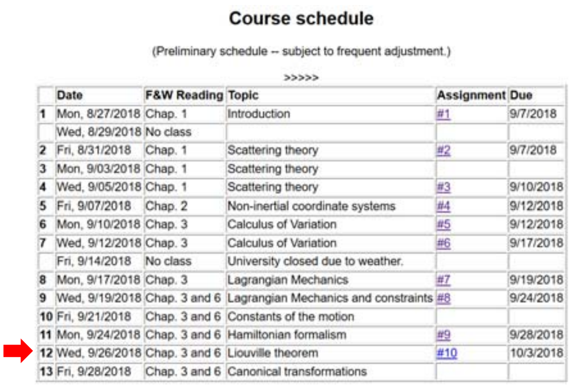
PHY 711 Classical Mechanics and Mathematical Methods
10-10:50 AM MWF Olin 103

Plan for Lecture 12:

Continue reading Chapter 3 & 6

1. **Hamiltonian formalism**
2. **Phase space & Liouville's theorem**
3. **Modern applications**



Course schedule

(Preliminary schedule -- subject to frequent adjustment.)

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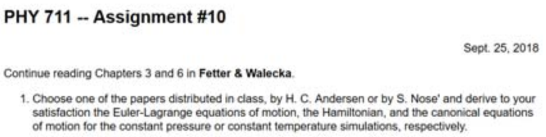
	Date	F&W Reading	Topic	Assignment	Due
1	Mon, 8/27/2018	Chap. 1	Introduction	#1	9/7/2018
	Wed, 8/29/2018	No class			
2	Fri, 8/31/2018	Chap. 1	Scattering theory	#2	9/7/2018
3	Mon, 9/03/2018	Chap. 1	Scattering theory		
4	Wed, 9/05/2018	Chap. 1	Scattering theory	#3	9/10/2018
5	Fri, 9/07/2018	Chap. 2	Non-inertial coordinate systems	#4	9/12/2018
6	Mon, 9/10/2018	Chap. 3	Calculus of Variation	#5	9/12/2018
7	Wed, 9/12/2018	Chap. 3	Calculus of Variation	#6	9/17/2018
	Fri, 9/14/2018	No class	University closed due to weather.		
8	Mon, 9/17/2018	Chap. 3	Lagrangian Mechanics	#7	9/19/2018
9	Wed, 9/19/2018	Chap. 3 and 6	Lagrangian Mechanics and constraints	#8	9/24/2018
10	Fri, 9/21/2018	Chap. 3 and 6	Constants of the motion		
11	Mon, 9/24/2018	Chap. 3 and 6	Hamiltonian formalism	#9	9/28/2018
12	Wed, 9/26/2018	Chap. 3 and 6	Liouville theorem	#10	10/3/2018
13	Fri, 9/28/2018	Chap. 3 and 6	Canonical transformations		



PHY 711 -- Assignment #10

Sept. 25, 2018

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

1. Choose one of the papers distributed in class, by H. C. Andersen or by S. Nose' and derive to your satisfaction the Euler-Lagrange equations of motion, the Hamiltonian, and the canonical equations of motion for the constant pressure or constant temperature simulations, respectively.

Hamiltonian formalism

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

Canonical equations of motion

$$\frac{dq_\sigma}{dt} = \frac{\partial H}{\partial p_\sigma}$$

$$\frac{dp_\sigma}{dt} = -\frac{\partial H}{\partial q_\sigma}$$

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.

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

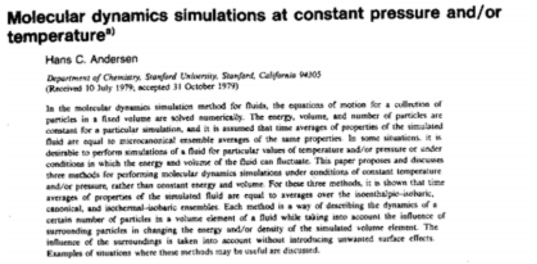
$$\boxed{\frac{dD}{dt} = 0}$$

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.

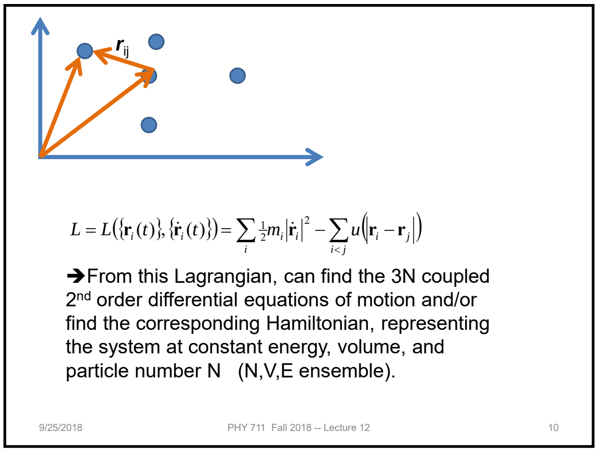
"Molecular dynamics" is a subfield of computational physics focused on analyzing the motions of atoms in fluids and solids with the goal of relating the atomistic and macroscopic properties of materials. Ideally molecular dynamics calculations can numerically realize the statistical mechanics viewpoint.

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

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

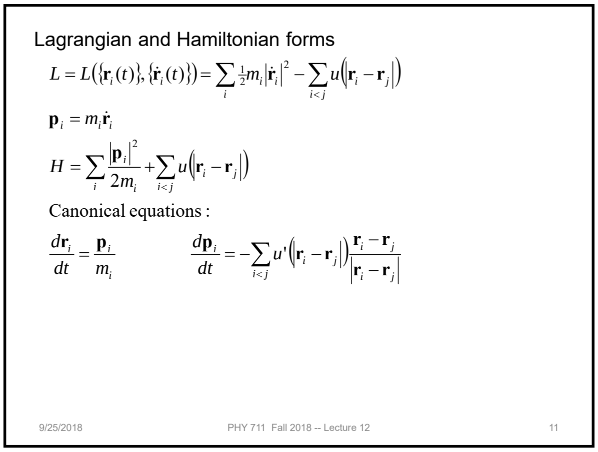
For simplicity, it is assumed that the potential interaction is a sum of pairwise interactions:

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



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

➔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

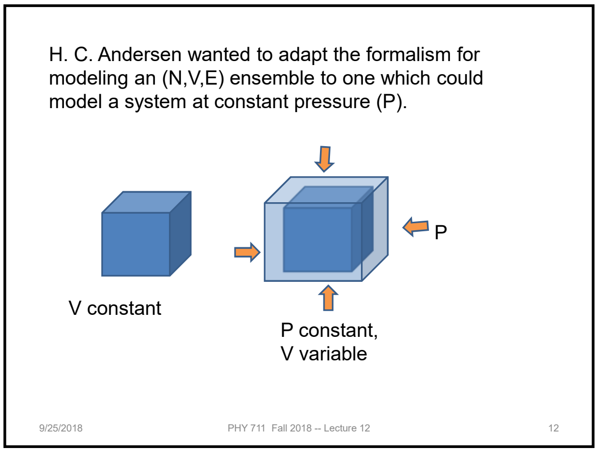
$$L = L\left(\{\mathbf{r}_i(t)\},\{\dot{\mathbf{r}}_i(t)\}\right) = \sum_i \tfrac{1}{2} m_i |\dot{\mathbf{r}}_i|^2 - \sum_{i<j} u\left(|\mathbf{r}_i - \mathbf{r}_j|\right)$$

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

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

Canonical equations :

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



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).

PV contribution to
potential energy

Andersen's clever transformation :

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

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

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

kinetic energy of
“balloon”

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

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

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

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

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

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

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

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:

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

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

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

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

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

Digression on numerical evaluation of differential equations

Example differential equation (one dimension);

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

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

Euler's method :

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

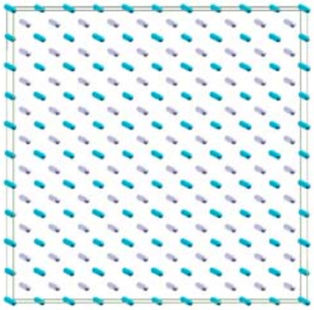
$$v_{n+1} = v_n + hf_n$$

Velocity Verlet algorithm :

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

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

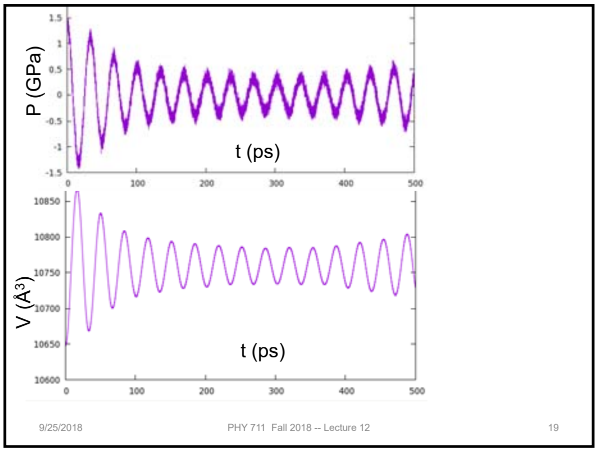
Example simulation for NPT molecular dynamics simulation of Li_2O using 1500 atoms with θ=0

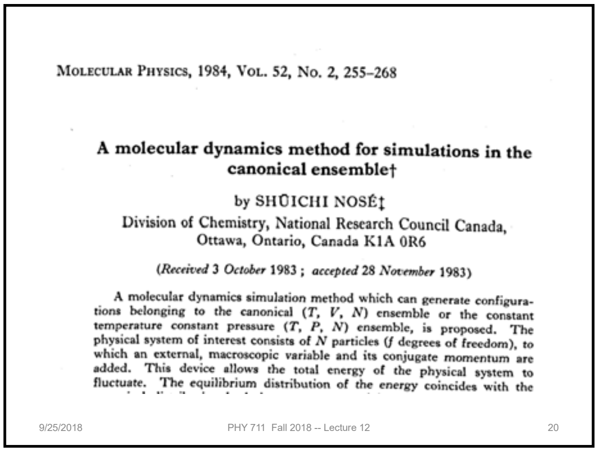


Pair interaction potential

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

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





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

A molecular dynamics method for simulations in the canonical ensemble†

by SHŪICHI NOSɇ‡
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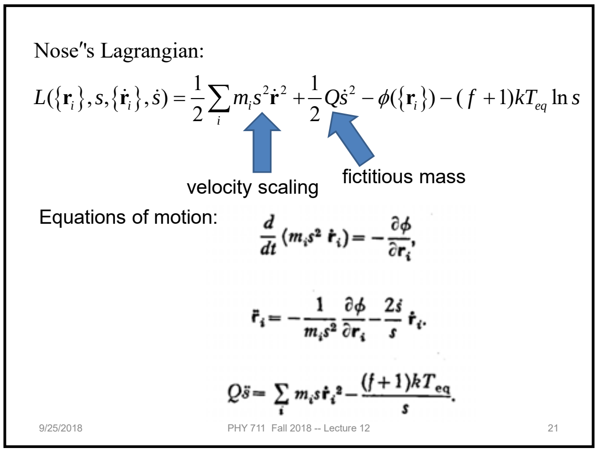
Ottawa, Ontario, Canada K1A 0R6

(*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:

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

velocity scaling

fictitious mass

Equations of motion:

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

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

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

Time averaged relationships

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

Hamiltonian

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

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:

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

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

From LAMMPS simulation (using modified Nose’ algorithm)