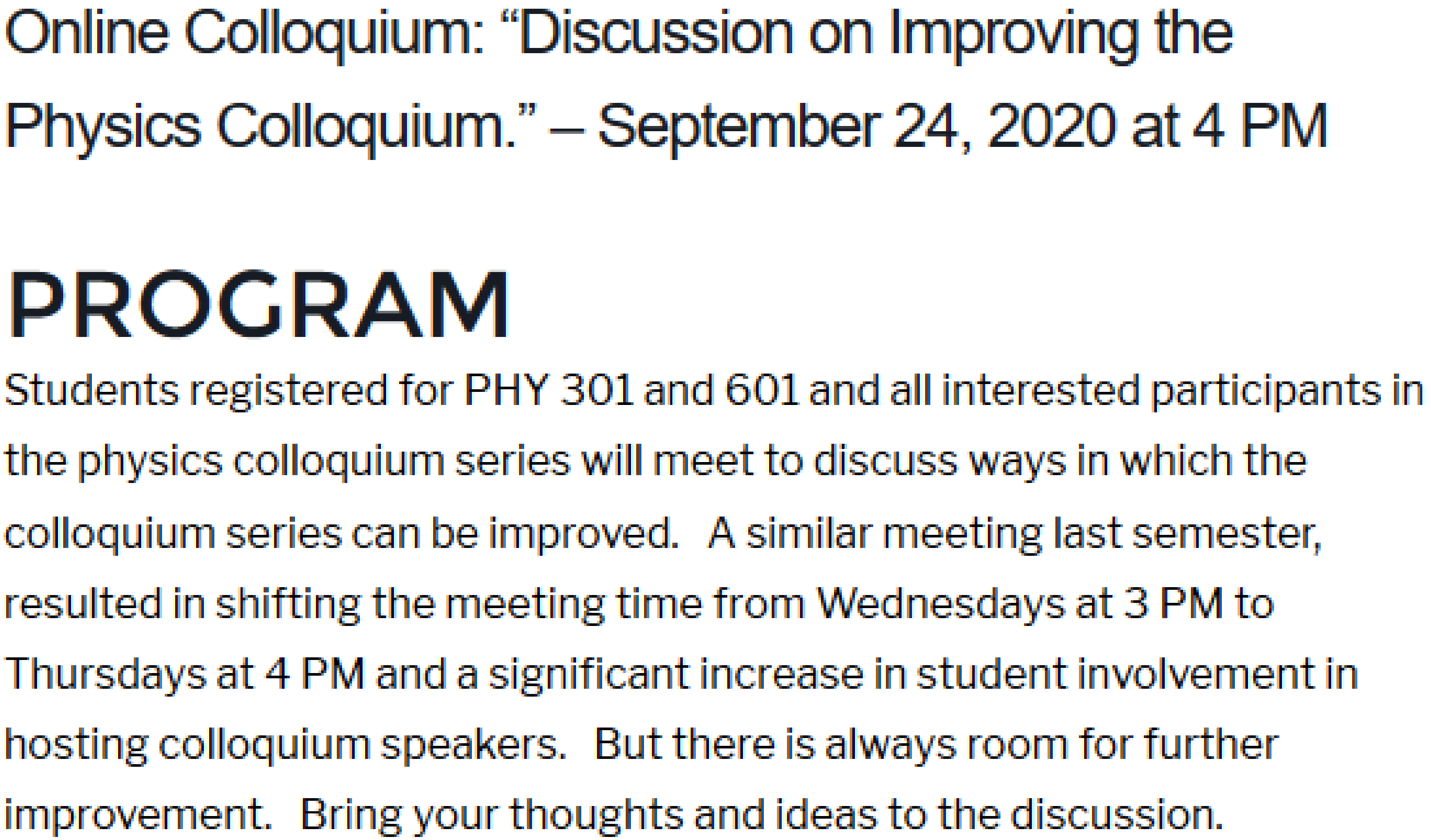
PHY 711 Classical Mechanics and Mathematical Methods

10-10:50 AM MWF Online or (occasional) in Olin 103

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

1. Phase space
2. Liouville theorem
3. Examples

Physics Colloquium – Thursday, September 24, 2020



Online Colloquium: "Discussion on Improving the Physics Colloquium." – September 24, 2020 at 4 PM

PROGRAM

Students registered for PHY 301 and 601 and all interested participants in the physics colloquium series will meet to discuss ways in which the colloquium series can be improved. A similar meeting last semester, resulted in shifting the meeting time from Wednesdays at 3 PM to Thursdays at 4 PM and a significant increase in student involvement in hosting colloquium speakers. But there is always room for further improvement. Bring your thoughts and ideas to the discussion.

-- Bring your ideas and suggestions --

Schedule for weekly one-on-one meetings

Nick – 11 AM Monday (ED/ST)
Tim – 9 AM Tuesday
Bamidele – 7 PM Tuesday
Zhi– 9 PM Tuesday
Jeanette – 11 AM Wednesday (this week only?)
Derek – 12 PM Friday

Your questions –
From Gao –

1. I have no questions about this lecture. Could you give a brief introduction to your research areas and their relationship with today's lecture if they have.

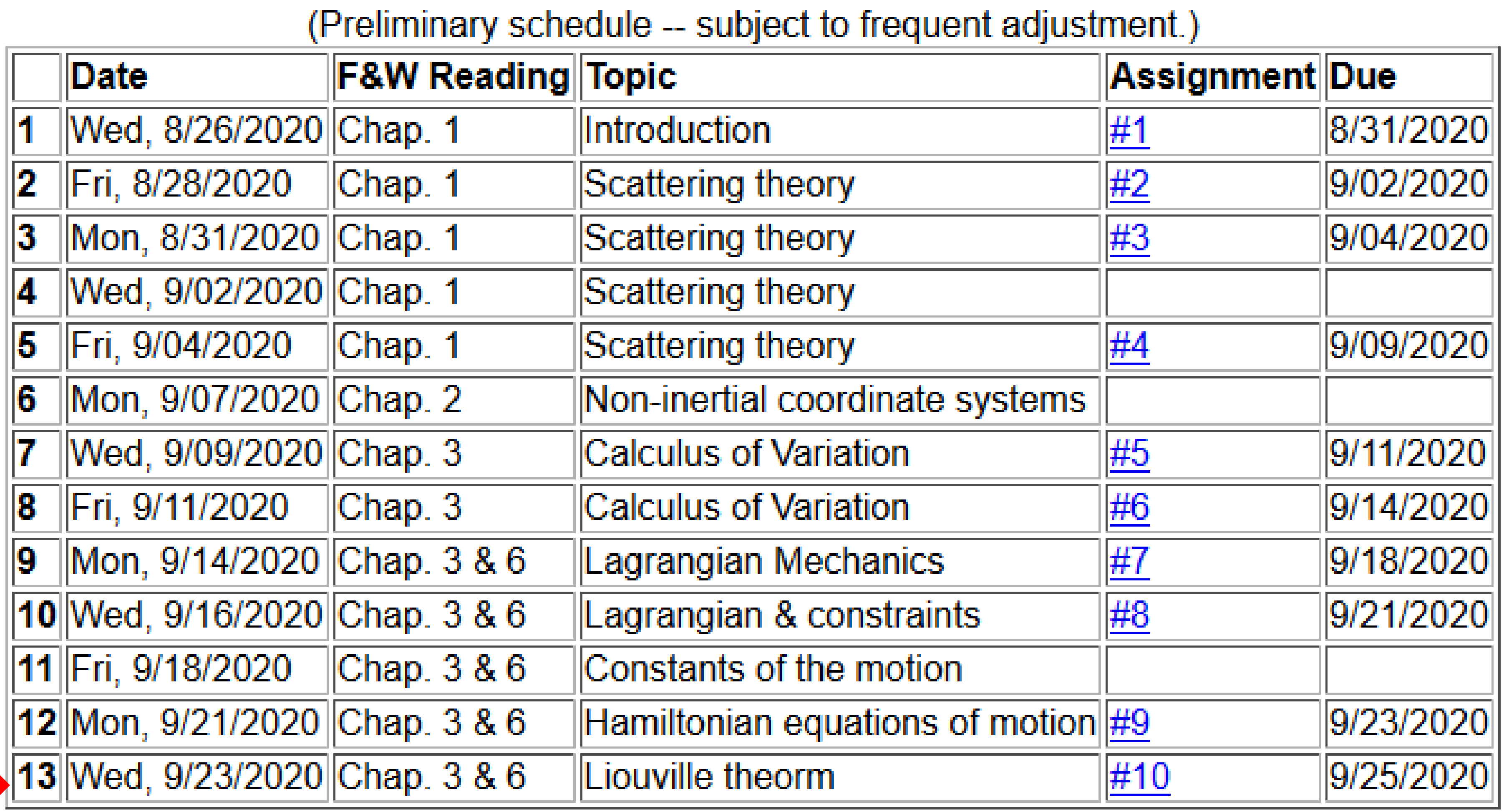
From Nick –

1. As of right now, Liouville's Theorem seems to make sense to me. But I wanted to ask, because I was intrigued by the numerical algorithms you slipped in there, are we going to be doing any more with numerical algorithms in this class? I was just wondering because I've seen Euler's method used in practice before but I have never used the Velocity Verlet algorithm.

From Tim –

1. For the homework due on Friday I am a little confused as to which Langrangian we are supposed to find the Hamiltonian for because all the Lagrangians I have found in the articles have already been solved.

Course schedule



(Preliminary schedule -- subject to frequent adjustment.)

	Date	F&W Reading	Topic	Assignment	Due
1	Wed, 8/26/2020	Chap. 1	Introduction	#1	8/31/2020
2	Fri, 8/28/2020	Chap. 1	Scattering theory	#2	9/02/2020
3	Mon, 8/31/2020	Chap. 1	Scattering theory	#3	9/04/2020
4	Wed, 9/02/2020	Chap. 1	Scattering theory		
5	Fri, 9/04/2020	Chap. 1	Scattering theory	#4	9/09/2020
6	Mon, 9/07/2020	Chap. 2	Non-inertial coordinate systems		
7	Wed, 9/09/2020	Chap. 3	Calculus of Variation	#5	9/11/2020
8	Fri, 9/11/2020	Chap. 3	Calculus of Variation	#6	9/14/2020
9	Mon, 9/14/2020	Chap. 3 & 6	Lagrangian Mechanics	#7	9/18/2020
10	Wed, 9/16/2020	Chap. 3 & 6	Lagrangian & constraints	#8	9/21/2020
11	Fri, 9/18/2020	Chap. 3 & 6	Constants of the motion		
12	Mon, 9/21/2020	Chap. 3 & 6	Hamiltonian equations of motion	#9	9/23/2020
13	Wed, 9/23/2020	Chap. 3 & 6	Liouville theorm	#10	9/25/2020

PHY 711 -- Assignment #10

Sept. 23, 2020

Continue reading Chapters 3 and 6 in **Fetter & Walecka**.

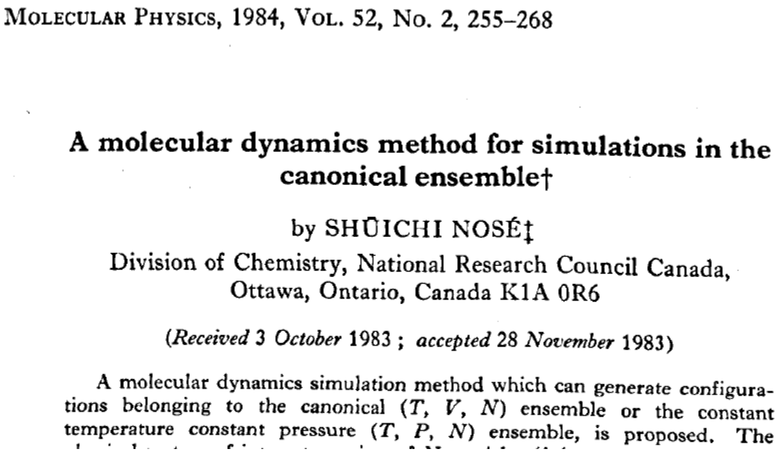
1. Choose one of the literature papers discussed class, by H. C. Andersen or by S. Nose' and derive to your satisfaction the Hamiltonian function from the given Lagrangian corresponding to constant pressure or constant temperature simulations, respectively.

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



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

Your question -- For the homework due on Friday I am a little confused as to which Langrangian we are supposed to find the Hamiltonian for because all the Lagrangians I have found in the articles have already been solved.

Comment -- It is true that in both papers a lot of the analysis is given in the texts. The point of the problem is for you to critically read one of the papers and make sure the derivations makes sense to you given what we have learned in this class.

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

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

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

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

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

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

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

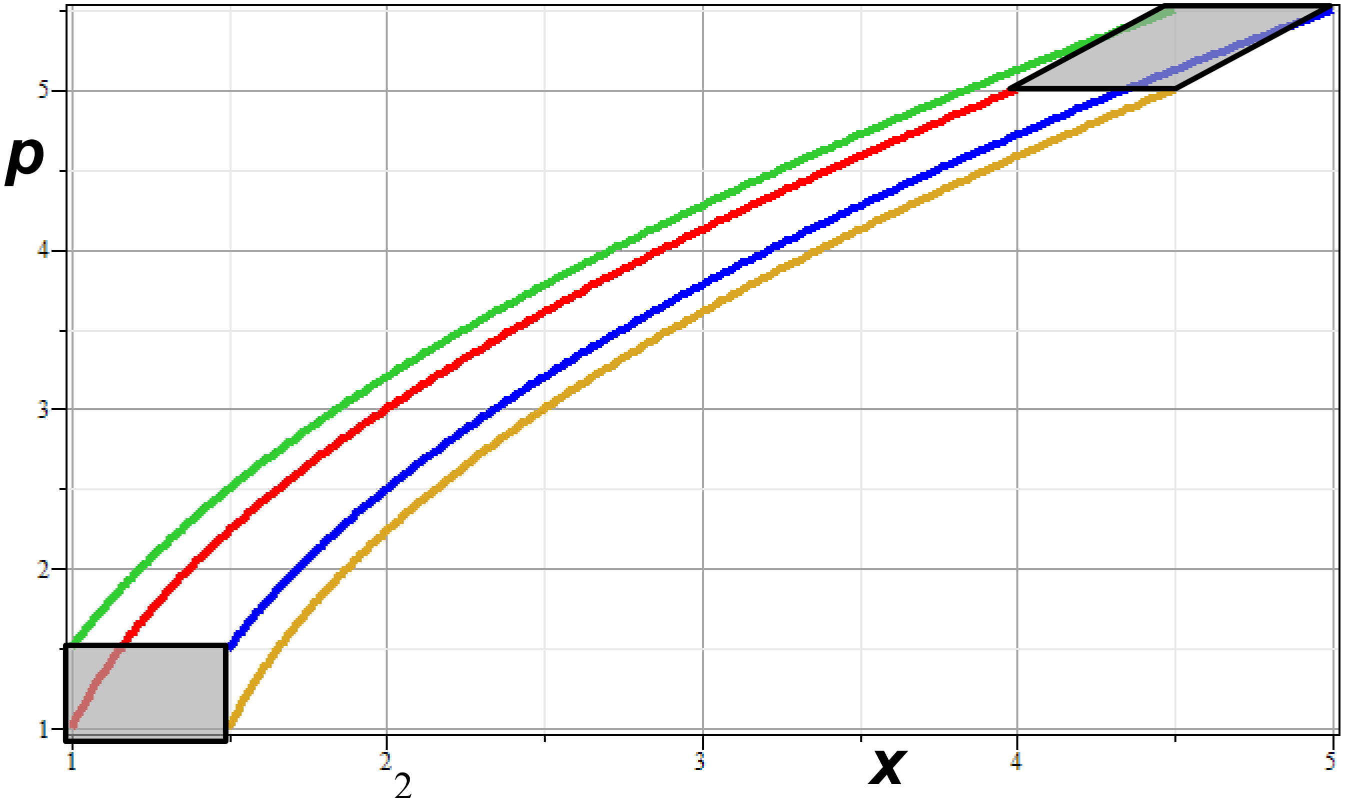
Phase space is defined at the set of all coordinates and momenta of a system:

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

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.

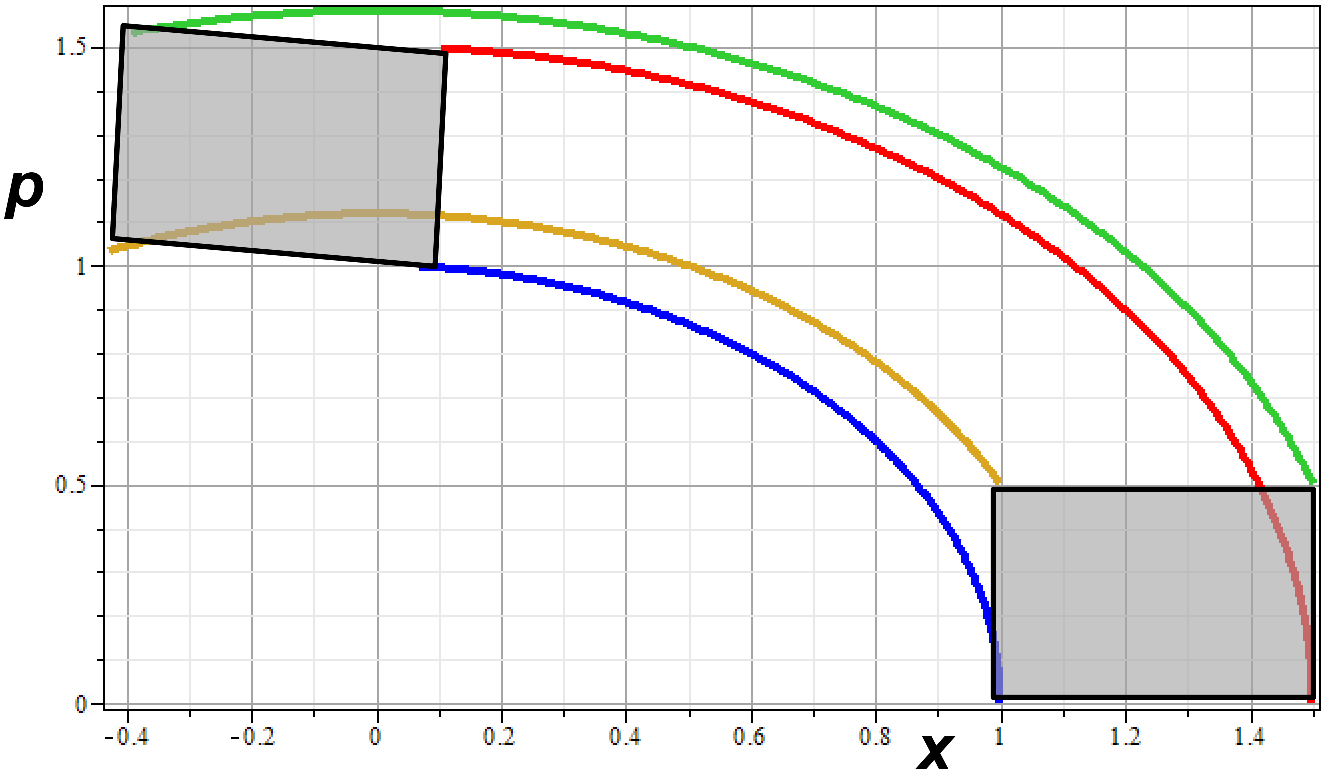
Phase space diagram for one-dimensional motion due to constant force



$$H\left(x,p\right)=\frac{p^2}{2m}-F_0x \qquad \dot{p}=F_0 \qquad \dot{x}=\frac{p}{m}$$

$$p_i(t)=p_{0i}+F_0t \qquad x_i(t)=x_{0i}+\frac{p_{0i}}{m}t+\frac{1}{2}F_0t^2$$

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



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

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

Liouville's Theorem (1838)

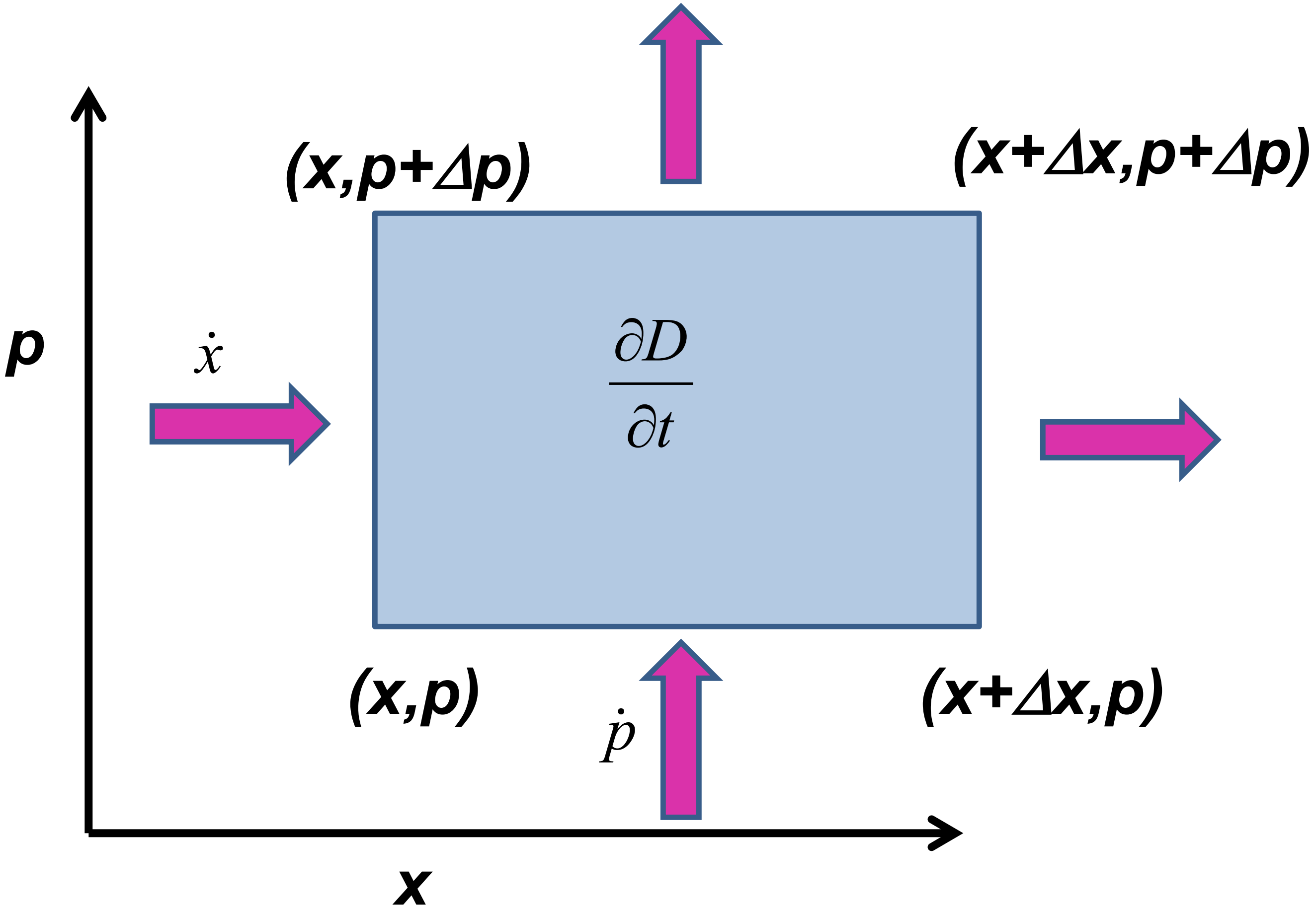
The density of representative points in phase space corresponding to the motion of a system of particles remains constant during the motion.

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

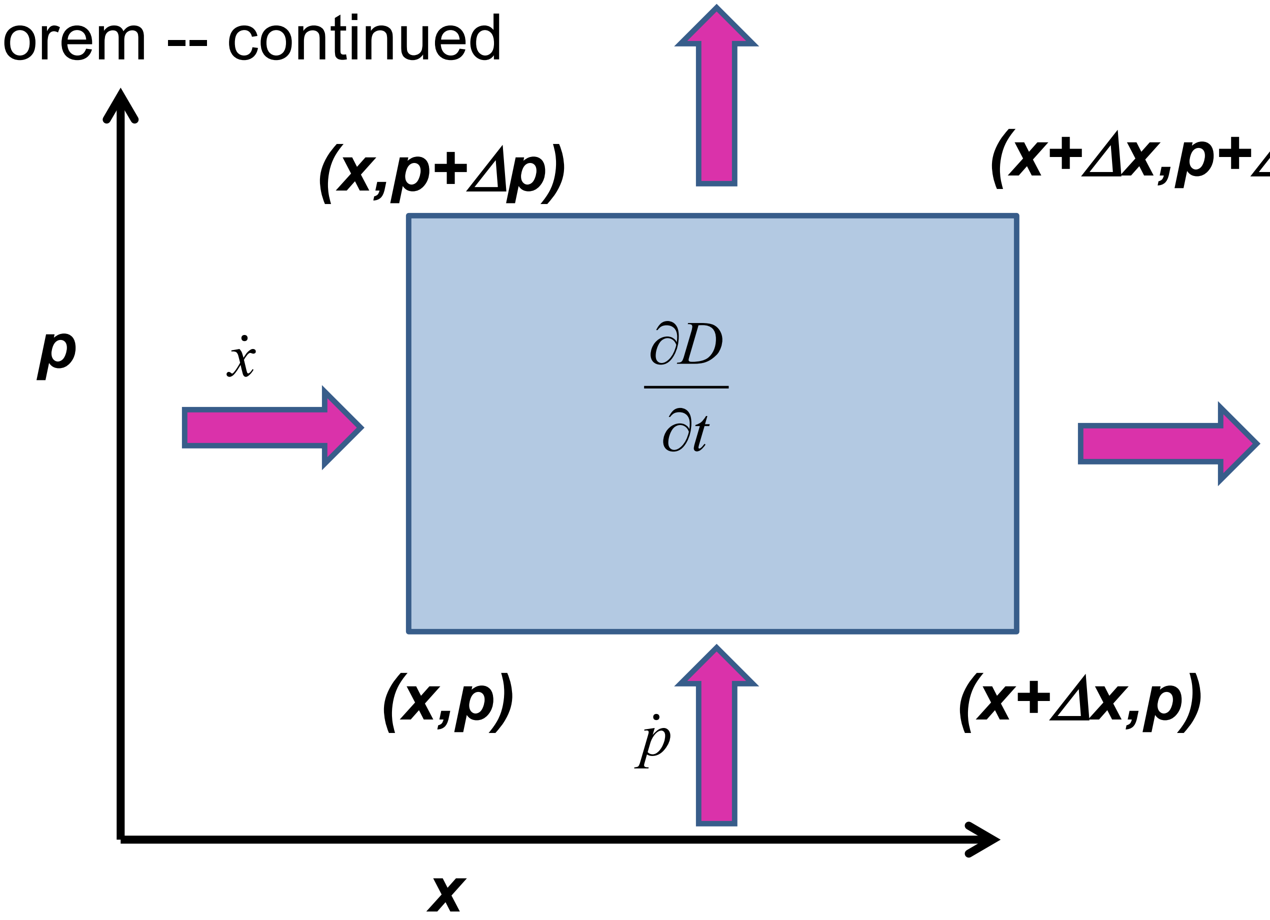
$$\frac{dD}{dt} = \sum_\sigma \left(\frac{\partial D}{\partial q_\sigma}\dot{q}_\sigma + \frac{\partial D}{\partial p_\sigma}\dot{p}_\sigma \right) + \frac{\partial D}{\partial t}$$

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

Liouville's theorem



Liouville's theorem -- continued

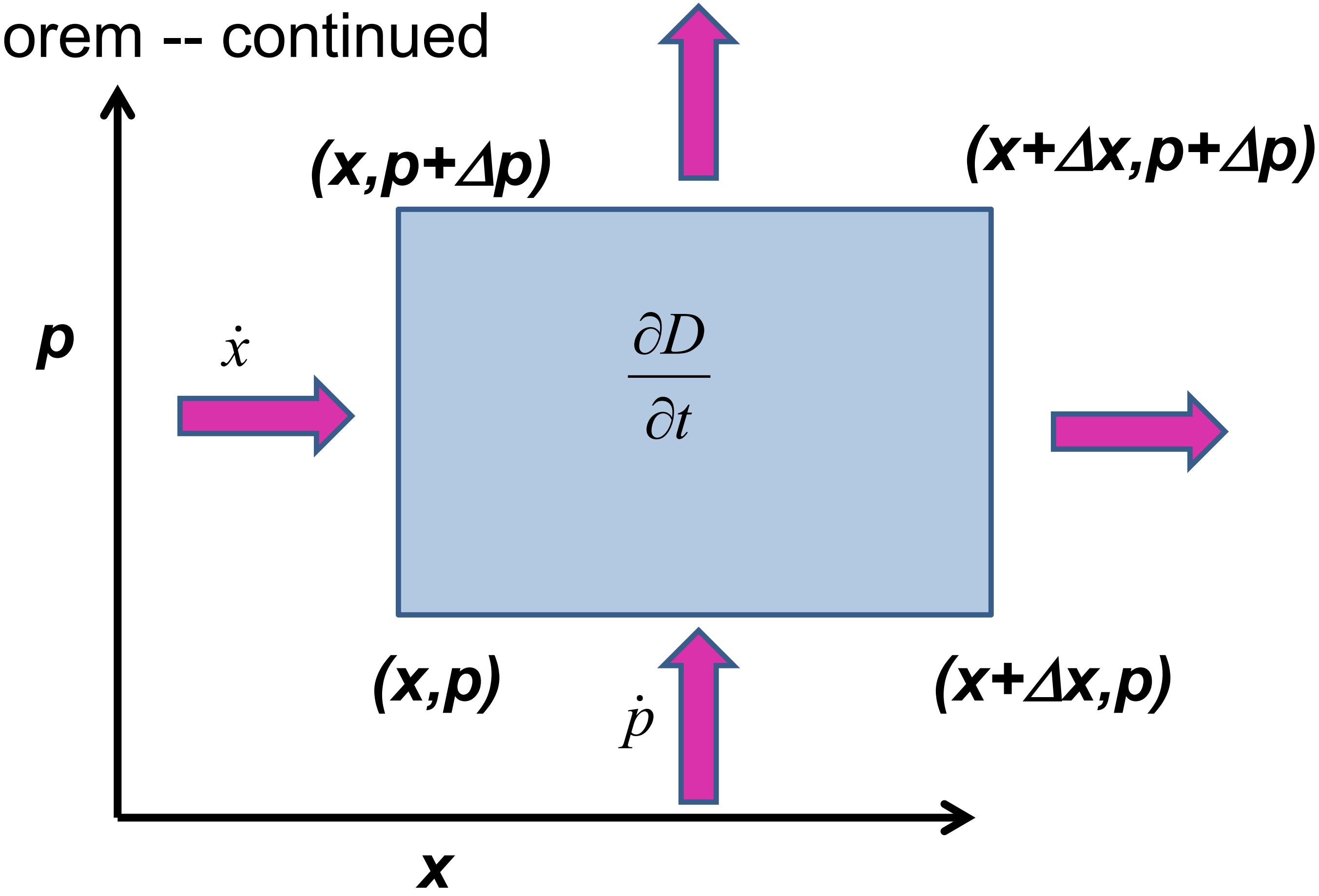


$$\frac{\partial D}{\partial t} \Rightarrow \text{time rate of change of particles within volume}$$

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

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

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:

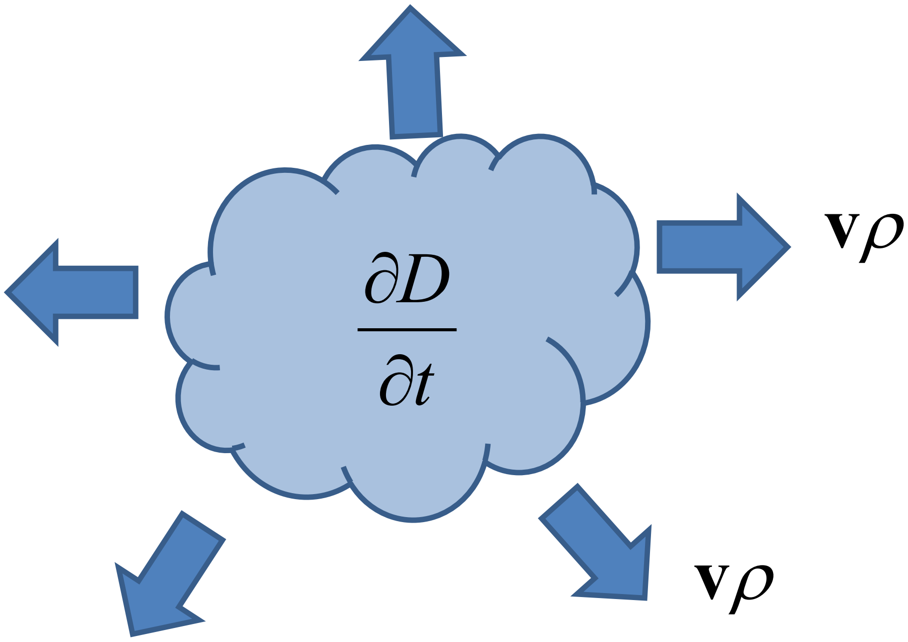
$$D = D\left(\{q_1 \cdots q_{3N}\}, \{p_1 \cdots p_{3N}\}, t\right)$$

Liouville's theorm shows that:

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

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 :

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

We also have a $6N$ dimensional gradient :

$$\nabla = \left(\nabla_{\mathbf{r}_1}, \nabla_{\mathbf{r}_2}, \ldots \nabla_{\mathbf{r}_\mathrm{N}}, \nabla_{\mathbf{p}_1}, \nabla_{\mathbf{p}_2}, \ldots \nabla_{\mathbf{p}_\mathrm{N}}\right)$$

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

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

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

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

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

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

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

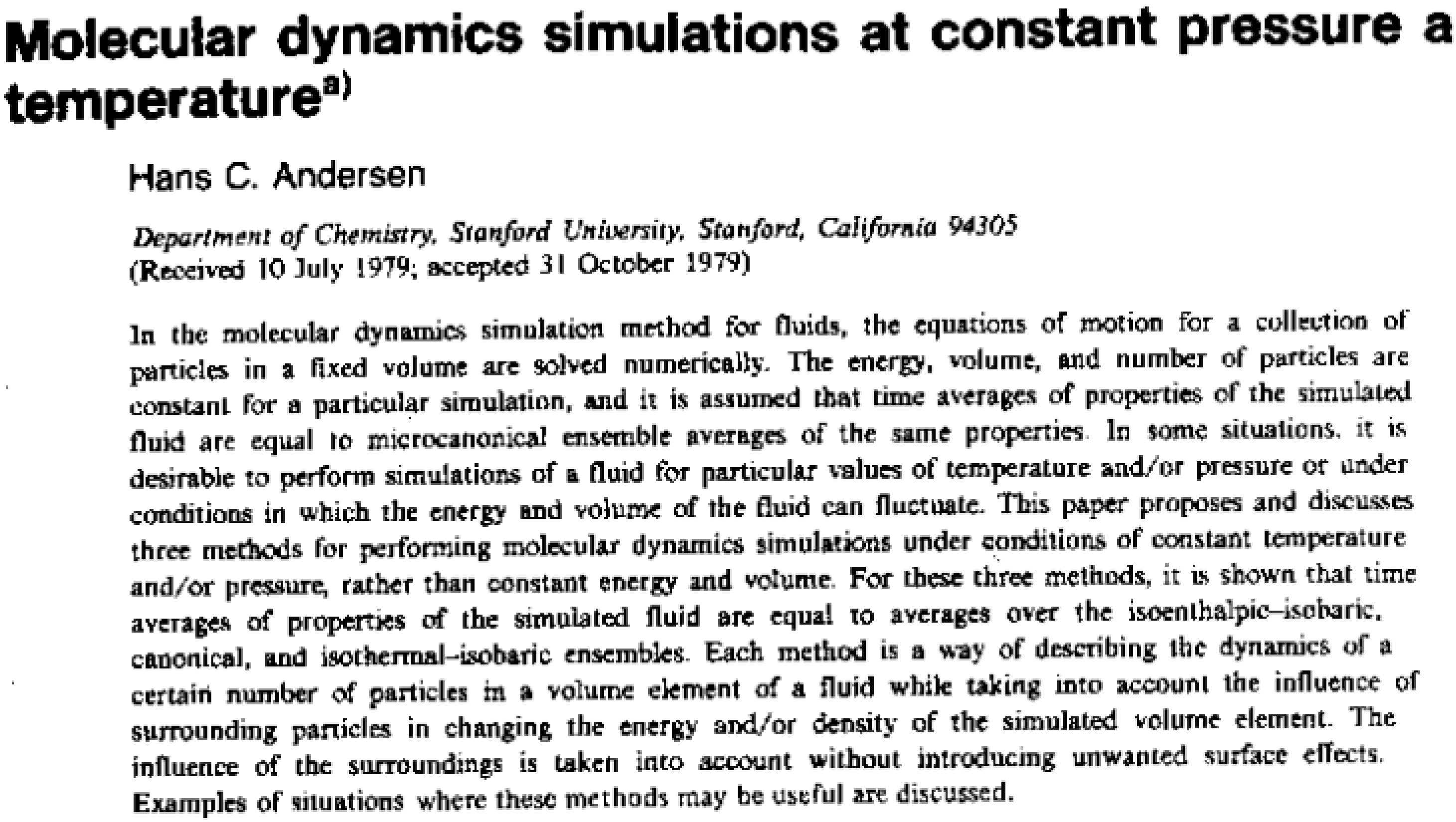
$$\boxed{\frac{dD}{dt}=0}$$

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.

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.

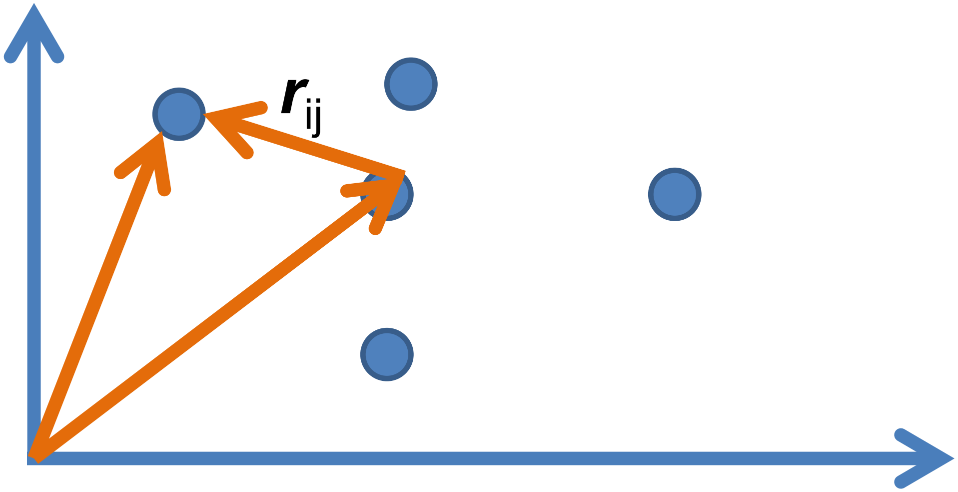
“Molecular dynamics” is a subfield of computational physics focused on analyzing the motions of atoms in fluids and solids with the goal of relating the atomistic and macroscopic properties of materials. Ideally molecular dynamics calculations can numerically realize the statistical mechanics viewpoint.

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:

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



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

➔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:

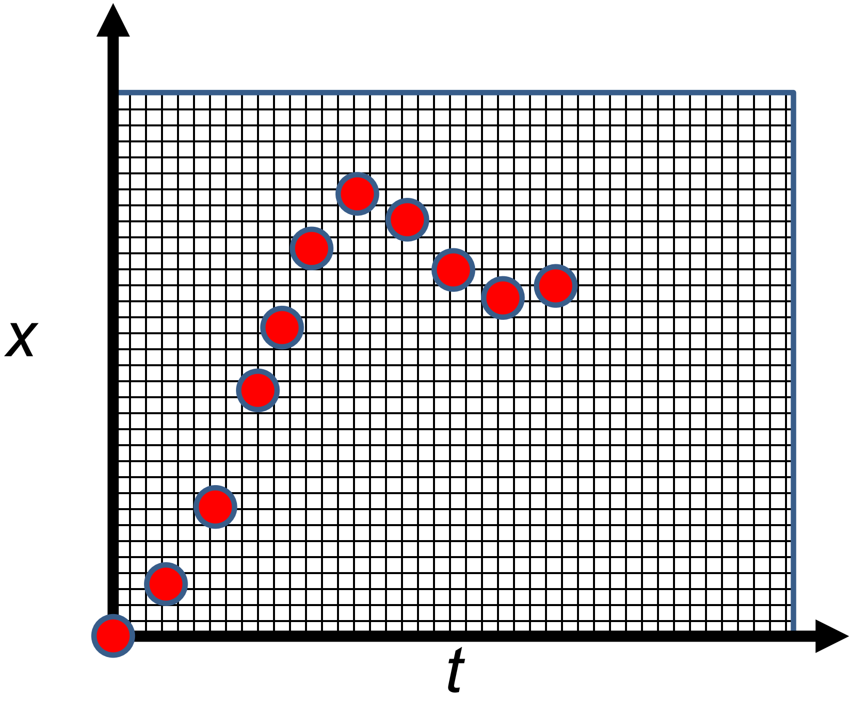
$$x_{n+1} = x_n + hv_n + \frac{1}{2}h^2 f_n$$

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

Velocity Verlet algorithm:

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

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



Your question –… I was intrigued by the numerical algorithms you slipped in there, are we going to be doing any more with numerical algorithms in this class? I was just wondering because I've seen Euler's method used in practice before but I have never used the Velocity Verlet algorithm.

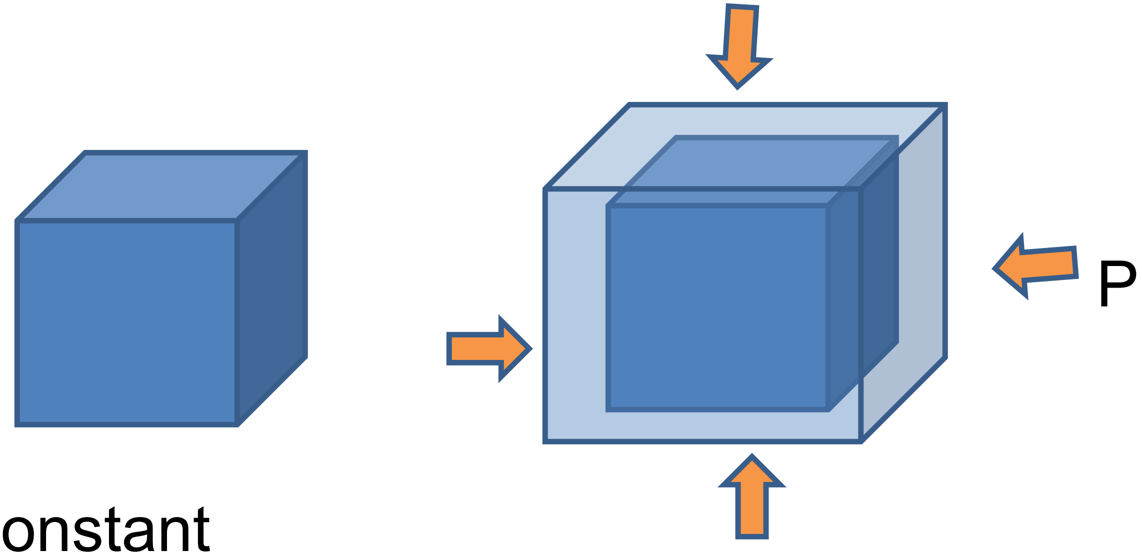
Comment – Numerical algorithms is a big subject and we might have some time in this class and in PHY 712 to cover some of the ideas. I would be glad to help you research some aspects for your “project” in this class. For a more comprehensive presentation I would recommend some classes in Math and Computer science and Professor Greg Cook in our department teaches a class every other year or so.

Your question – a related question about research expertise.

Comment – I do not view myself as an expert in molecular dynamics which we are discussing, despite having used some of these techniques. Professors Sam Cho and Fred Salsbury have much more experience in these areas than I do. My main goal in presenting these ideas here is to help you understand that the seemingly dusty topic of classical mechanics and old ideas developed over a century ago can be useful in modern times.

In defense of numerical evaluation, here is a quote from Richard Feynman: First you guess. Don’t laugh, this is the most important step. Then you compute the consequences. Compare the consequences to experience. If it disagrees with experience, the guess is wrong. In that simple statement is the key to science. It doesn’t matter how beautiful your guess is or how smart you are or what your name is. If it disagrees with experience, it’s wrong. That’s all there is to it.

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).



V constant

P constant,
V variable

PV contribution to potential energy

Andersen's clever transformation :

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

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

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

kinetic energy of "balloon"

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

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

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

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

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

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

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

Relationship between system representations

Scaled Original

$$Q(t) \quad = \quad V(t)$$

$$Q^{1/3}\boldsymbol{\rho}_i(t) \quad = \quad \mathbf{r}_i(t)$$

$$\boldsymbol{\pi}_i / Q^{1/3} \quad = \quad \mathbf{p}_i$$

Equations of motion in “original” coordinates:

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

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

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

Physical interpretation:

$\alpha \Leftrightarrow$ Imposed (target) pressure

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

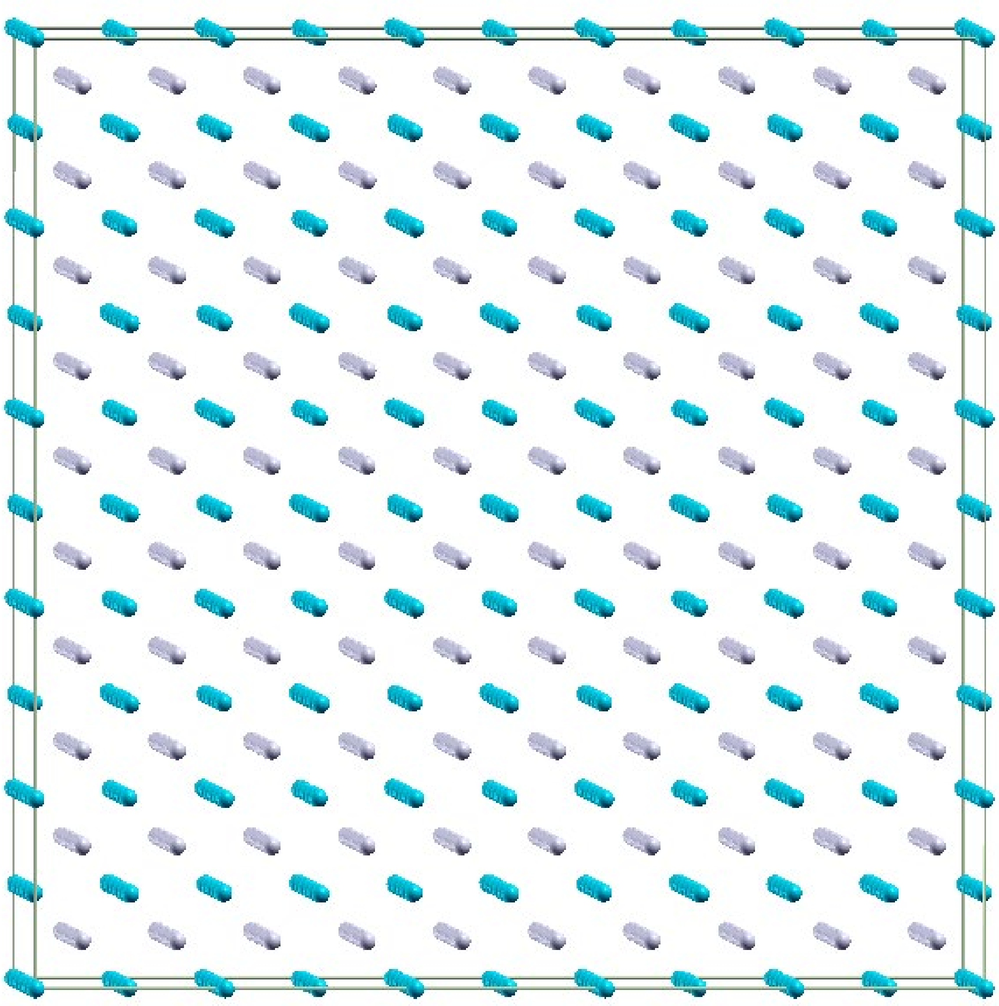
Time dependence

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

Averaged over many time steps:

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

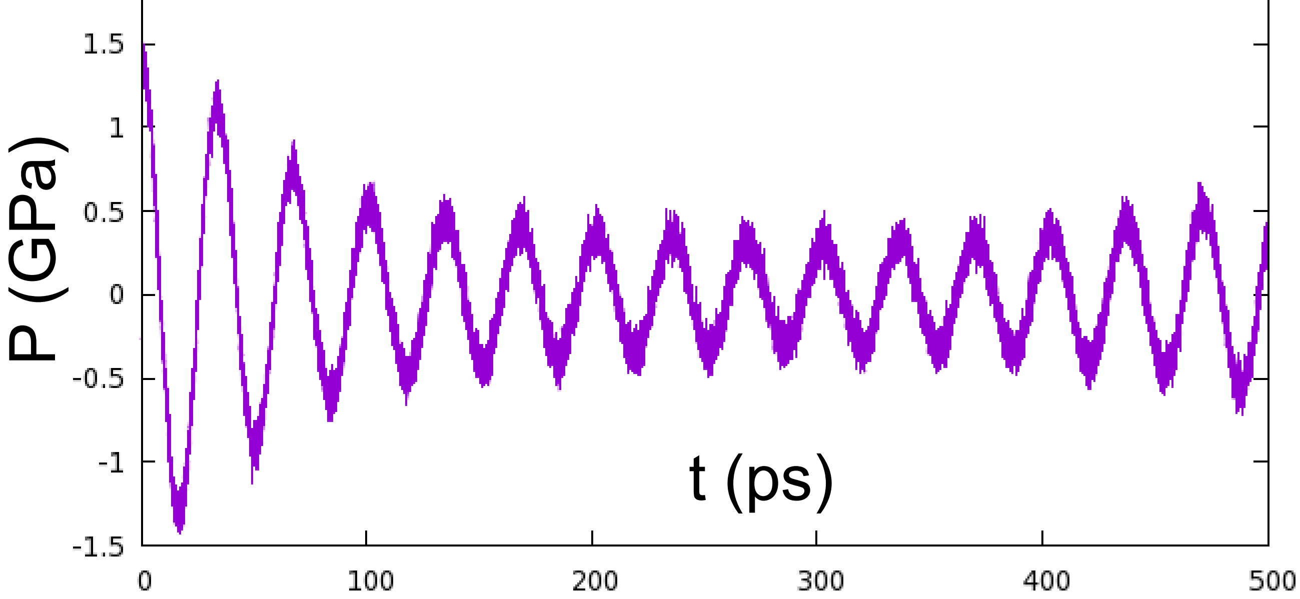
Example simulation for NPT molecular dynamics simulation of Li_2O using 1500 atoms with θ=0



Pair interaction potential

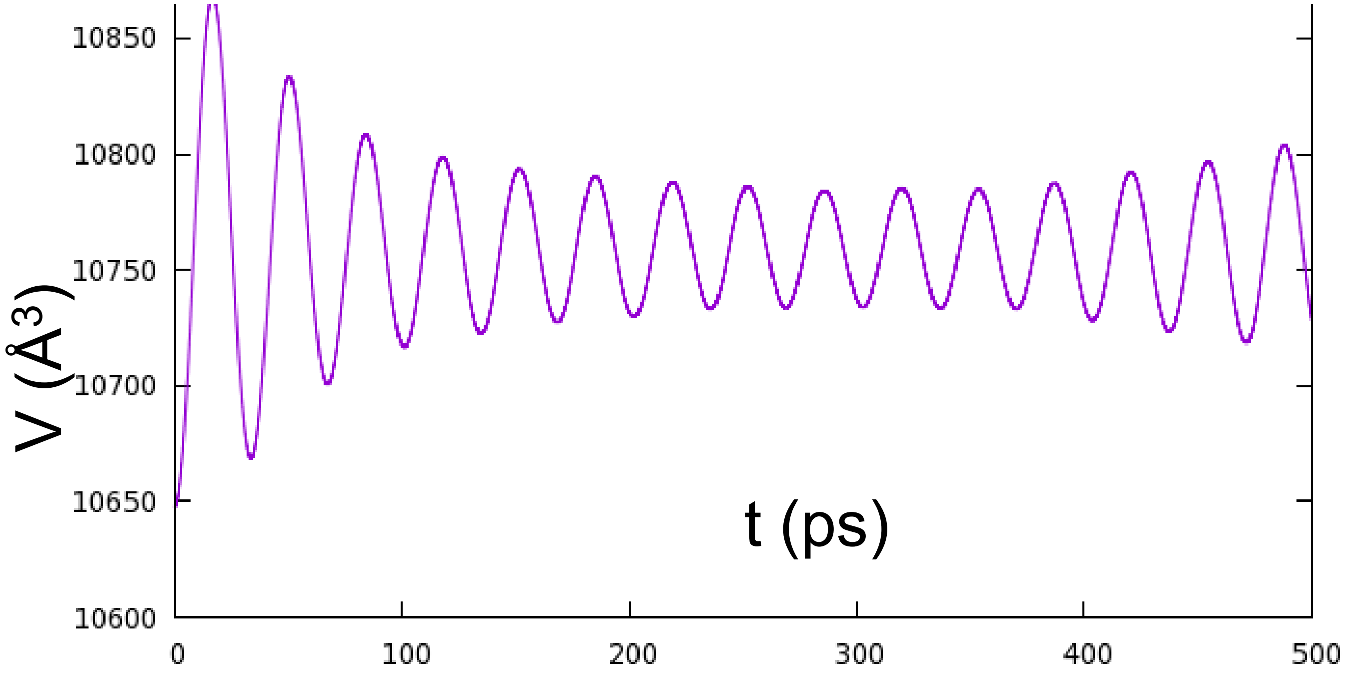
$$u_{ij}(r_{ij}) = A_{ij}e^{-r_{ij}/\rho_{ij}} - \frac{C_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}}$$

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

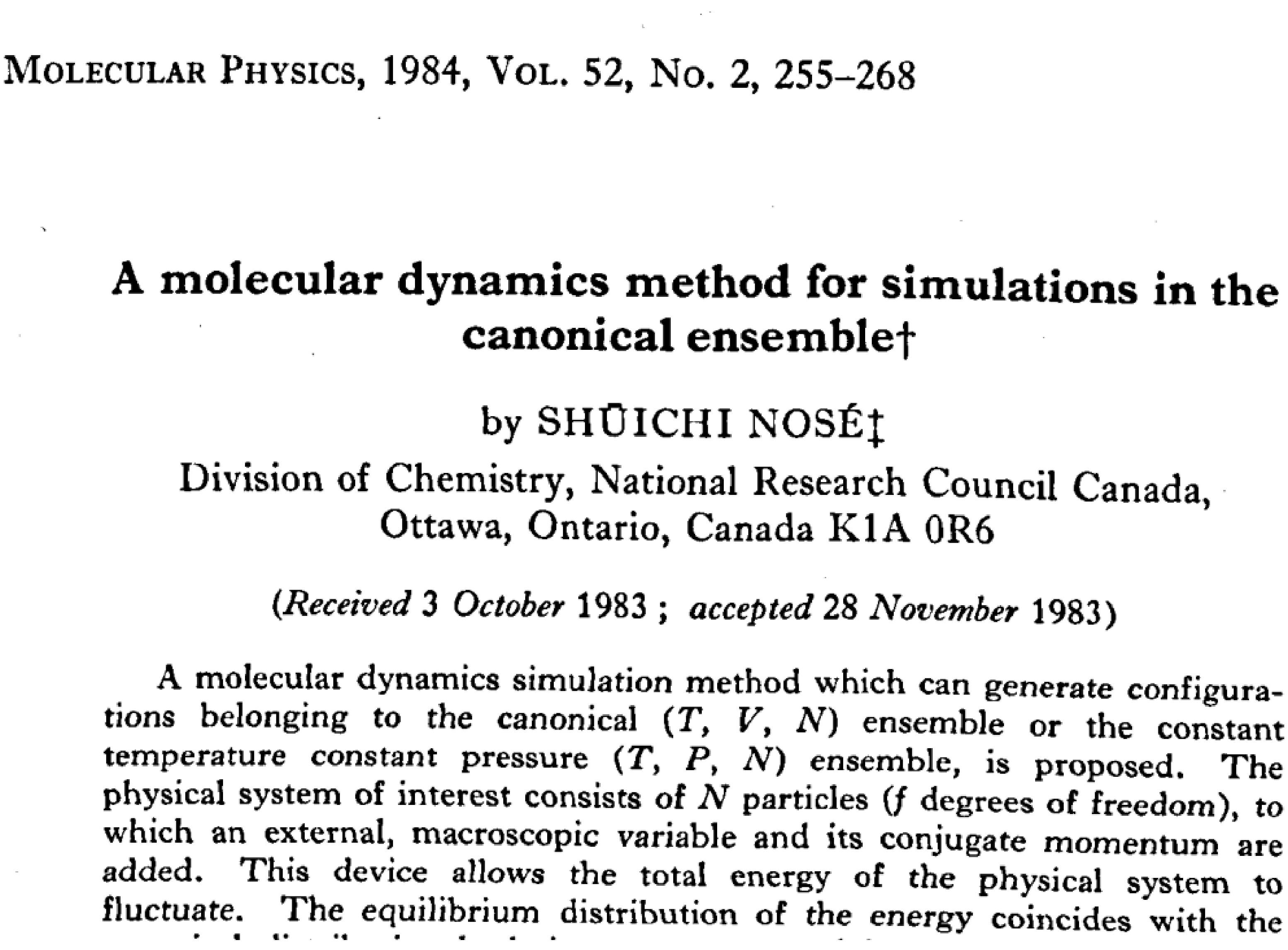


P (GPa)
1.5
1
0.5
0
-0.5
-1
-1.5
t (ps)
0
100
200
300
400
500

α=0



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



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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

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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

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

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

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

Time averaged relationships

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

Hamiltonian

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

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:

$$Z = \underbrace{\frac{1}{(f+1)}\left(\frac{2\pi Q}{kT_{\mathrm{eq}}}\right)^{1/2} \exp\left(E/kT_{\mathrm{eq}}\right)}_{\text{constant factor}} Z_{\mathrm{c}}.$$

Some details:

Starting with partition for microcanonical ensemble:

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

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

Change variables: $\overline{\mathbf{p}}_i=\frac{\mathbf{p}_i}{s} \qquad \overline{\mathbf{r}}_i=\mathbf{r}_i$

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

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

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

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

When the dust clears --

$$Z=\underbrace{\frac{1}{(f+1)}\left(\frac{2\pi Q}{kT_{\mathrm{eq}}}\right)^{1/2}\exp\left(E/kT_{\mathrm{eq}}\right)}_{\text{constant factor}}Z_{\mathrm{c}}.$$

➔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)