PHY 711 Classical Mechanics and Mathematical Methods
10-10:50 AM MWF in Olin 103

Discussion of Lecture 13 – Chap. 3&6 (F&W)

1. Phase space
2. Liouville theorem
3. Examples

9	Fri, 9/09/2022	Chap. 3 & 6	Lagrangian Mechanics		
10	Mon, 9/12/2022	Chap. 3 & 6	Lagrangian Mechanics	#8	9/14/2022
11	Wed, 9/14/2022	Chap. 3 & 6	Constants of the motion	#9	9/16/2022
12	Fri, 9/16/2022	Chap. 3 & 6	Hamiltonian equations of motion		
13	Mon, 9/19/2022	Chap. 3 & 6	Liouville theorm	#10	9/21/2022
14	Wed, 9/21/2022	Chap. 3 & 6	Canonical transformations		
15	Fri, 9/23/2022	Chap. 4	Small oscillations about equilibrium		
16	Mon, 9/26/2022	Chap. 4	Normal modes of vibration		
17	Wed, 9/28/2022	Chap. 4	Normal modes of more complicated systems		
18	Fri, 9/30/2022	Chap. 7	Motion of strings		
19	Mon, 10/03/2022	Chap. 7	Sturm-Liouville equations		
20	Wed, 10/05/2022	Chap. 7	Sturm-Liouville equations		
21	Fri, 10/07/2022	Chap. 1-4,6-7	Review		
	Mon, 10/10/2022	No class	Take home exam		
	Wed, 10/12/2022	No class	Take home exam		
	Fri, 10/14/2022	No class	Fall break		
22	Mon, 10/17/2022	Chap. 7s	Class resumes		

Take home exam due by 5 PM on 10/14/2022

PHY 711 – Assignment #10

September 19, 2022

1. This problem uses a simplification of the ideas of Nosé. Consider a Lagrangian describing one dimensional motion of a particle of mass m in a mechanical potential $V(x)$ with an addition time dependent function $s(t)$ and extra constants Q and K having the form

$$L(x, \dot{x}, s, \dot{s}) = \frac{1}{2} m s^2 \dot{x}^2 - V(x) + Q\dot{s}^2 - K \ln(s).$$

   (a) Write down the the Euler-Lagrange equations for this system. (It is not necessary to solve them.)

   (b) Assuming that the time average of $\ddot{s} = 0$ ($\langle \ddot{s} \rangle = 0$), show that the average kinetic energy of the system is proportional to the constant K.

   (c) Find the Hamiltonian for this system in canonical form $H(x, p_x, s, p_s)$.

With the Hamiltonian formalism comes the notion of phase space --

$$H = H\left(\{q_\sigma(t)\},\{p_\sigma(t)\},t\right)$$

$$\frac{dq_\sigma}{dt} = \frac{\partial H}{\partial p_\sigma} \quad \Rightarrow \text{constant } q_\sigma \text{ if } \frac{\partial H}{\partial p_\sigma} = 0$$

$$\frac{dp_\sigma}{dt} = -\frac{\partial H}{\partial q_\sigma} \quad \Rightarrow \text{constant } p_\sigma \text{ if } \frac{\partial H}{\partial q_\sigma} = 0$$

$$\frac{dH}{dt} = \sum_\sigma \left(\frac{\partial H}{\partial q_\sigma}\dot{q}_\sigma + \frac{\partial H}{\partial p_\sigma}\dot{p}_\sigma \right) + \frac{\partial H}{\partial t}$$

Similarly for an arbitrary function : $F = F\left(\{q_\sigma(t)\},\{p_\sigma(t)\},t\right)$

$$\frac{dF}{dt} = \sum_\sigma \left(\frac{\partial F}{\partial q_\sigma}\dot{q}_\sigma + \frac{\partial F}{\partial p_\sigma}\dot{p}_\sigma \right) + \frac{\partial F}{\partial t} = \sum_\sigma \left(\frac{\partial F}{\partial q_\sigma}\frac{\partial H}{\partial p_\sigma} - \frac{\partial F}{\partial p_\sigma}\frac{\partial H}{\partial q_\sigma} \right) + \frac{\partial F}{\partial t}$$

For an arbitrary function: $F = F\left(\{q_\sigma(t)\},\{p_\sigma(t)\},t\right)$

$$\frac{dF}{dt} = \sum_\sigma \left(\frac{\partial F}{\partial q_\sigma}\dot{q}_\sigma + \frac{\partial F}{\partial p_\sigma}\dot{p}_\sigma \right) + \frac{\partial F}{\partial t} = \sum_\sigma \left(\frac{\partial F}{\partial q_\sigma}\frac{\partial H}{\partial p_\sigma} - \frac{\partial F}{\partial p_\sigma}\frac{\partial H}{\partial q_\sigma} \right) + \frac{\partial F}{\partial t}$$

Short and notation -- Poisson brackets

$$\left[F,G\right]_{PB} \equiv \sum_\sigma \left(\frac{\partial F}{\partial q_\sigma}\frac{\partial G}{\partial p_\sigma} - \frac{\partial F}{\partial p_\sigma}\frac{\partial G}{\partial q_\sigma} \right) = -\left[G,F\right]_{PB}$$

So that: $$\frac{dF}{dt} = \left[F,H\right]_{PB} + \frac{\partial F}{\partial t}$$

Poisson brackets -- continued:

$$[F,G]_{PB} \equiv \sum_{\sigma}\left(\frac{\partial F}{\partial q_\sigma}\frac{\partial G}{\partial p_\sigma}-\frac{\partial F}{\partial p_\sigma}\frac{\partial G}{\partial q_\sigma}\right)=-[G,F]_{PB}$$

Examples:

$$[x,x]_{PB}=0 \qquad [x,p_x]_{PB}=1 \qquad [x,p_y]_{PB}=0$$

$$[L_x,L_y]_{PB}=L_z$$

Liouville theorem

Let $D \equiv$ density of particles in phase space:

$$\frac{dD}{dt}=[D,H]_{PB}+\frac{\partial D}{\partial t}=0$$

In the following slides we will justify this statement using several approaches.

Phase space

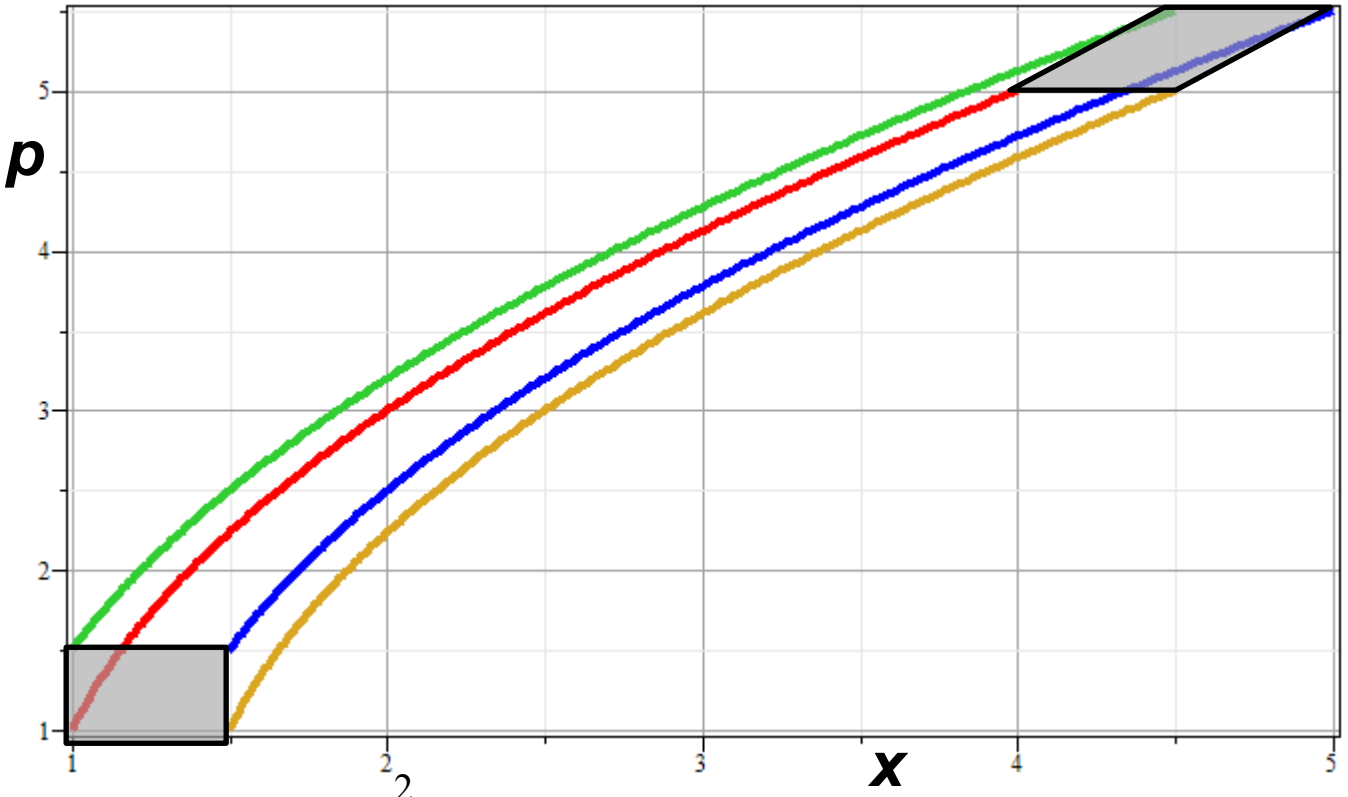
Phase space is defined at the set of all coordinates and momenta of a system:

$$\left(\{q_\sigma(t)\},\{p_\sigma(t)\}\right)$$

For a d dimensional system with N particles, the phase space corresponds to $2dN$ degrees of freedom.

The notion of density of particles in phase space is simply the ratio of the number of particles per unit phase space volume. It seems reasonable that under conditions where there are no sources or sinks for the particles, that the density should remain constant in time.

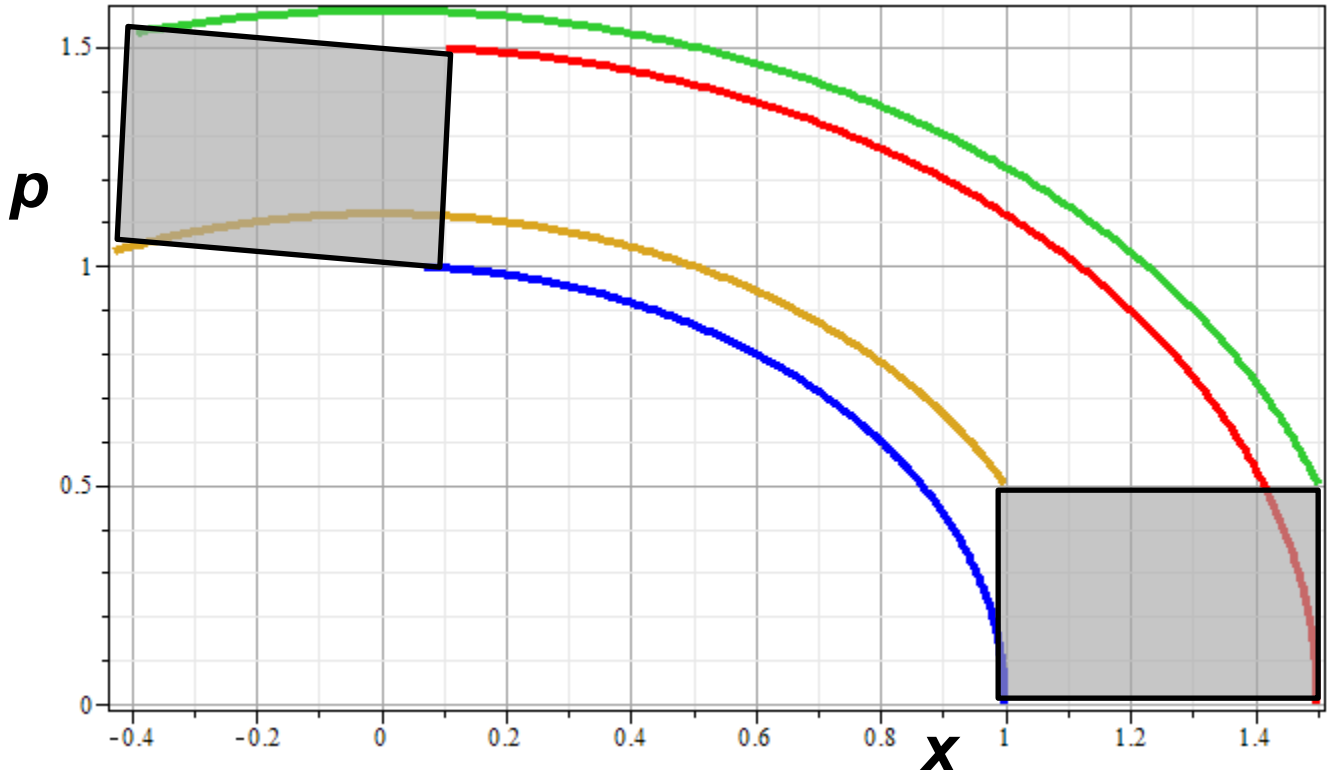
Phase space diagram for one-dimensional motion due to constant force



$$H(x,p) = \frac{p^2}{2m} - F_0 x \qquad \dot{p} = F_0 \qquad \dot{x} = \frac{p}{m}$$

$$p_i(t) = p_{0i} + F_0 t \qquad x_i(t) = x_{0i} + \frac{p_{0i}}{m} t + \frac{1}{2} F_0 t^2$$

Phase space diagram for one-dimensional motion due to spring force



$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \qquad \dot{p} = -m\omega^2 x \qquad \dot{x} = \frac{p}{m}$$

$$p_i(t) = p_{0i}\cos(\omega t + \theta_{0i}) \qquad x_i(t) = \frac{p_{0i}}{m\omega}\sin(\omega t + \theta_{0i})$$

Liouville's Theorem (1838)

The density of representative points in phase space corresponding to the motion of a system of particles remains constant during the motion.

Joseph Liouville

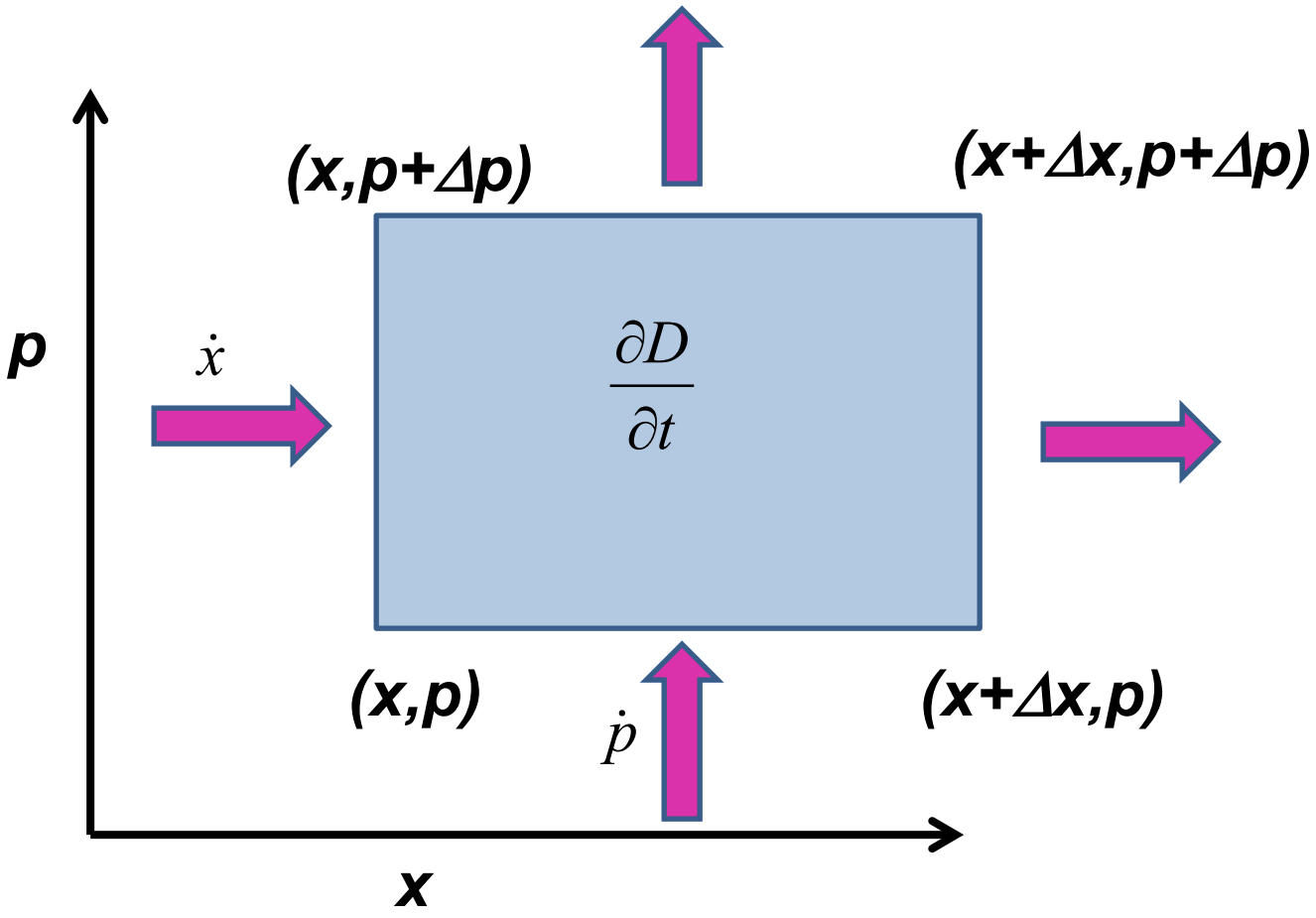
lived from 1809 to 1882

Denote the density of particles in phase space: $D = D\left(\{q_\sigma(t)\}, \{p_\sigma(t)\}, t\right)$

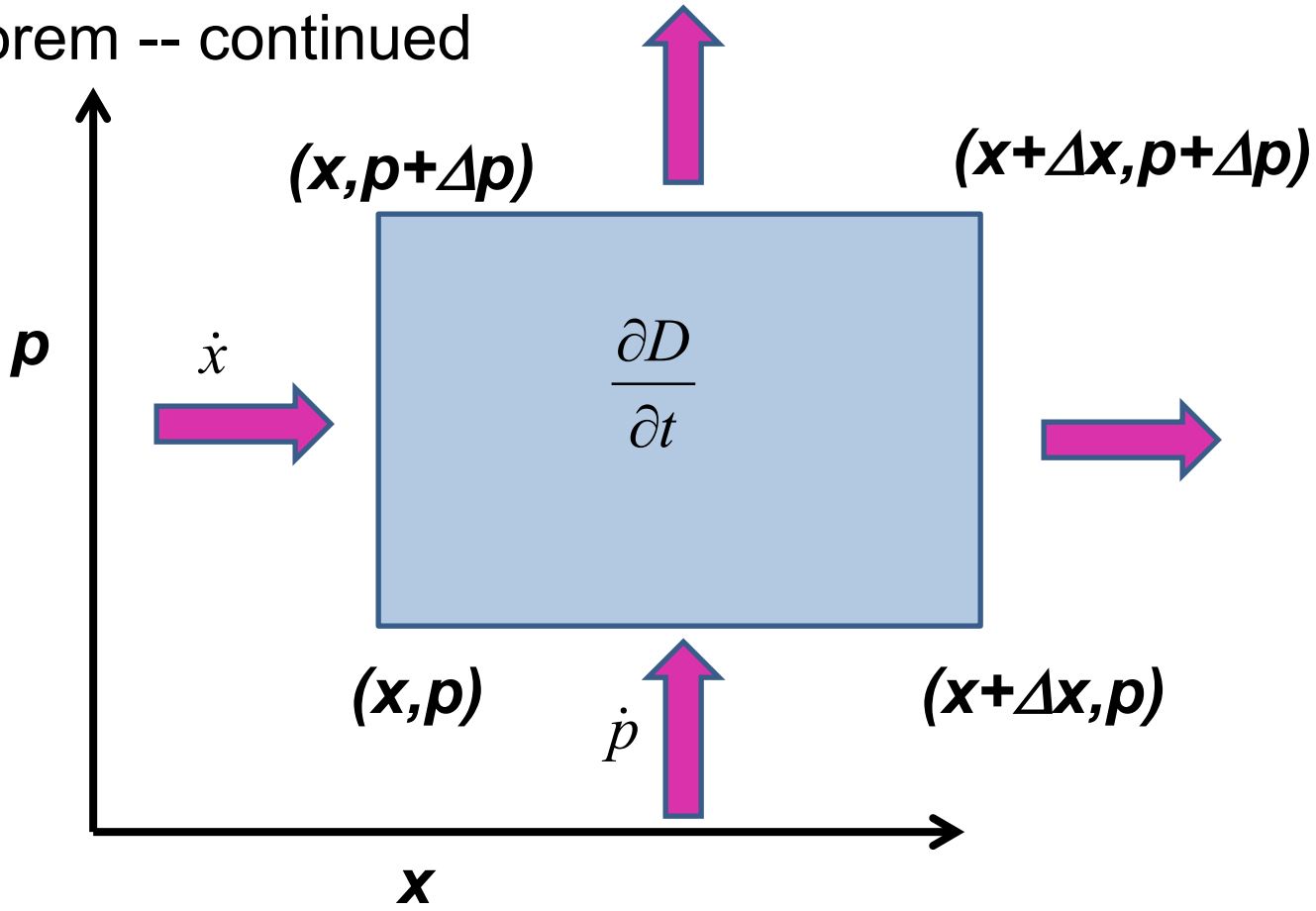
$$\frac{dD}{dt} = \sum_\sigma \left(\frac{\partial D}{\partial q_\sigma} \dot{q}_\sigma + \frac{\partial D}{\partial p_\sigma} \dot{p}_\sigma \right) + \frac{\partial D}{\partial t}$$

According to Liouville's theorem: $\frac{dD}{dt} = 0$

Liouville's theorem



Liouville's theorem -- continued

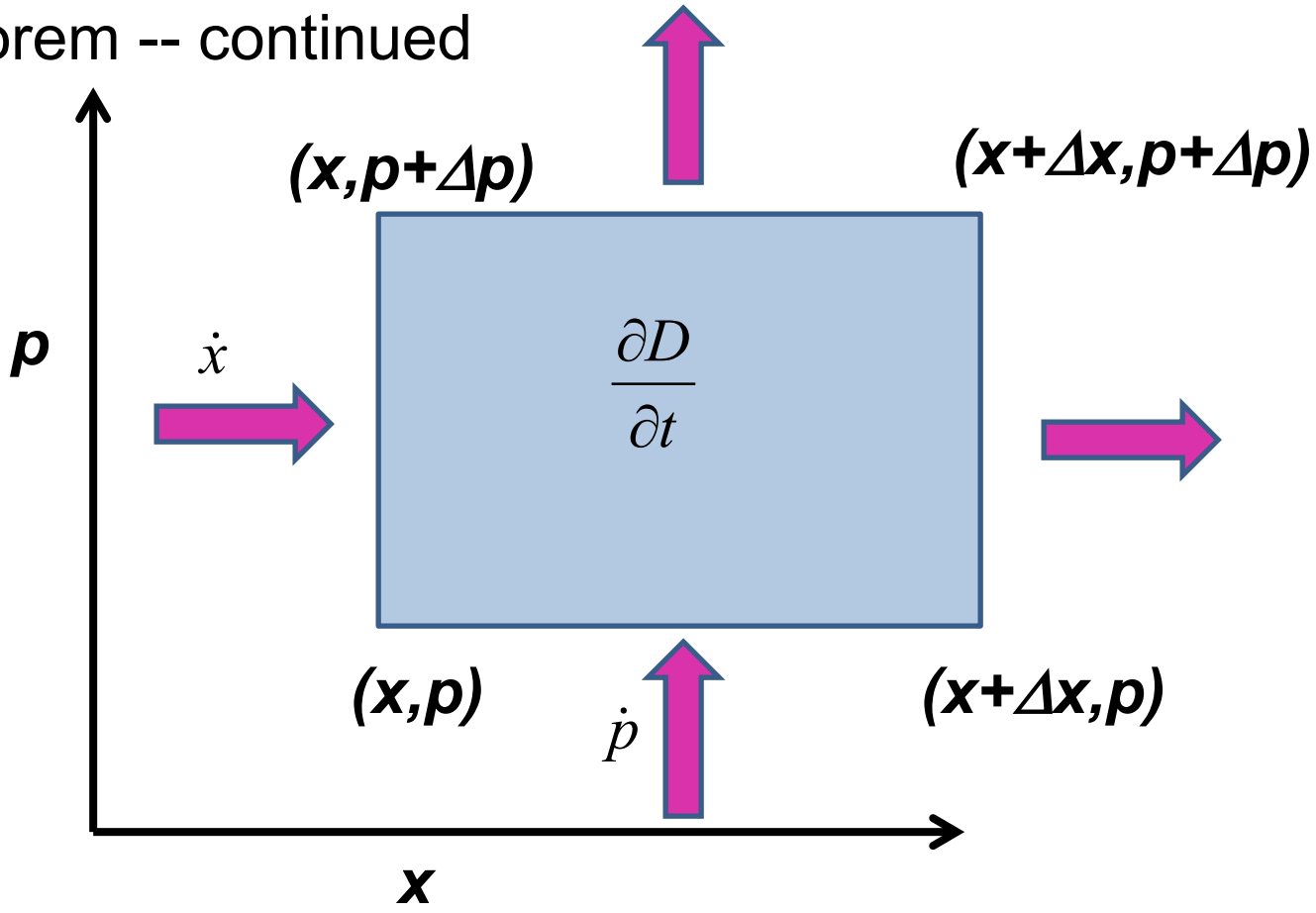


$$\frac{\partial D}{\partial t} \Rightarrow \text{time rate of change of particles within volume}$$

$$= \text{time rate of particle entering minus particles leaving}$$

$$= -\frac{\partial D}{\partial x}\dot{x} - \frac{\partial D}{\partial p}\dot{p}$$

Liouville's theorem -- continued



$$\frac{\partial D}{\partial t} = -\frac{\partial D}{\partial x}\dot{x} - \frac{\partial D}{\partial p}\dot{p}$$

$$\frac{\partial D}{\partial t} + \frac{\partial D}{\partial x}\dot{x} + \frac{\partial D}{\partial p}\dot{p} = 0 = \frac{dD}{dt}$$

Review:

Liouville's theorem:

Imagine a collection of particles obeying the Canonical equations of motion in phase space.

Let D denote the "distribution" of particles in phase space:

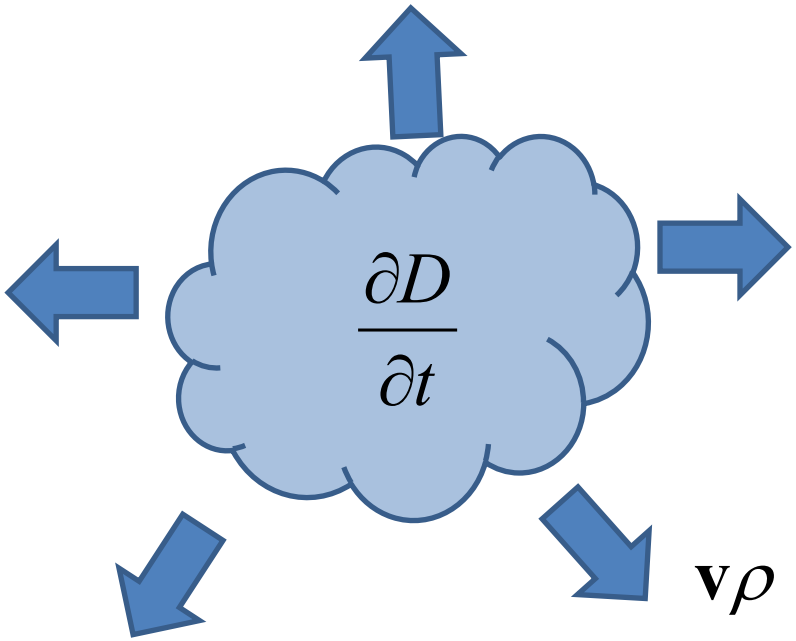
$$D = D\left(\{q_1 \cdots q_{3N}\}, \{p_1 \cdots p_{3N}\}, t\right)$$

Liouville's theorm shows that:

$$\frac{dD}{dt} = 0 \qquad \Rightarrow D \text{ is constant in time}$$

Note that we are assuming that no particles are created or destroyed in these processes.

Another proof of Liouville's theorem:



Continuity equation :

$$\frac{\partial D}{\partial t} = -\nabla \cdot (\mathbf{v} D)$$

Note : in this case, the velocity is the $6N$ dimensional vector :

$$\mathbf{v} = (\dot{\mathbf{r}}_1, \dot{\mathbf{r}}_2, \ldots \dot{\mathbf{r}}_N, \dot{\mathbf{p}}_1, \dot{\mathbf{p}}_2, \ldots \dot{\mathbf{p}}_N)$$

We also have a $6N$ dimensional gradient :

$$\nabla = (\nabla_{\mathbf{r}_1}, \nabla_{\mathbf{r}_2}, \ldots \nabla_{\mathbf{r}_N}, \nabla_{\mathbf{p}_1}, \nabla_{\mathbf{p}_2}, \ldots \nabla_{\mathbf{p}_N})$$

$$\frac{\partial D}{\partial t} = -\nabla \cdot (\mathbf{v} D)$$

$$= -\sum_{j=1}^{3N} \left[\frac{\partial}{\partial q_j} (\dot{q}_j D) + \frac{\partial}{\partial p_j} (\dot{p}_j D) \right]$$

$$= -\sum_{j=1}^{3N} \left[\frac{\partial D}{\partial q_j} \dot{q}_j + \frac{\partial D}{\partial p_j} \dot{p}_j \right] - D \sum_{j=1}^{3N} \left[\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} \right]$$

$$\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} = \frac{\partial^2 H}{\partial q_j \partial p_j} + \left(- \frac{\partial^2 H}{\partial p_j \partial q_j} \right) = 0$$

0

$$\frac{\partial D}{\partial t} = -\sum_{j=1}^{3N}\left[\frac{\partial D}{\partial q_j}\dot{q}_j + \frac{\partial D}{\partial p_j}\dot{p}_j\right] - D\sum_{j=1}^{3N}\left[\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j}\right]$$

$$\frac{\partial D}{\partial t} = -\sum_{j=1}^{3N}\left[\frac{\partial D}{\partial q_j}\dot{q}_j + \frac{\partial D}{\partial p_j}\dot{p}_j\right]$$

$$\Rightarrow \frac{\partial D}{\partial t} + \sum_{j=1}^{3N}\left[\frac{\partial D}{\partial q_j}\dot{q}_j + \frac{\partial D}{\partial p_j}\dot{p}_j\right] = \frac{dD}{dt} = 0$$

$$\frac{dD}{dt} = 0$$

Importance of Liouville's theorem to statistical mechanical analysis:

In statistical mechanics, we need to evaluate the probability of various configurations of particles. The fact that the density of particles in phase space is constant in time, implies that each point in phase space is equally probable and that the time average of the evolution of a system can be determined by an average of the system over phase space volume. Computationally this can be approximated using molecular dynamics or sampling methods.

Modern usage of Lagrangian and Hamiltonian formalisms

J. Chem. Physics **72** 2384-2393 (1980)

Molecular dynamics simulations at constant pressure and/or temperature[a)]

Hans C. Andersen

Department of Chemistry, Stanford University, Stanford, California 94305
(Received 10 July 1979; accepted 31 October 1979)

In the molecular dynamics simulation method for fluids, the equations of motion for a collection of particles in a fixed volume are solved numerically. The energy, volume, and number of particles are constant for a particular simulation, and it is assumed that time averages of properties of the simulated fluid are equal to microcanonical ensemble averages of the same properties. In some situations, it is desirable to perform simulations of a fluid for particular values of temperature and/or pressure or under conditions in which the energy and volume of the fluid can fluctuate. This paper proposes and discusses three methods for performing molecular dynamics simulations under conditions of constant temperature and/or pressure, rather than constant energy and volume. For these three methods, it is shown that time averages of properties of the simulated fluid are equal to averages over the isoenthalpic–isobaric, canonical, and isothermal–isobaric ensembles. Each method is a way of describing the dynamics of a certain number of particles in a volume element of a fluid while taking into account the influence of surrounding particles in changing the energy and/or density of the simulated volume element. The influence of the surroundings is taken into account without introducing unwanted surface effects. Examples of situations where these methods may be useful are discussed.

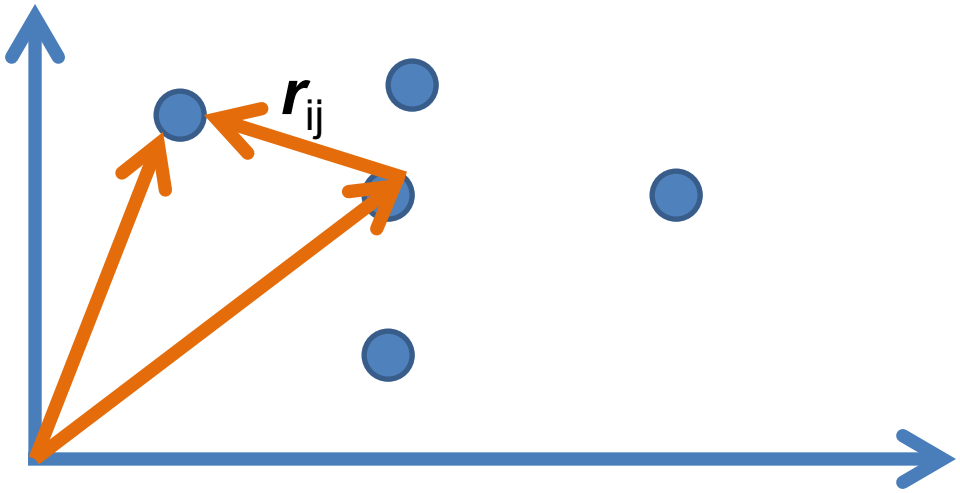
"Molecular dynamics" is a subfield of computational physics focused on analyzing the motions of atoms in fluids and solids with the goal of relating the atomistic and macroscopic properties of materials. Ideally molecular dynamics calculations can numerically realize the statistical mechanics viewpoint.

Imagine that the generalized coordinates $\{q_\sigma(t)\}$ represent N atoms, each with 3 spacial coordinates:

$$L = L\left(\{q_\sigma(t)\},\{\dot{q}_\sigma(t)\},t\right) = T - U$$

For simplicity, it is assumed that the potential interaction is a sum of pairwise interactions:

$$U(r^N) = \sum_{i<j} u(r_{ij}) \,. \qquad (2.1)$$



$$L = L\left(\{\mathbf{r}_i(t)\},\{\dot{\mathbf{r}}_i(t)\}\right) = \sum_i \tfrac{1}{2} m_i \left|\dot{\mathbf{r}}_i\right|^2 - \sum_{i<j} u\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)$$

➔From this Lagrangian, can find the 3N coupled 2nd order differential equations of motion and/or find the corresponding Hamiltonian, representing the system at constant energy, volume, and particle number N (N,V,E ensemble).

Lagrangian and Hamiltonian forms

$$L = L\left(\{\mathbf{r}_i(t)\},\{\dot{\mathbf{r}}_i(t)\}\right) = \sum_i \tfrac{1}{2} m_i \left|\dot{\mathbf{r}}_i\right|^2 - \sum_{i<j} u\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)$$

Euler-Lagrange equations:

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = -\sum_{i<j} u'\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) \frac{\mathbf{r}_i - \mathbf{r}_j}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

Hamiltonian formulation:

$$\mathbf{p}_i = m_i \dot{\mathbf{r}}_i$$

$$H = \sum_i \frac{\left|\mathbf{p}_i\right|^2}{2m_i} + \sum_{i<j} u\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)$$

Canonical equations:

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} \qquad \frac{d\mathbf{p}_i}{dt} = -\sum_{i<j} u'\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) \frac{\mathbf{r}_i - \mathbf{r}_j}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

Digression on numerical evaluation of differential equations

Example differential equation (one dimension);

$$\frac{d^2x}{dt^2} = f(t) \qquad \text{Let} \quad t = nh \qquad (n = 1, 2, 3\ldots)$$

$$x_n \equiv x(nh); \qquad f_n \equiv f(nh)$$

Euler's method :

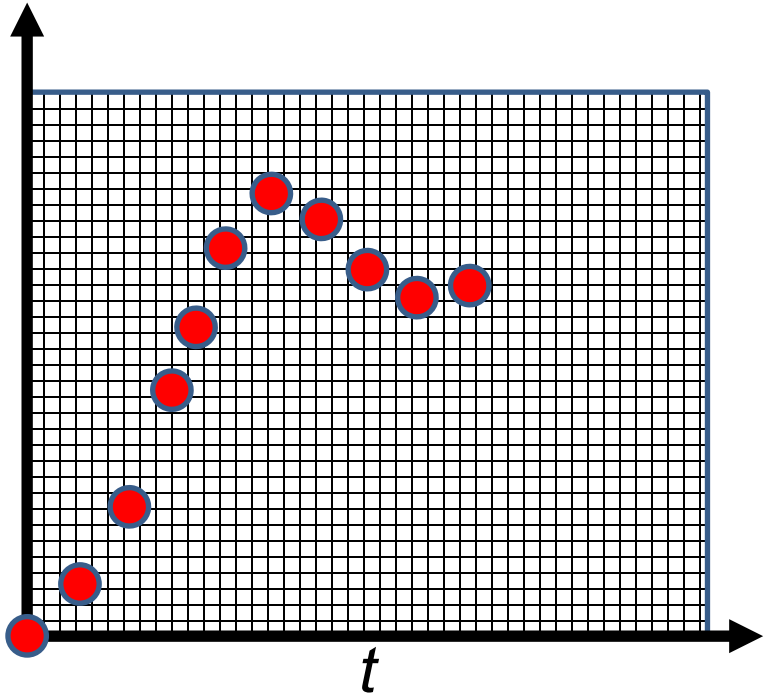
$$x_{n+1} = x_n + hv_n + \frac{1}{2}h^2 f_n$$

$$v_{n+1} = v_n + hf_n$$

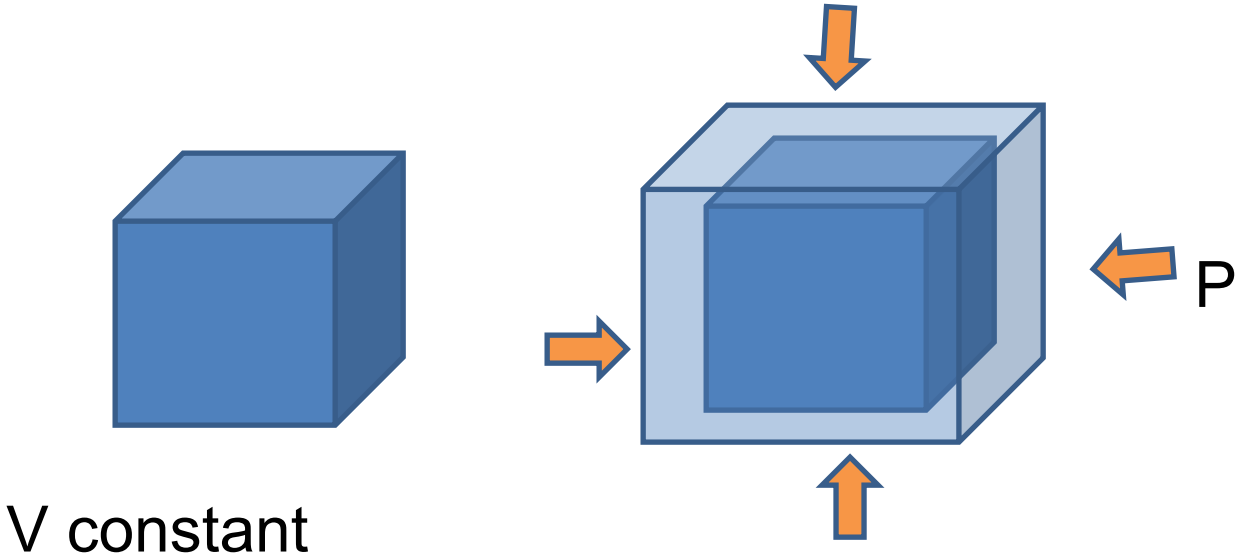
Velocity Verlet algorithm :

$$x_{n+1} = x_n + hv_n + \frac{1}{2}h^2 f_n$$

$$v_{n+1} = v_n + \frac{1}{2}h(f_n + f_{n+1})$$



H. C. Andersen wanted to adapt the formalism for modeling an (N,V,E) ensemble to one which could model a system at constant pressure (P).



Andersen's clever transformation :

Let $\boldsymbol{\rho}_i = \mathbf{r}_i / Q^{1/3}$

$$L = L\left(\{\mathbf{r}_i(t)\},\{\dot{\mathbf{r}}_i(t)\}\right) = \sum_i \tfrac{1}{2} m_i \left|\dot{\mathbf{r}}_i\right|^2 - \sum_{i<j} u\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)$$

$$L = L\left(\{\boldsymbol{\rho}_i(t)\},\{\dot{\boldsymbol{\rho}}_i(t)\},Q,\dot{Q}\right) = Q^{2/3}\sum_i \tfrac{1}{2} m_i \left|\dot{\boldsymbol{\rho}}_i\right|^2 - \sum_{i<j} u\left(Q^{1/3}\left|\boldsymbol{\rho}_i - \boldsymbol{\rho}_j\right|\right) + \tfrac{1}{2} M\dot{Q}^2 - \alpha Q$$

PV contribution to potential energy

kinetic energy of "balloon"

$$L = L\left(\{\boldsymbol{\rho}_i(t)\},\{\dot{\boldsymbol{\rho}}_i(t)\},Q,\dot{Q}\right) = Q^{2/3}\sum_i \tfrac{1}{2}m_i\left|\dot{\boldsymbol{\rho}}_i\right|^2 - \sum_{i<j} u\left(Q^{1/3}\left|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j\right|\right) + \tfrac{1}{2}M\dot{Q}^2 - \alpha Q$$

$$\boldsymbol{\pi}_i = \frac{\partial L}{\partial \dot{\boldsymbol{\rho}}_i} = mQ^{2/3}\dot{\boldsymbol{\rho}}_i$$

$$\Pi = \frac{\partial L}{\partial \dot{Q}} = M\dot{Q}$$

$$H = \sum_i \frac{\left|\boldsymbol{\pi}_i\right|^2}{2m_iQ^{2/3}} + \sum_{i<j} u\left(Q^{1/3}\left|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j\right|\right) + \frac{\Pi^2}{2M} + \alpha Q$$

$$\frac{d\boldsymbol{\rho}_i}{dt} = \frac{\boldsymbol{\pi}_i}{m_iQ^{2/3}} \qquad \frac{dQ}{dt} = \frac{\Pi}{M}$$

$$\frac{d\boldsymbol{\pi}_i}{dt} = -Q^{1/3}\sum_{i<j} u'\left(Q^{1/3}\left|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j\right|\right)\frac{\boldsymbol{\rho}_i-\boldsymbol{\rho}_j}{\left|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j\right|}$$

$$\frac{d\Pi}{dt} = \frac{2}{3Q}\sum_i \frac{\left|\boldsymbol{\pi}_i\right|^2}{2m_iQ^{2/3}} - \frac{1}{3Q^{2/3}}\sum_{i<j} u'\left(Q^{1/3}\left|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j\right|\right)\left|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j\right| - \alpha$$

Relationship between system representations

Scaled		Original
$Q(t)$	$=$	$V(t)$
$Q^{1/3}\boldsymbol{\rho}_i(t)$	$=$	$\mathbf{r}_i(t)$
$\boldsymbol{\pi}_i / Q^{1/3}$	$=$	$\mathbf{p}_i$

Equations of motion in "original" coordinates:

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} + \frac{1}{3}\mathbf{r}_i \frac{d\ln V}{dt}$$

$$\frac{d\mathbf{p}_i}{dt} = -\sum_{j<i} \frac{\mathbf{r}_i - \mathbf{r}_j}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} u'\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) - \frac{1}{3}\mathbf{p}_i \frac{d\ln V}{dt}$$

$$M\frac{d^2V}{dt^2} = -\alpha + \frac{1}{V}\left(\frac{2}{3}\sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{m_i} - \frac{1}{3}\sum_{j<i}\left|\mathbf{r}_i - \mathbf{r}_j\right| u'\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)\right)$$

Physical interpretation:

$\alpha \Leftrightarrow$ Imposed (target) pressure

$$\frac{1}{V}\left(\frac{2}{3}\sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{m_i} - \frac{1}{3}\sum_{j<i}\left|\mathbf{r}_i - \mathbf{r}_j\right| u'\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)\right) \Leftrightarrow \text{Internal pressure of system}$$

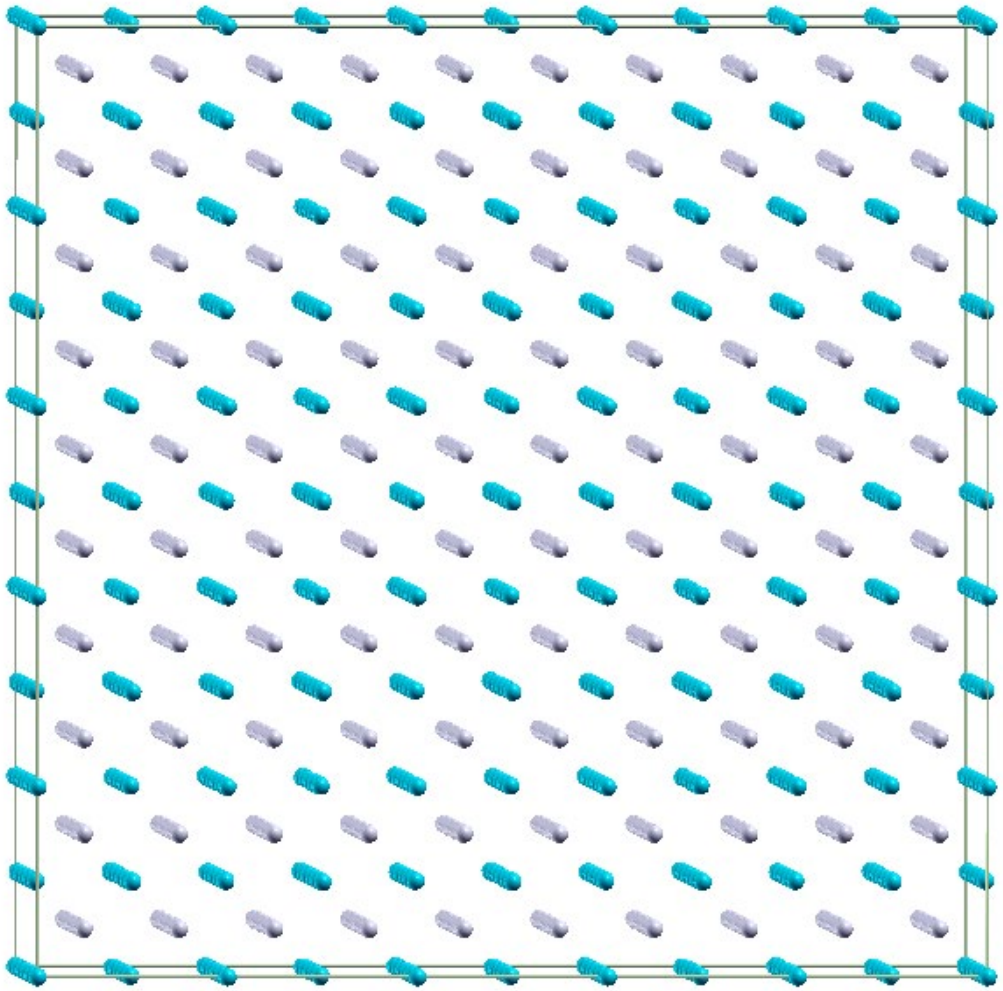
Time dependence

$$M\frac{d^2V}{dt^2} = -\alpha + \frac{1}{V}\left(\frac{2}{3}\sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{m_i} - \frac{1}{3}\sum_{j<i}\left|\mathbf{r}_i - \mathbf{r}_j\right| u'\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)\right)$$

Averaged over many time steps:

$$\left\langle M\frac{d^2V}{dt^2}\right\rangle = 0 \quad \Rightarrow \quad \alpha = \left\langle \frac{1}{V}\left(\frac{2}{3}\sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{m_i} - \frac{1}{3}\sum_{j<i}\left|\mathbf{r}_i - \mathbf{r}_j\right| u'\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)\right)\right\rangle$$

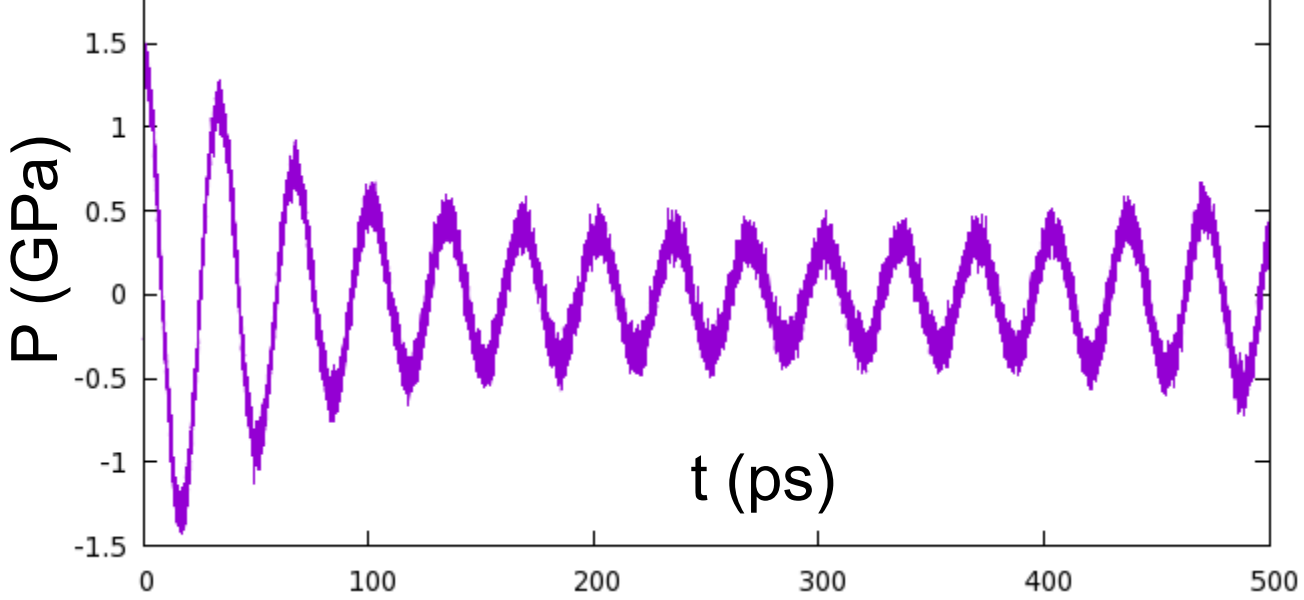
Example simulation for NPT molecular dynamics simulation of Li_2O using 1500 atoms with α=0



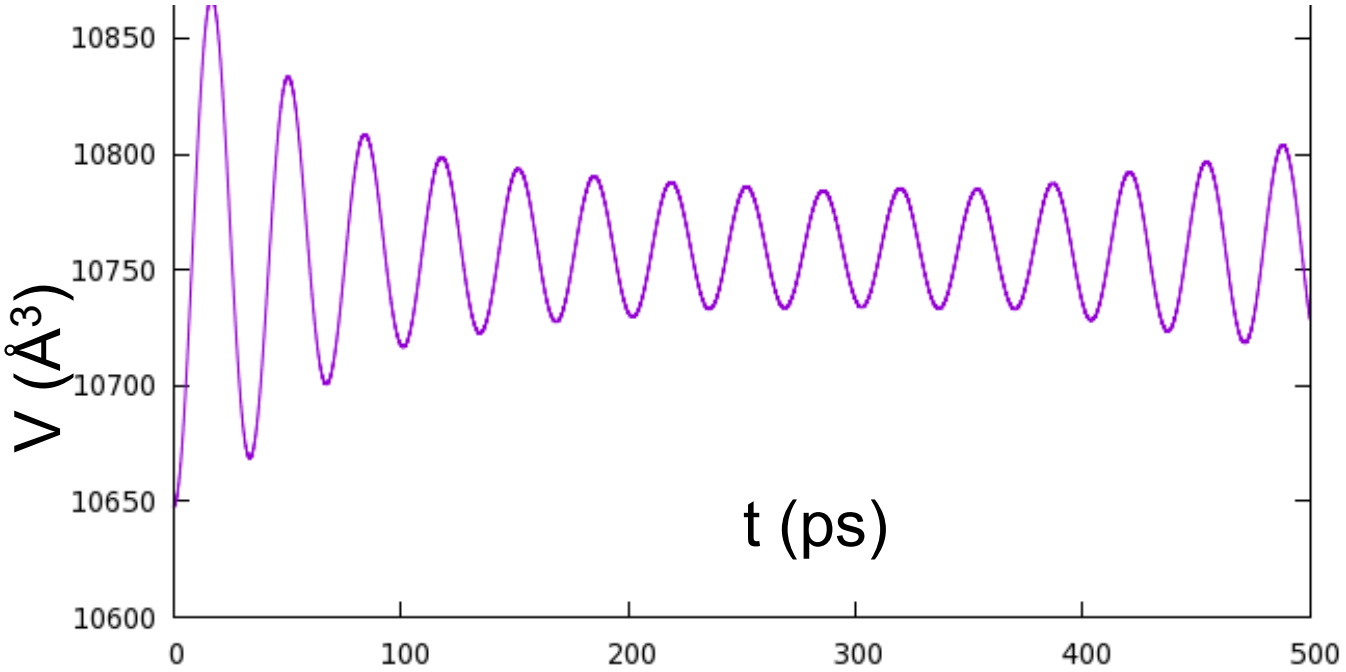
Pair interaction potential

$$u_{ij}(r_{ij}) = A_{ij} e^{-r_{ij}/\rho_{ij}} - \frac{C_{ij}}{r_{ij}^{\,6}} + \frac{q_i q_j}{r_{ij}}$$

Use LAMMPS code
http://LAMMPS.sandia.gov


P (GPa)
1.5
1
0.5
0
-0.5
-1
-1.5
0
100
200
300
400
500
t (ps)

α=0


V (Å^3)
10850
10800
10750
10700
10650
10600
0
100
200
300
400
500
t (ps)

MOLECULAR PHYSICS, 1984, VOL. 52, NO. 2, 255–268

A molecular dynamics method for simulations in the canonical ensemble†

by SHŪICHI NOSÉ‡
Division of Chemistry, National Research Council Canada,
Ottawa, Ontario, Canada K1A 0R6

(*Received* 3 *October* 1983 ; *accepted* 28 *November* 1983)

A molecular dynamics simulation method which can generate configurations belonging to the canonical (T, V, N) ensemble or the constant temperature constant pressure (T, P, N) ensemble, is proposed. The physical system of interest consists of N particles (f degrees of freedom), to which an external, macroscopic variable and its conjugate momentum are added. This device allows the total energy of the physical system to fluctuate. The equilibrium distribution of the energy coincides with the

Nose′s Lagrangian:

$$L(\{\mathbf{r}_i\}, s, \{\dot{\mathbf{r}}_i\}, \dot{s}) = \frac{1}{2}\sum_i m_i s^2 \dot{\mathbf{r}}_i^2 + \frac{1}{2} Q \dot{s}^2 - \phi(\{\mathbf{r}_i\}) - (f+1) kT_{eq} \ln s$$

velocity scaling

fictitious mass

Equations of motion:

$$\frac{d}{dt}(m_i s^2 \dot{\mathbf{r}}_i) = -\frac{\partial \phi}{\partial \mathbf{r}_i},$$

$$\ddot{\mathbf{r}}_i = -\frac{1}{m_i s^2}\frac{\partial \phi}{\partial \mathbf{r}_i} - \frac{2\dot{s}}{s}\dot{\mathbf{r}}_i.$$

$$Q\ddot{s} = \sum_i m_i s \dot{\mathbf{r}}_i^2 - \frac{(f+1)kT_{eq}}{s}.$$

Time averaged relationships

$$Q\ddot{s} = \sum_i m_i s\dot{\mathbf{r}}_i^2 - \frac{(f+1)kT_{eq}}{s}$$

$$\langle Q\ddot{s} \rangle = 0 \quad \Rightarrow \left\langle \sum_i m_i s\dot{\mathbf{r}}_i^2 \right\rangle = \left\langle \frac{(f+1)kT_{eq}}{s} \right\rangle$$

$$\left\langle \frac{\sum_i m_i s^2 \dot{\mathbf{r}}_i^2}{s} \right\rangle = (f+1)kT_{eq} \left\langle \frac{1}{s} \right\rangle$$

Time averaged relationships

$$\left\langle \frac{\sum_i m_i s^2 \dot{\mathbf{r}}_i^2}{s} \right\rangle = (f+1) k T_{\text{eq}} \left\langle \frac{1}{s} \right\rangle$$

Hamiltonian

$$\mathscr{H}_1 = \sum_i \frac{\mathbf{p}_i^2}{2 m_i s^2} + \phi(\mathbf{r}) + \frac{p_s^2}{2Q} + (f+1) k T_{\text{eq}} \ln s,$$

where $\mathbf{p}_i = m_i s^2 \dot{\mathbf{r}}_i$ $\qquad p_s = Q\dot{s}$

In statistical mechanics, the thermodynamic functions can be analyzed in terms of a partition function. A canonical partition function for a system with N particles at a temperature T_{eq} can be determined from the phase space integral:

$$Z_c = \frac{1}{N!}\int d^{3N}\overline{r}\; d^{3N}\overline{p}\; e^{-\mathcal{H}(\{\overline{\mathbf{r}}_i\},\{\overline{\mathbf{p}}_i\})/kT_{eq}}$$

where $\mathcal{H}(\{\overline{\mathbf{r}}_i\},\{\overline{\mathbf{p}}_i\}) \equiv \sum_i \frac{\overline{\mathbf{p}}_i^2}{2m_i} + \phi(\{\overline{\mathbf{r}}_i\})$

For such a canonical distribution the average value of a quantity $F(\{\overline{\mathbf{r}}_i\},\{\overline{\mathbf{p}}_i\})$ is given by

$$\left\langle F(\{\overline{\mathbf{r}}_i\},\{\overline{\mathbf{p}}_i\})\right\rangle_c = \frac{1}{Z_c}\frac{1}{N!}\int d^{3N}\overline{r}\; d^{3N}\overline{p}\; e^{-\mathcal{H}(\{\overline{\mathbf{r}}_i\},\{\overline{\mathbf{p}}_i\})/kT_{eq}} F(\{\overline{\mathbf{r}}_i\},\{\overline{\mathbf{p}}_i\})$$

Nose' was able to show that his effective Hamiltonian well approximates such a canonical distribution.

Relationship between Nose"s partition function and the canonical partition function:

$$Z = \frac{1}{(f+1)} \left(\frac{2\pi Q}{kT_{eq}} \right)^{1/2} \exp\left(E/kT_{eq}\right) Z_c.$$

constant factor

Some details:

Starting with partition for microcanonical ensemble:

$$Z = \frac{1}{N!} \int dp_s \int ds \int d\mathbf{p} \int d\mathbf{r}\, \delta\left(\sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \phi(\mathbf{r}) + \frac{p_s^2}{2Q} + (f+1)kT_{eq} \ln s - E \right).$$

$$Z = \frac{1}{N!}\int dp_s \int ds \int d\mathbf{p} \int d\mathbf{r}\ \delta\left(\sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \phi(\mathbf{r}) + \frac{p_s^2}{2Q} + (f+1)kT_{\text{eq}} \ln s - E\right).$$

Change variables: $\bar{\mathbf{p}}_i = \dfrac{\mathbf{p}_i}{s}$ $\qquad$ $\bar{\mathbf{r}}_i = \mathbf{r}_i$

$$Z = \frac{1}{N!}\int dp_s\ ds\ d^{3N}\bar{p}\ d^{3N}\bar{r}\ s^f \delta\left(\sum_i \frac{\bar{\mathbf{p}}_i^2}{2m_i} + \phi\left(\{\bar{\mathbf{r}}\}\right) + \frac{p_s^2}{2Q} + (f+1)kT_{eq} \ln s - E\right)$$

Note that $\int ds\ \delta(g(s)) = \int ds\ \dfrac{\delta(s-s_0)}{|g'(s_0)|}$

where $(f+1)kT_{eq} \ln s_0 = E - \dfrac{p_s^2}{2Q} - \sum_i \dfrac{\bar{\mathbf{p}}_i^2}{2m_i} - \phi\left(\{\bar{\mathbf{r}}_i\}\right)$

$$s_0 = \exp\left(\frac{E - \dfrac{p_s^2}{2Q} - \sum_i \dfrac{\bar{\mathbf{p}}_i^2}{2m_i} - \phi\left(\{\bar{\mathbf{r}}_i\}\right)}{(f+1)kT_{eq}}\right)$$

When the dust clears --

$$Z = \frac{1}{(f+1)} \left(\frac{2\pi Q}{kT_{eq}} \right)^{1/2} \exp\left(E/kT_{eq}\right) Z_c .$$

constant factor

➔The Nose' ensemble should sample phase space in the same way as does the canonical ensemble at T_{eq}.

From LAMMPS simulation (using modified Nose' algorithm)