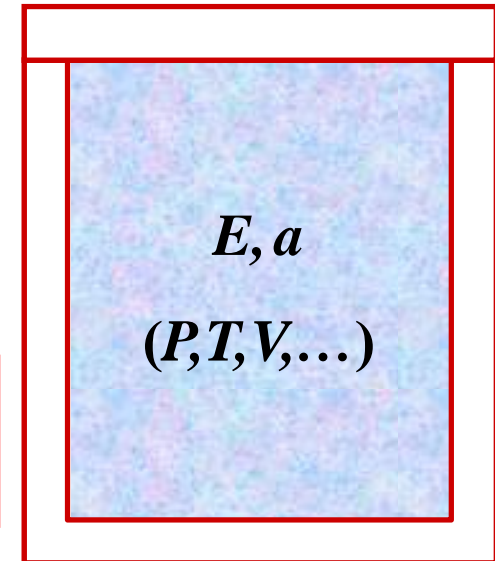
and finally:

$$w(p, q) = \frac{1}{\Omega(E, a)} \delta(E - H(p, q, a))$$

where Ω is the normalization factor,

$$\Omega(E, a) = \int_{(p, q)} \delta(E - H(p, q, a)) dp dq$$

Within the microcanonical ensemble, all the energetically allowed microstates have an equal probability to occur.



Microcanonical Distribution: Integral Over States

The normalization factor Ω is given by

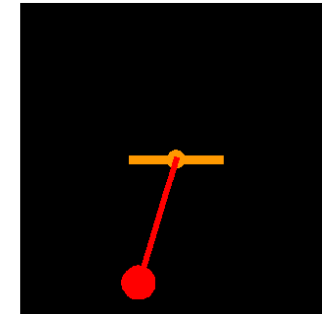
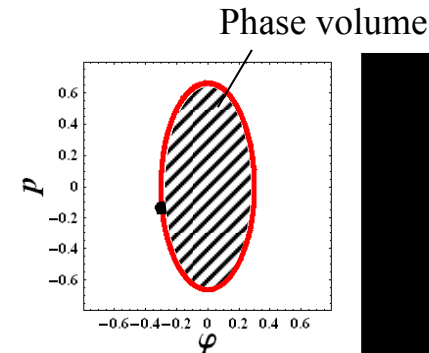
$$\Omega(E, a) = \left(\frac{\partial \Gamma(E, a)}{\partial E} \right)_a$$

where Γ is the **integral over states**,
or **phase integral**:

$$\Gamma(E, a) = \frac{1}{(2\pi\hbar)^{fN} N!} \int_{H(p, q, a) < E} dp dq$$

$$= \frac{1}{(2\pi\hbar)^{fN} N!} \int_{(p, q)} \theta(E - H(p, q)) d\mathbf{p}_1 \dots d\mathbf{p}_N d\mathbf{q}_1 \dots d\mathbf{q}_N$$

$$\theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x \geq 0 \end{cases}, \quad \hbar - \text{Planck's constant}, \quad j - \text{number of DOF per particle}$$



$\Gamma(E, a)$ represents the normalized phase volume, enclosed within the hypersurface of given energy determined by the equation $H(X, a) = E$.

Phase integral Γ is a dimensionless quantity.

Thus the normalization factor Ω shows the *rate* at which the phase volume varies due to a change of total energy at fixed external parameters.

Microcanonical Distribution: Integral Over States

The integral over states is a major *calculation characteristic* of the microcanonical ensemble. The knowledge of Γ allows computing thermodynamic parameters of the closed adiabatic system:

$$S = k \ln \Gamma, \quad T = \left(\frac{\partial S}{\partial E} \right)^{-1}, \quad P = \frac{1}{\Omega(E, V)} \left(\frac{\partial \Gamma}{\partial V} \right)_E$$

(These are the major results in terms of practical calculations over microcanonical ensembles.)

Summary:

micro-canonical ensemble (N,V,E)

Partition function:

$$Q(N,V,E) = \frac{1}{h^{3N} N!} \iint d\mathbf{p}^N d\mathbf{r}^N \delta(H(\mathbf{p}^N, \mathbf{r}^N) - E)$$

Probability to find a particular configuration

$$P(\Gamma) \propto 1$$

Free energy

$$\beta S = \ln Q_{N,V,E}$$

Microcanonical Ensemble: Illustrative Examples

We will consider one-dimensional illustrative examples of computing the phase integral, entropy and temperature for microcanonical ensembles:

Spring-mass harmonic oscillator

Pendulum (non-harmonic oscillator)

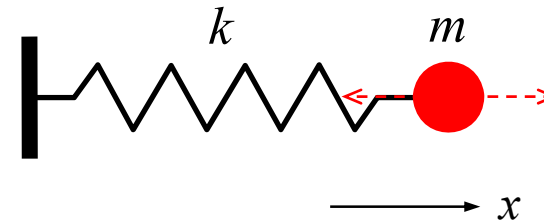
We will use the Hamiltonian equations of motion to get the phase space trajectory, and then evaluate the phase integral.

Harmonic Oscillator: Hamiltonian

Hamiltonian: general form $H = T(p) + U(x)$

Kinetic energy $T = \frac{p^2}{2m}$

Potential energy $U = \frac{kx^2}{2}$



Potential energy is a quadratic function of the coordinate (displacement from the equilibrium position)

The total Hamiltonian

$$H(p, x) = \frac{p^2}{2m} + \frac{kx^2}{2}$$

Parameters:

$$m = 10^{-21} \text{ kg}, \quad k = 25 \times 10^{-21} \text{ N/m}$$

Harmonic Oscillator: Equations of Motion and Solution

Hamiltonian and equations motion:

Parameters:

$$m = 10^{-21} \text{ kg}, \quad k = 25 \times 10^{-21} \text{ N/m}$$

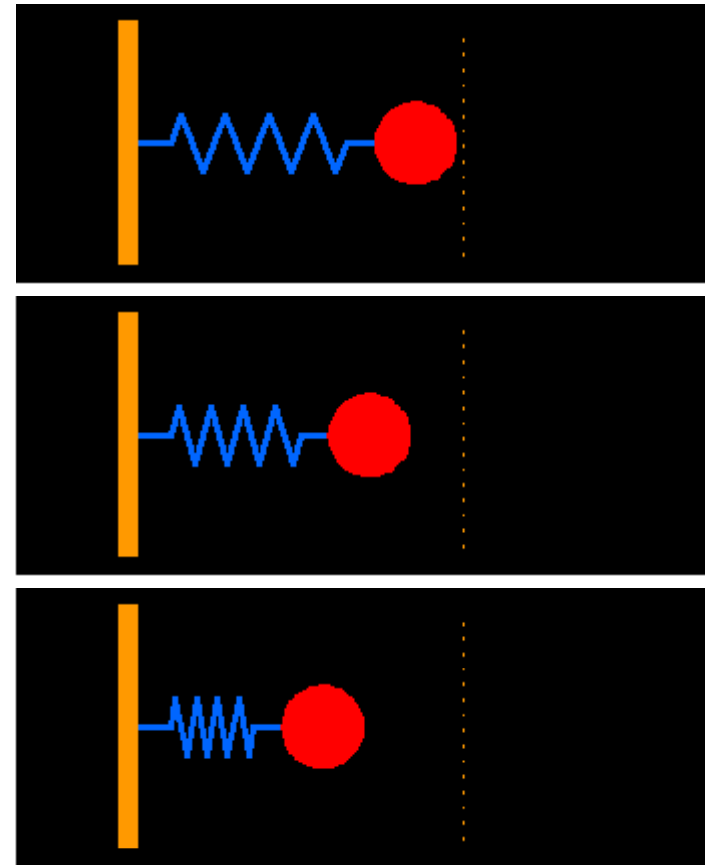
$$H(x, p) = \frac{p^2}{2m} + \frac{kx^2}{2} \Rightarrow \dot{x} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial x} \Rightarrow \boxed{\dot{x} = \frac{p}{m}, \quad \dot{p} = -kx}$$

Initial conditions (m, m/s):

$$x(0) = -0.2, \quad \dot{x}(0) = 0$$

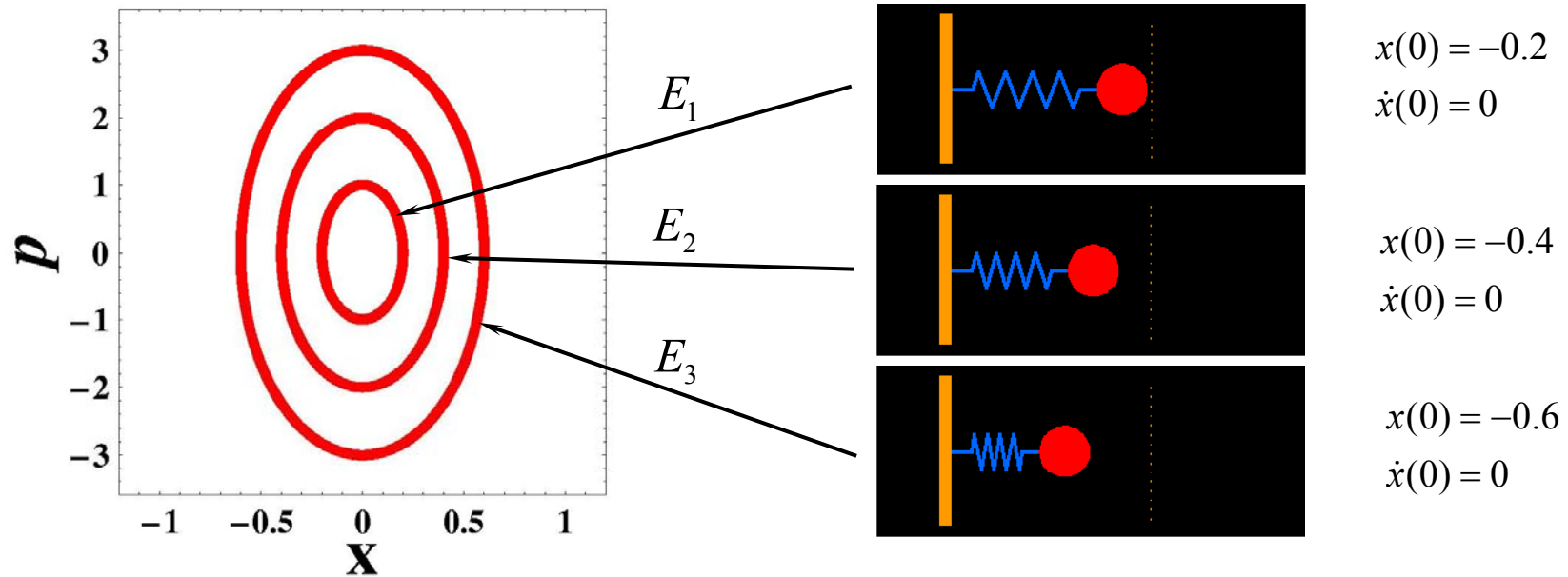
$$x(0) = -0.4, \quad \dot{x}(0) = 0$$

$$x(0) = -0.6, \quad \dot{x}(0) = 0$$



Harmonic Oscillator: Total Energy

Total energy: $E = H(x, p) = \text{Const}$ (at any $x(t), p(t)$)

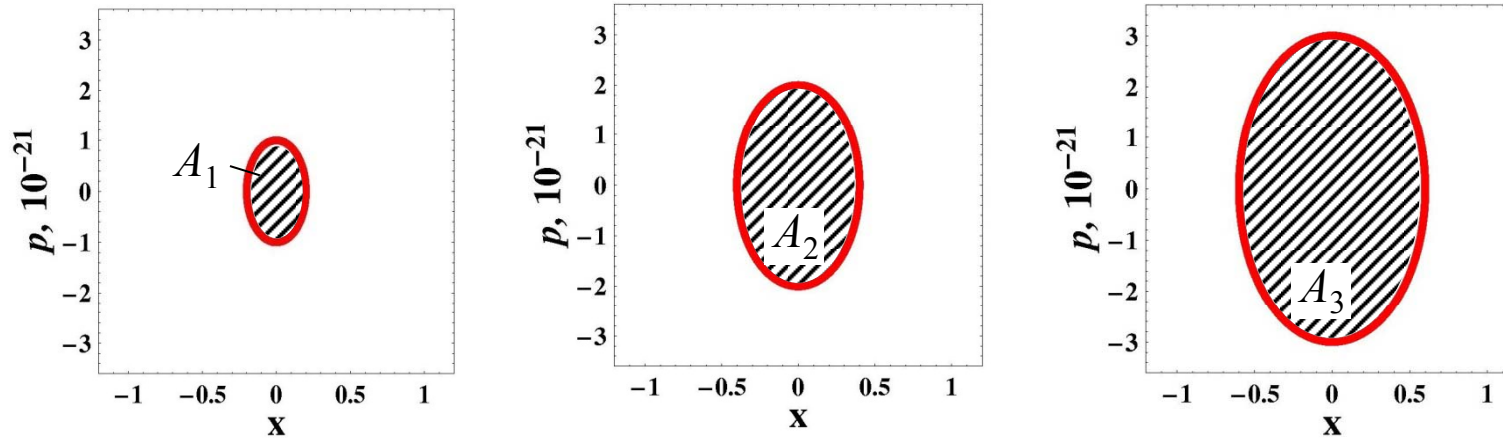


$$E_1 = 0.5 \times 10^{-21} \text{ J}, \quad E_2 = 2.0 \times 10^{-21} \text{ J}, \quad E_3 = 4.5 \times 10^{-21} \text{ J}$$

Phase integral: Harmonic Oscillator: Phase Integral

$$\Gamma(E) = \frac{1}{2\pi\hbar} A(E), \quad A(E) = \int_{(x,p)} \theta(E - H(x, p)) dx dp \approx \frac{\delta_x \delta_p}{2\pi\hbar} \sum_{i=0}^N \sum_{j=0}^N \theta(E - H(i\delta_x, j\delta_p))$$

$\delta_x = 2x_{\max} / N$ – step for x , $\delta_p = 2p_{\max} / N$ – step for p , N – number of integration steps

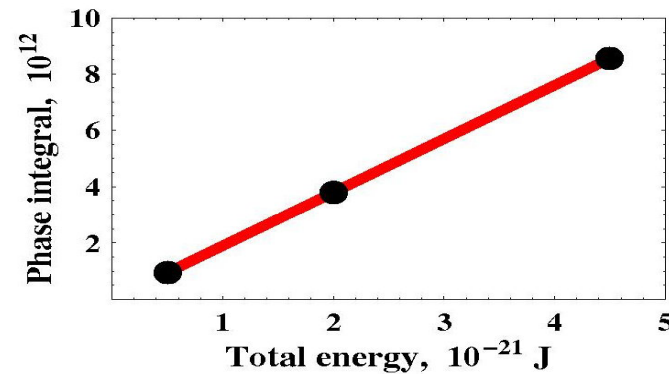


$$\Gamma_1 = 0.95 \times 10^{12}$$

$$\Gamma_2 = 3.80 \times 10^{12}$$

$$\Gamma_3 = 8.54 \times 10^{12}$$

For the harmonic oscillator, phase volume grows linearly with the increase of total energy.



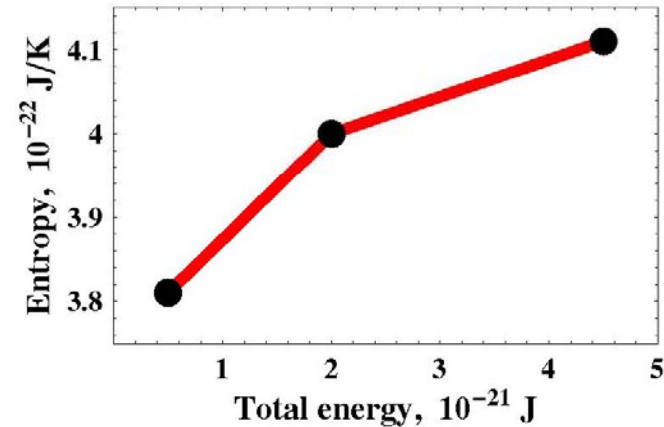
Harmonic Oscillator: Entropy and Temperature

Entropy: $S = k \ln \Gamma$, $k = 1.38 \times 10^{-23}$ J/K

$$S_1 = 3.81 \times 10^{-22} \text{ J/K}$$

$$S_2 = 4.00 \times 10^{-22} \text{ J/K}$$

$$S_3 = 4.11 \times 10^{-22} \text{ J/K}$$



Temperature: $T = \left(\frac{\partial S}{\partial E} \right)^{-1}$

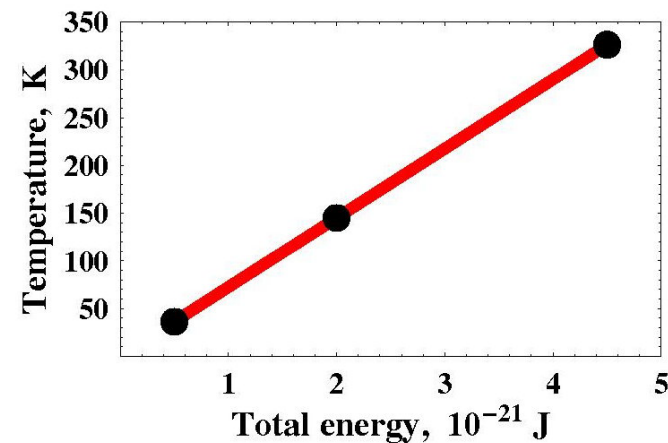
We perturb the initial conditions (on 0.1% or less) and compute new values \tilde{E} and \tilde{S} . The temperature is computed then, as

$$T \approx \left(\frac{\tilde{S} - S}{\tilde{E} - E} \right)^{-1} \quad (\text{benchmark: } T = \frac{2}{k} \bar{E}^{\text{kin}})$$

$$T_1 = 36.3 \text{ K}$$

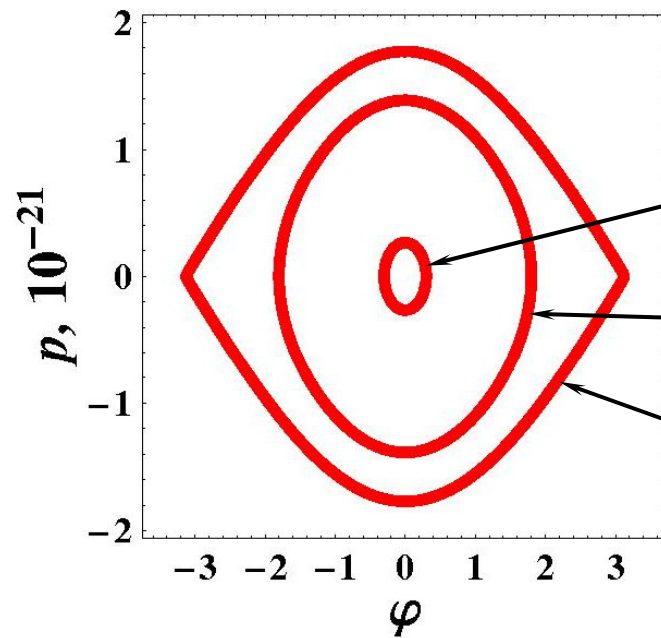
$$T_2 = 145.1 \text{ K}$$

$$T_3 = 326.5 \text{ K}$$

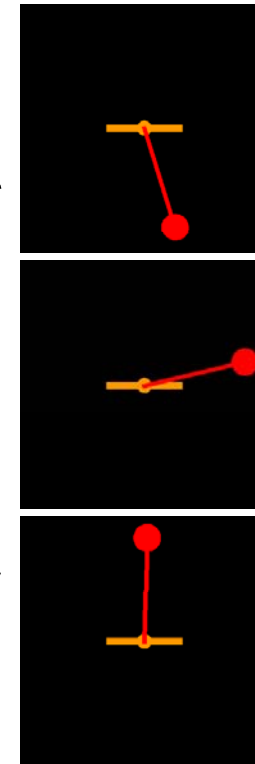


Pendulum: Total Energy

Total energy: $E = H(\varphi, p) = \frac{p^2}{2ml^2} - mgl \cos \varphi = \text{Const}$ (at any $\varphi(t), p(t)$)



$p = \dot{\varphi}l$ - angular momentum



$\varphi(0) = 0.3$
 $\dot{\varphi}(0) = 0$

$\varphi(0) = 1.8$
 $\dot{\varphi}(0) = 0$

$\varphi(0) = 3.12$
 $\dot{\varphi}(0) = 0$

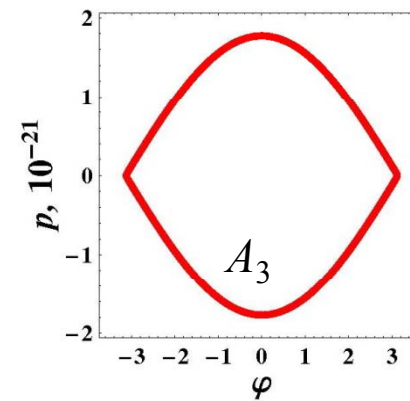
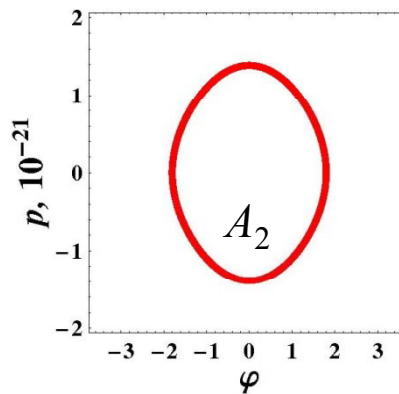
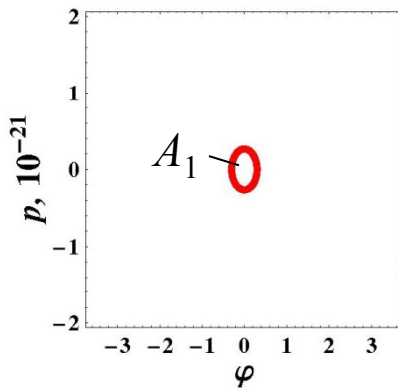
$E_1 = -1.87 \times 10^{-21} \text{ J}, \quad E_2 = 0.45 \times 10^{-21} \text{ J}, \quad E_3 = 1.96 \times 10^{-21} \text{ J}$

Phase integral:

Pendulum: Phase Integral

$$\Gamma(E) = \frac{1}{2\pi\hbar} A(E), \quad A(E) = \int_{(\varphi,p)} \theta(E - H(\varphi, p)) d\varphi dp \approx \frac{\delta_\varphi \delta_p}{2\pi\hbar} \sum_{i=0}^N \sum_{j=0}^N \theta(E - H(i\delta_\varphi, j\delta_p))$$

$\delta_\varphi = 2x_{\max} / N$ – step for φ , $\delta_p = 2p_{\max} / N$ – step for p , N – number of steps

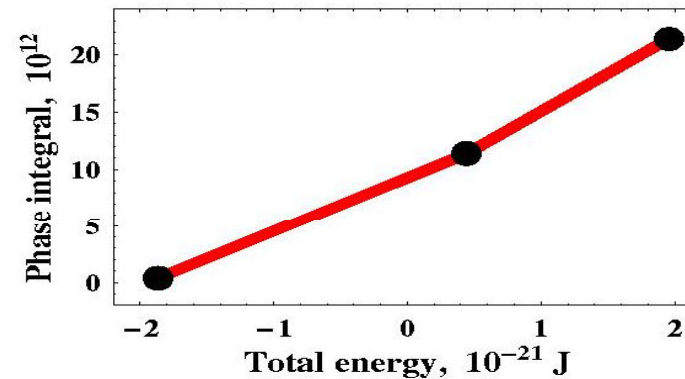


$$\Gamma_1 = 0.4 \times 10^{12}$$

$$\Gamma_2 = 11.2 \times 10^{12}$$

$$\Gamma_3 = 21.4 \times 10^{12}$$

For the pendulum, phase volume grows NON-linearly with the increase of total energy at large amplitudes.



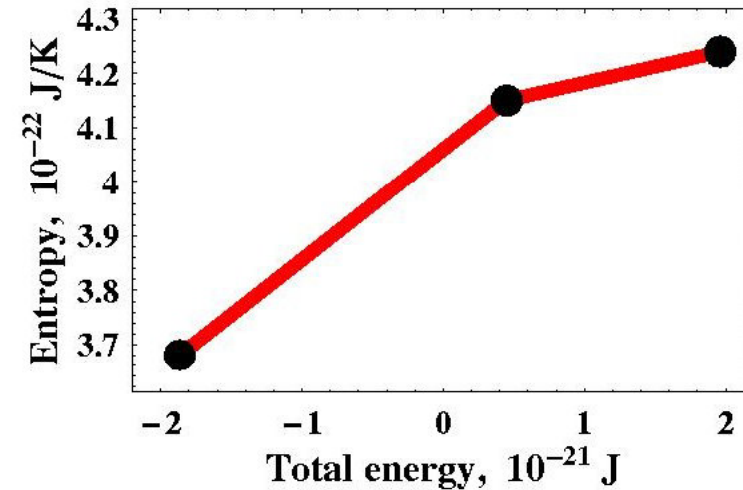
Pendulum: Entropy and Temperature

Entropy: $S = k \ln \Gamma$, $k = 1.38 \times 10^{-23}$ J/K

$$S_1 = 3.68 \times 10^{-22} \text{ J/K}$$

$$S_2 = 4.15 \times 10^{-22} \text{ J/K}$$

$$S_3 = 4.24 \times 10^{-22} \text{ J/K}$$



Temperature: $T = \left(\frac{\partial S}{\partial E} \right)^{-1}$

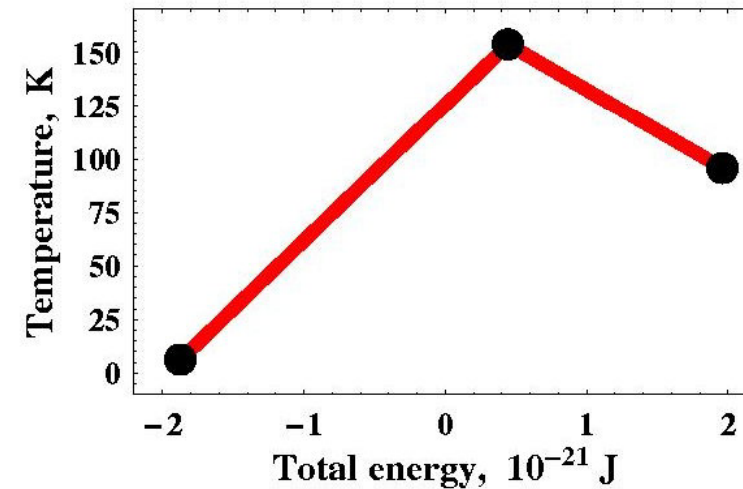
We perturb the initial conditions (on 0.1% or less) and compute new values \tilde{E} and \tilde{S} . The temperature is computed then, as

$$T \approx \left(\frac{\tilde{S} - S}{\tilde{E} - E} \right)^{-1} \quad (\text{benchmark: } T = \frac{2}{k} \bar{E}^{\text{kin}})$$

$$T_1 = 6.3 \text{ K}$$

$$T_2 = 153.8 \text{ K}$$

$$T_3 = 96.0 \text{ K}$$



Summary of the Statistical Method: Microcanonical Distribution

1. Analyze the physical model; justify applicability of the microcanonical distribution.
2. Model individual particles and boundaries.
3. Model interaction between particles and between particles and boundaries.
4. Set up initial conditions and solve for the deterministic trajectories (MD).
5. Compute two values of the total energy and the phase integral – for the original and perturbed initial conditions.
6. Using the method of thermodynamic parameters, compute entropy, temperature and other thermodynamic parameters. If possible compare the obtained value of temperature with benchmark values.

$$S = k \ln \Gamma, \quad T = \left(\frac{\partial S}{\partial E} \right)^{-1}, \quad P = \frac{1}{\Omega(E, V)} \left(\frac{\partial \Gamma}{\partial V} \right)_E$$

7. If required, accomplish an extended analysis of macroscopic properties (e.g. functions $T(E)$, $S(E)$, $S(T)$, etc.) by repeating the steps 4-7.

Free Energy and Isothermal Processes

Free energy, also **Helmholtz potential** is of importance for the description of isothermal processes. It is defined as the difference between internal energy and the product of temperature and entropy.

$$F = U - TS$$

Since free energy is a thermodynamic potential, the function $F(T, V, N, \dots)$ guarantees the full knowledge of all thermodynamic quantities.

Physical content of free energy: the change of the free energy dF of a system at constant temperature, represents the *work* accomplished by, or over, the system. Indeed,

$$\begin{aligned} dF &= dU - TdS - SdT \quad (dU = TdS - \delta W) \\ &= -SdT - \delta W \end{aligned}$$

$$\boxed{dF = -\delta W}$$

Isothermal processes tend to a minimum of free energy, i.e. due to the definition, simultaneously to a minimum of internal energy and maximum of entropy.