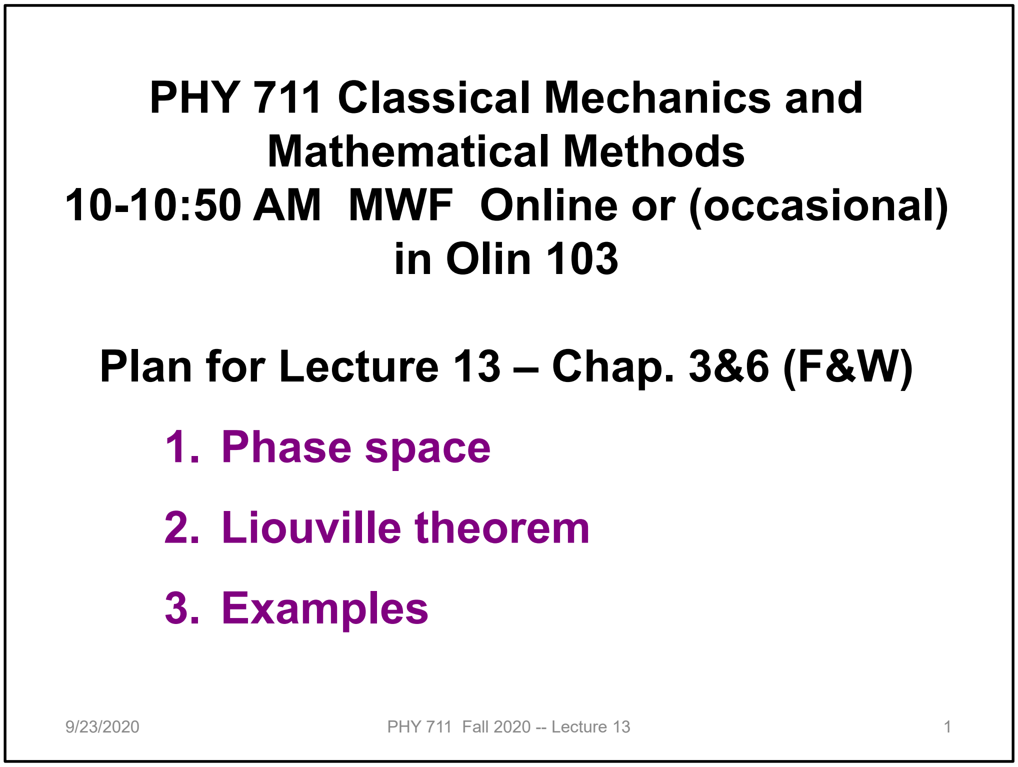
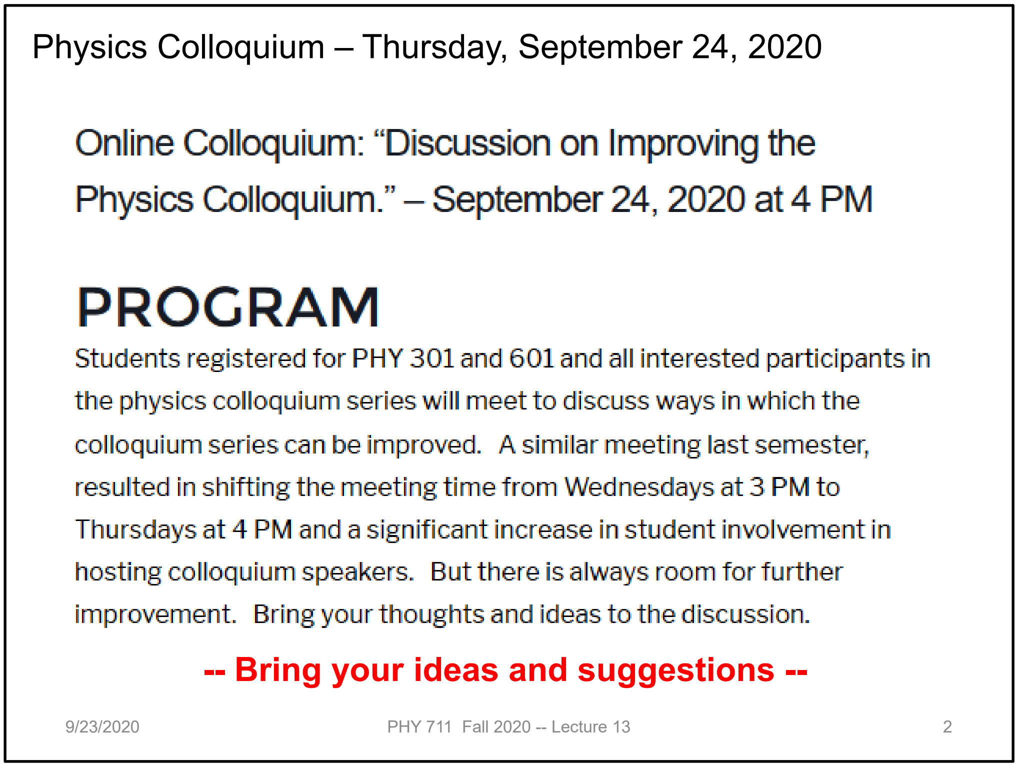


PHY 711 Classical Mechanics and Mathematical Methods
10-10:50 AM MWF Online or (occasional) in Olin 103

Plan for Lecture 13 – Chap. 3&6 (F&W)

1. Phase space
2. Liouville theorem
3. Examples

In this lecture we will introduce the notion of phase space, prove an important theorem concerning the density of particles in phase space, and show some interesting examples. The slides at the end are included only for those of you who may be interested in statistical mechanics.



Physics Colloquium – Thursday, September 24, 2020

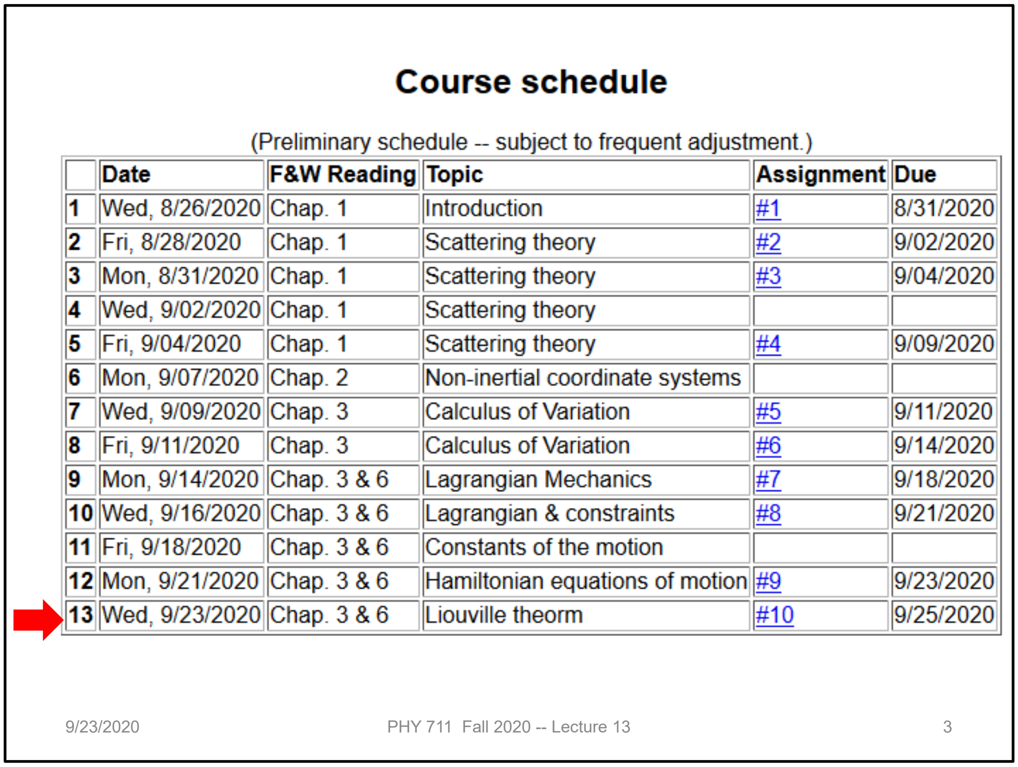
Online Colloquium: “Discussion on Improving the Physics Colloquium.” – September 24, 2020 at 4 PM

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 --

Reminder about colloquium on Thursday.

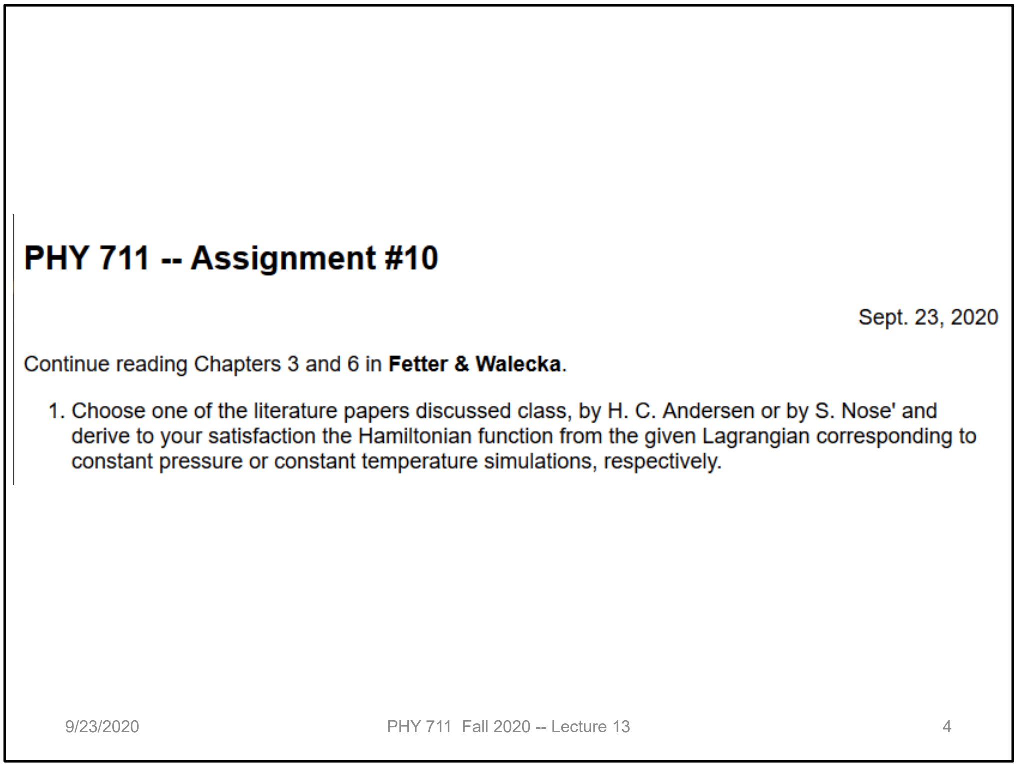


Course schedule

(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

There is a short homework problem due Friday.



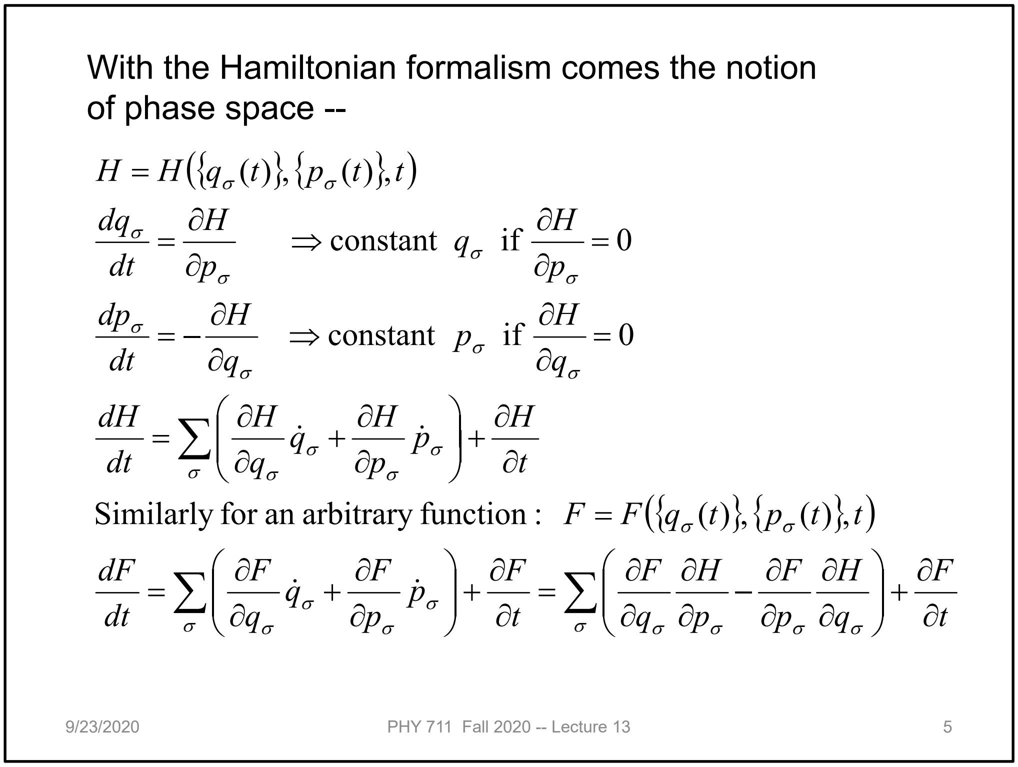
PHY 711 -- Assignment #10

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.

Note you need only read a small part of one of the papers. Of course perhaps you will be interested to read more…. The papers are available from our webpage.



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

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

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

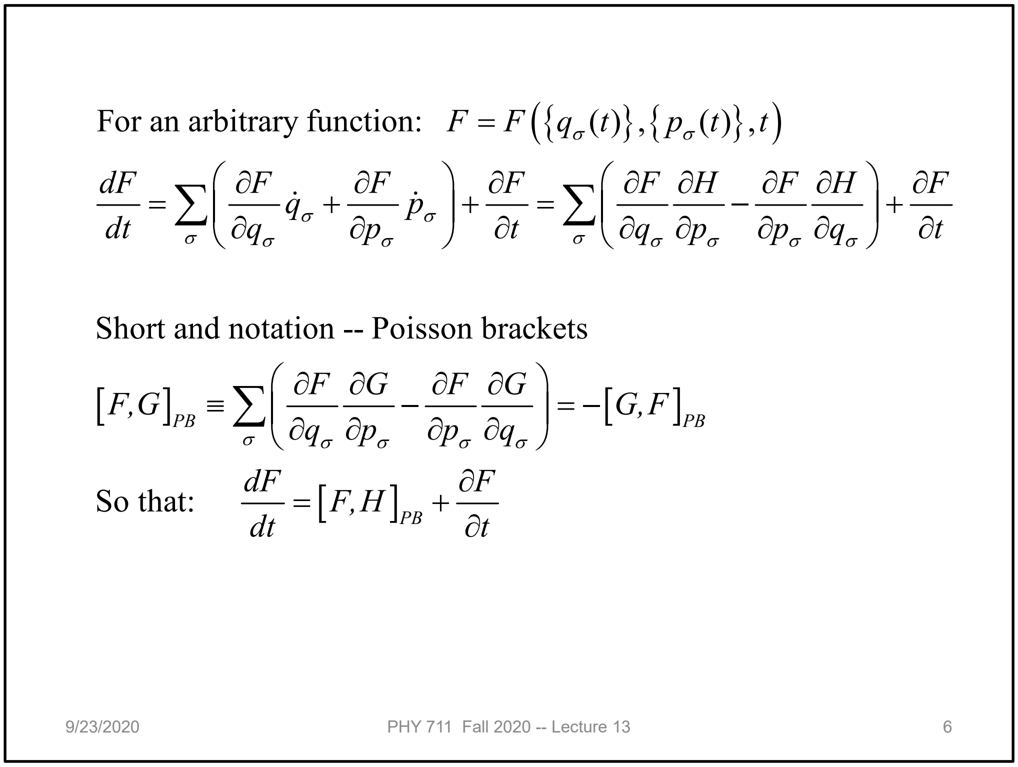
$$\frac{dp_\sigma}{dt} = -\frac{\partial H}{\partial q_\sigma} \qquad \Rightarrow \text{constant } \; p_\sigma \; \text{ if } \frac{\partial H}{\partial q_\sigma} = 0$$

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

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

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

Now an interesting addition property of the Hamiltonian formulation.



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

Introducing the Poisson Bracket.

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:

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

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

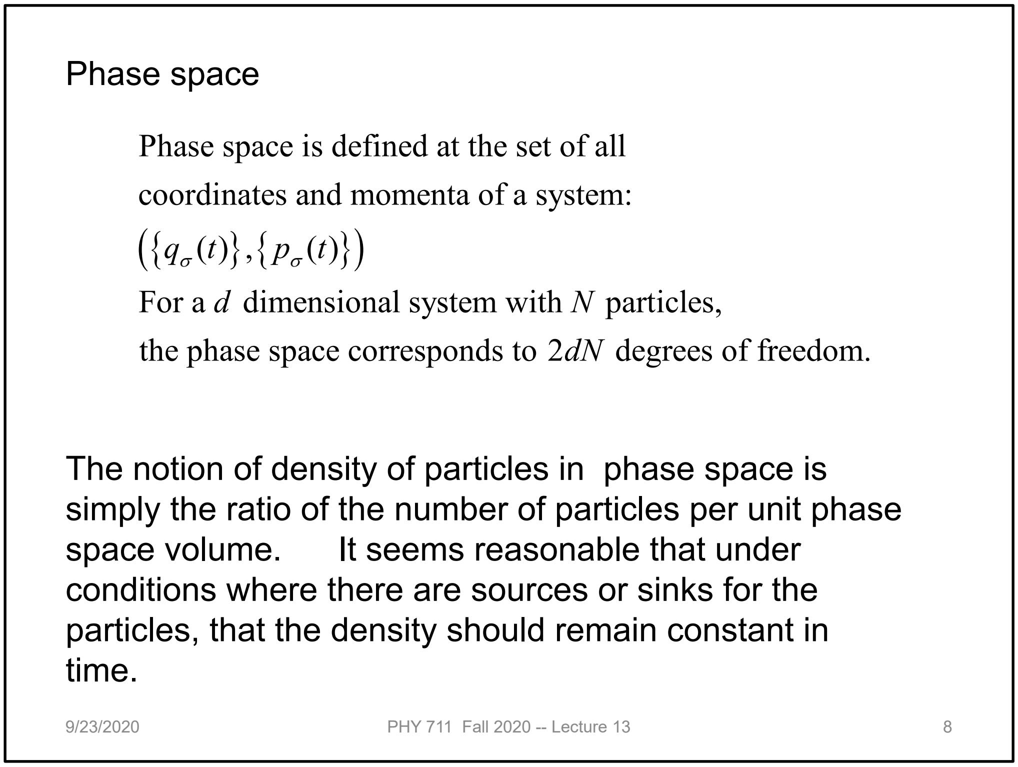
Liouville theorem

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.

Examples followed by introducing the Liouville theorem.



Phase space

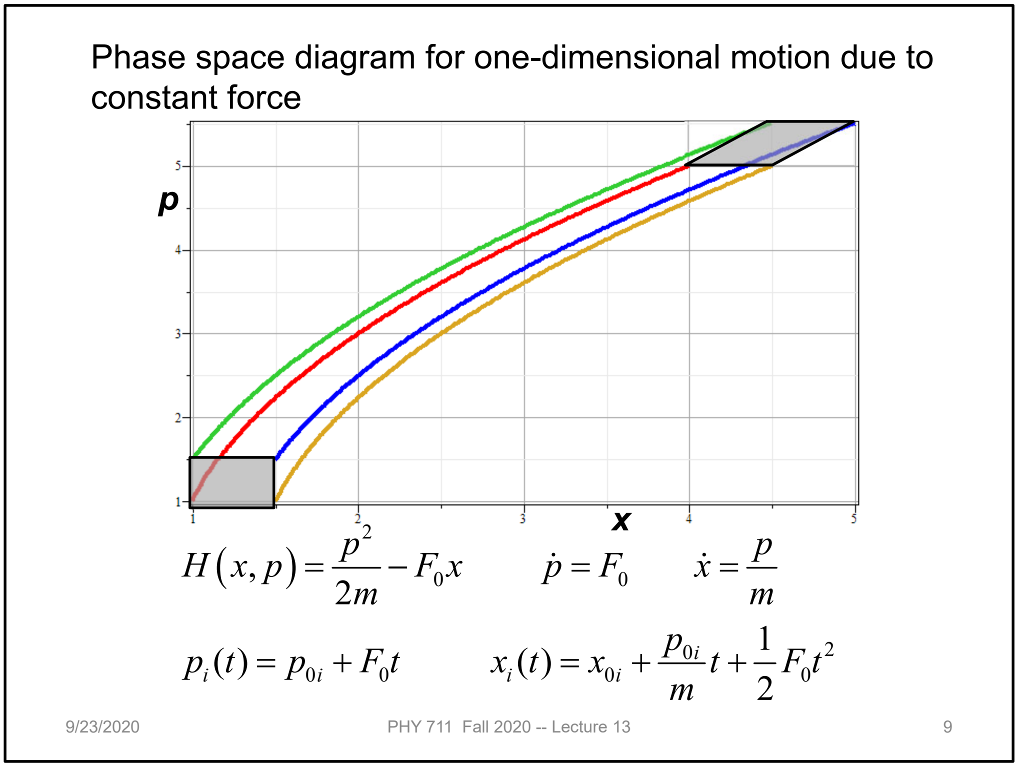
Phase space is defined at the set of all coordinates and momenta of a system:

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

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 sources or sinks for the particles, that the density should remain constant in time.

Notion of phase space



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

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

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

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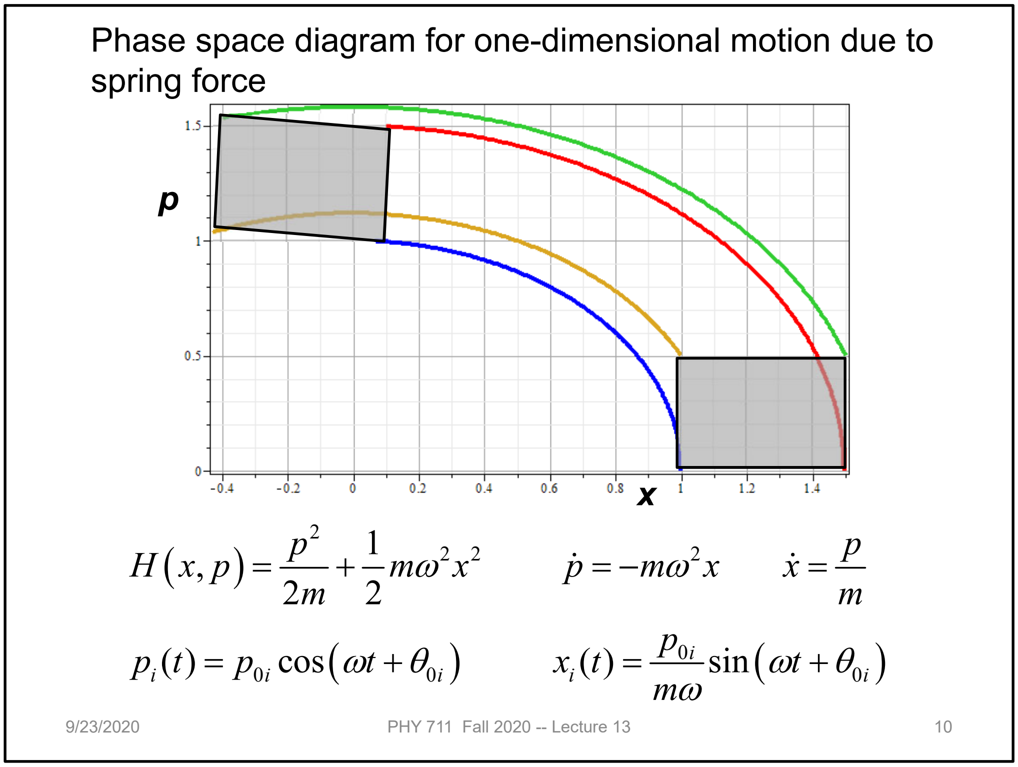
Example of time evolution of phase space.

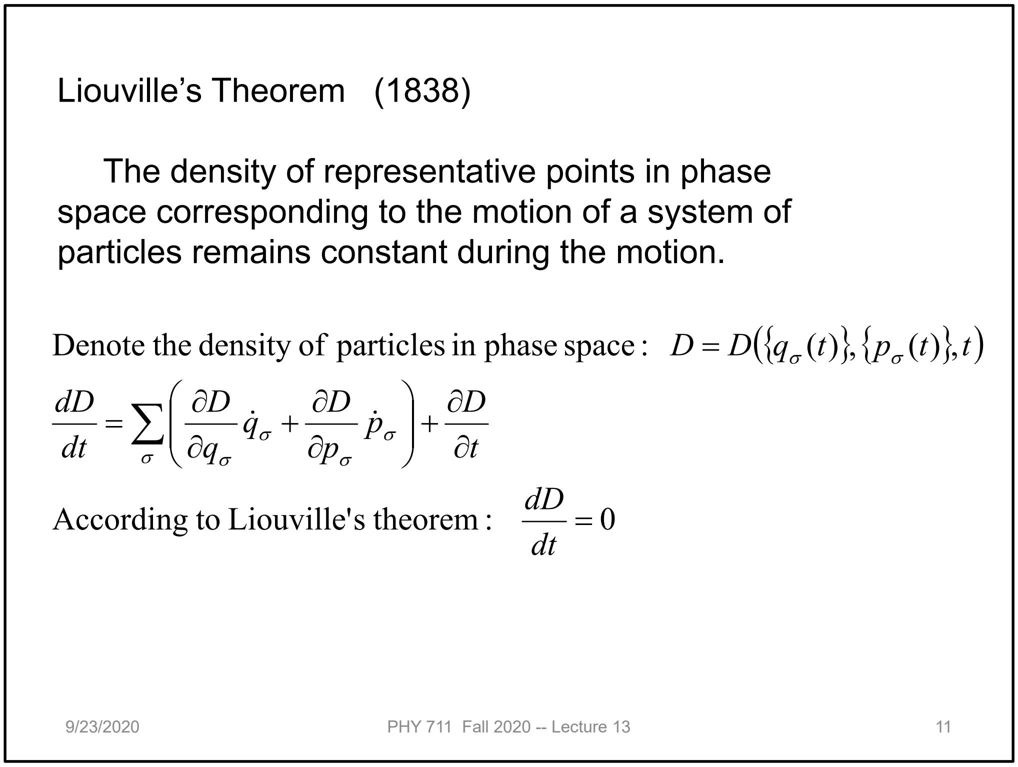


Phase space diagram for one-dimensional motion due to spring force

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

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

Another example of time evolution of phase space.



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

Application to the density of phase space – Liouville theorm.

Liouville's theorem

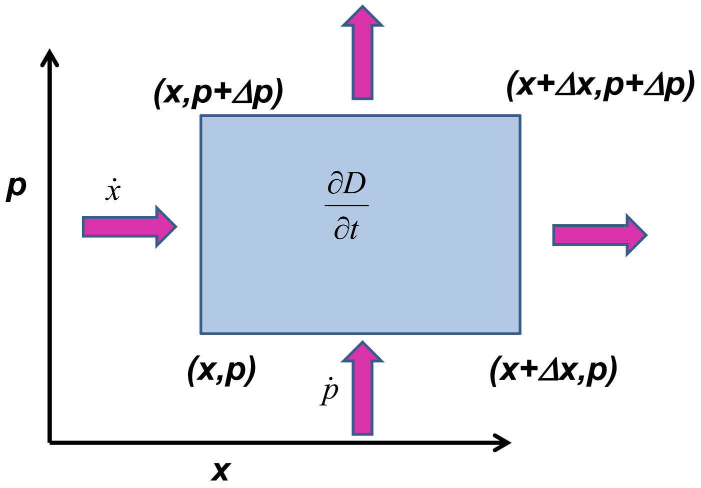
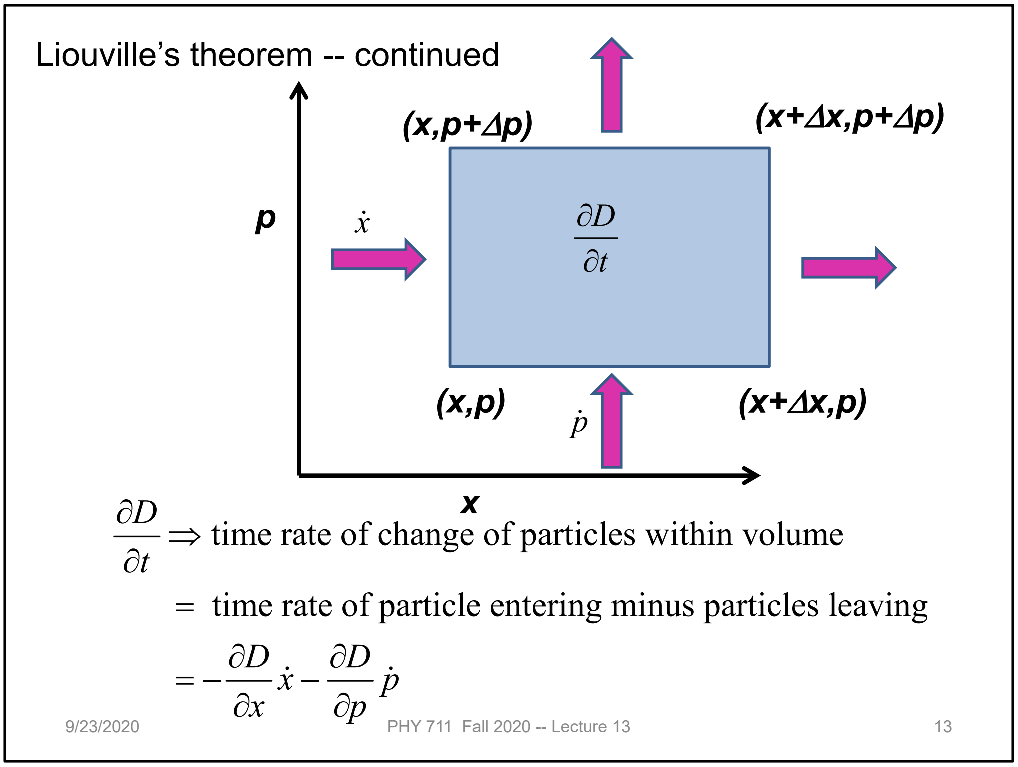


Diagram of flow in phase space.



Liouville's theorem -- continued

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

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

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

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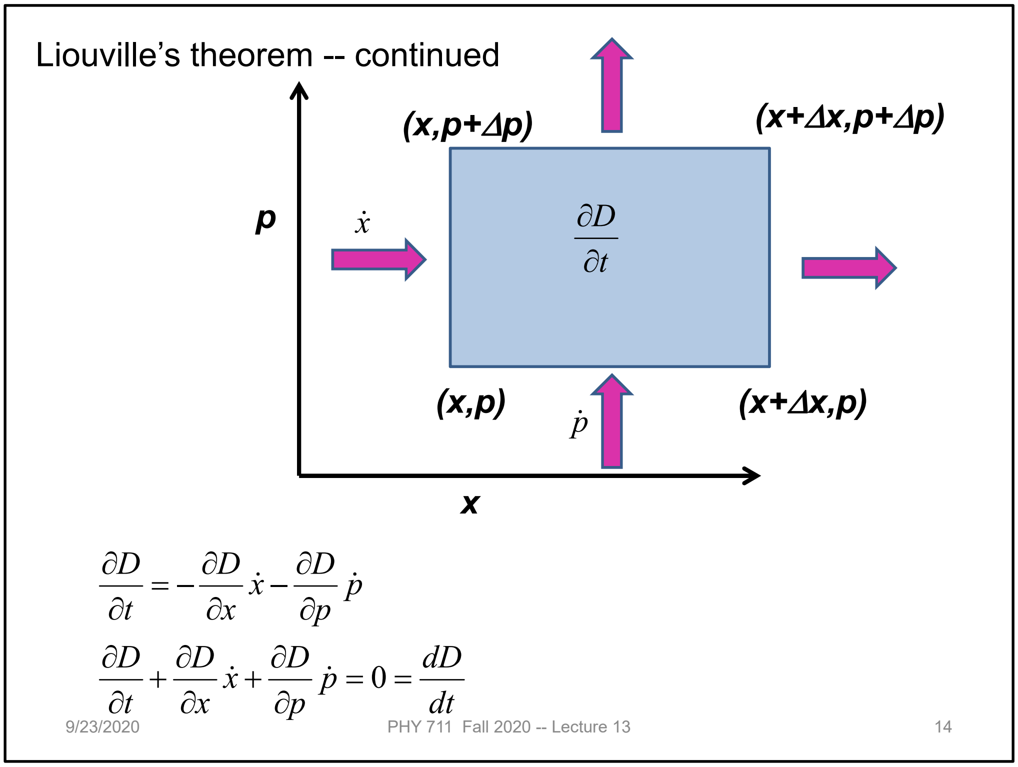
Some details.

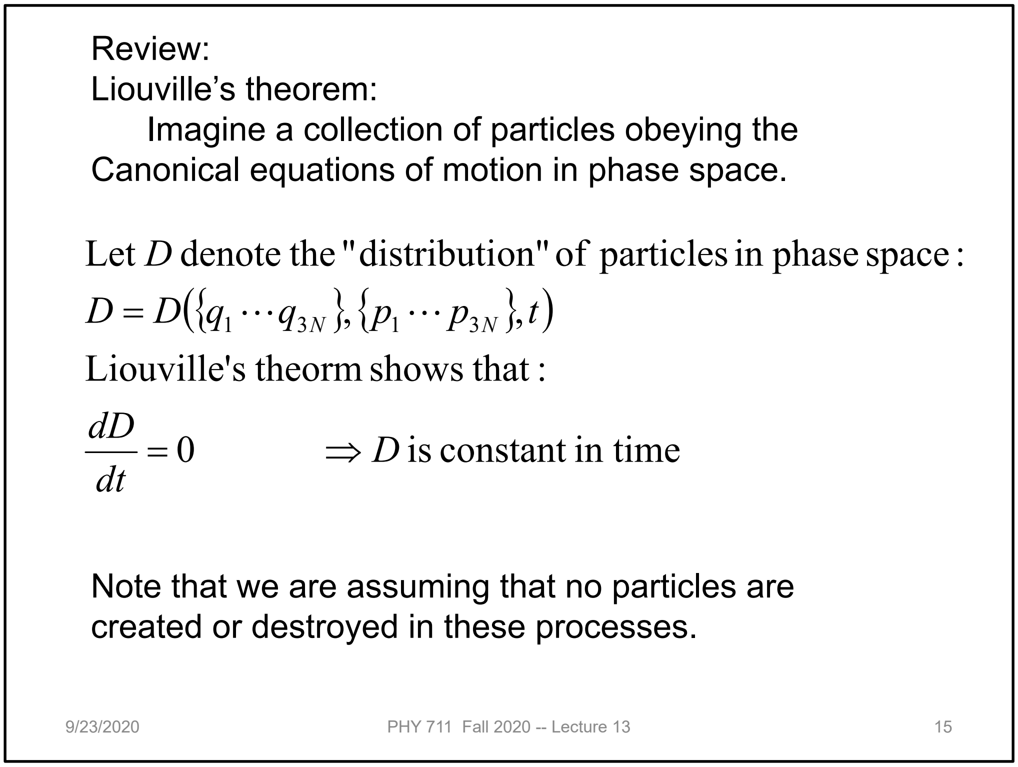


Liouville's theorem -- continued

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

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

More details.



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:

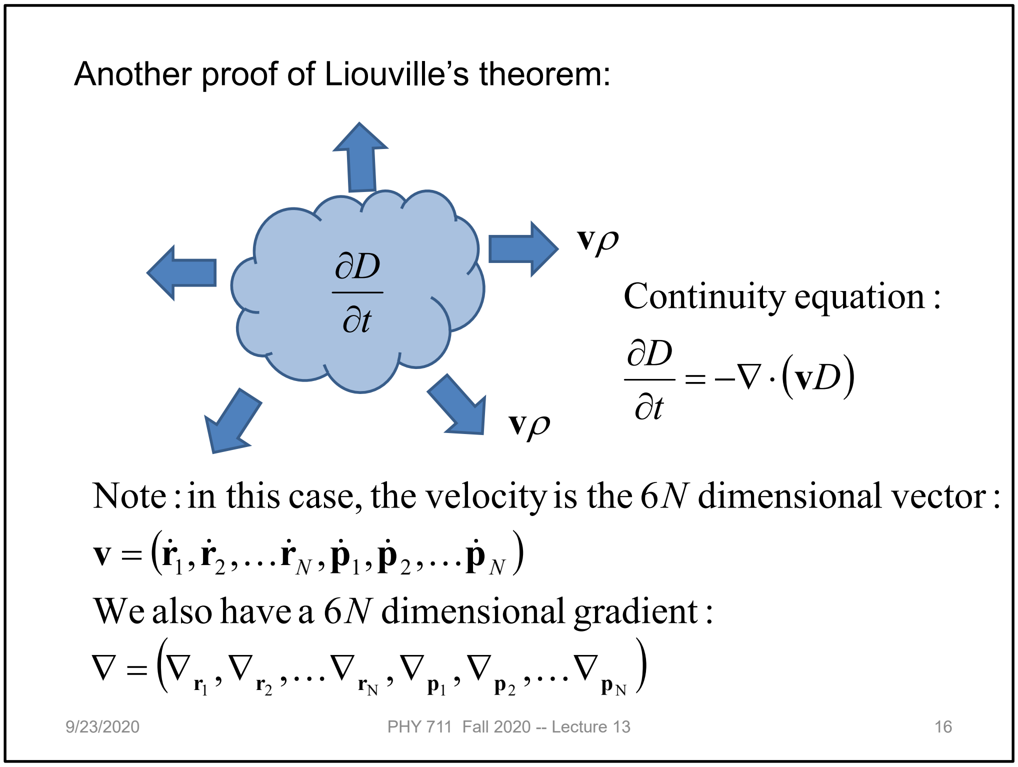
$$D = D\left(\{q_1 \cdots q_{3N}\}, \{p_1 \cdots p_{3N}\}, t\right)$$

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.

Summary of Liouville theorem.



Another proof of Liouville's theorem:

Continuity equation:

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

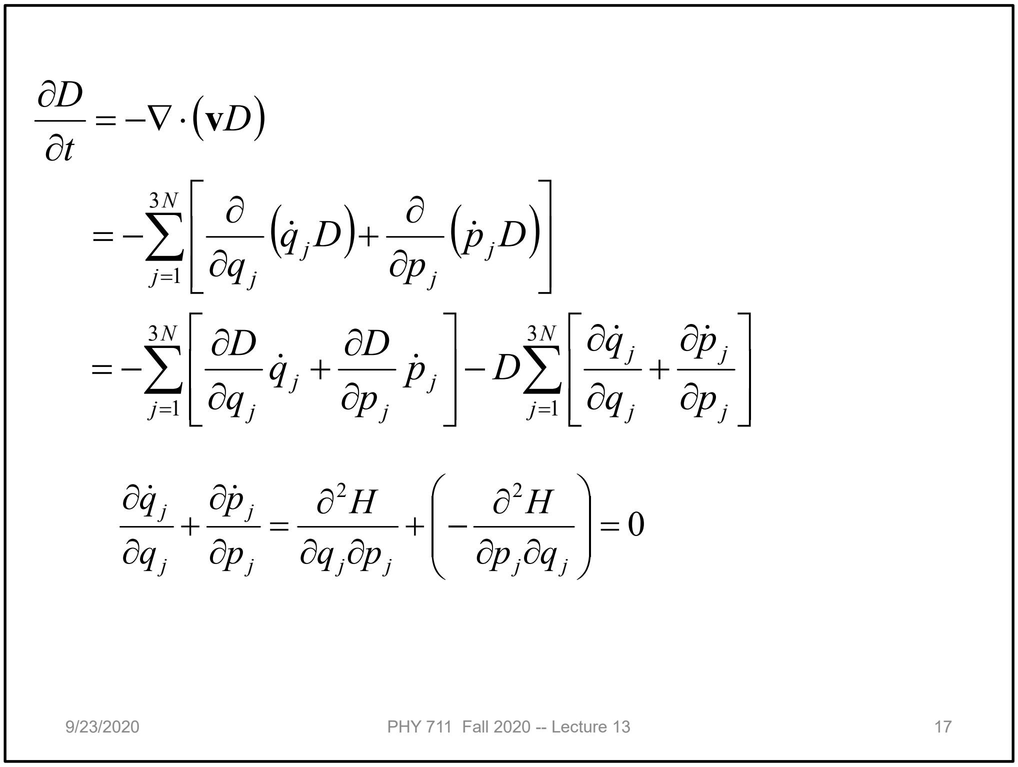
Note: in this case, the velocity is the $6N$ dimensional vector:

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

We also have a $6N$ dimensional gradient:

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

Another more formal derivation of Liouville



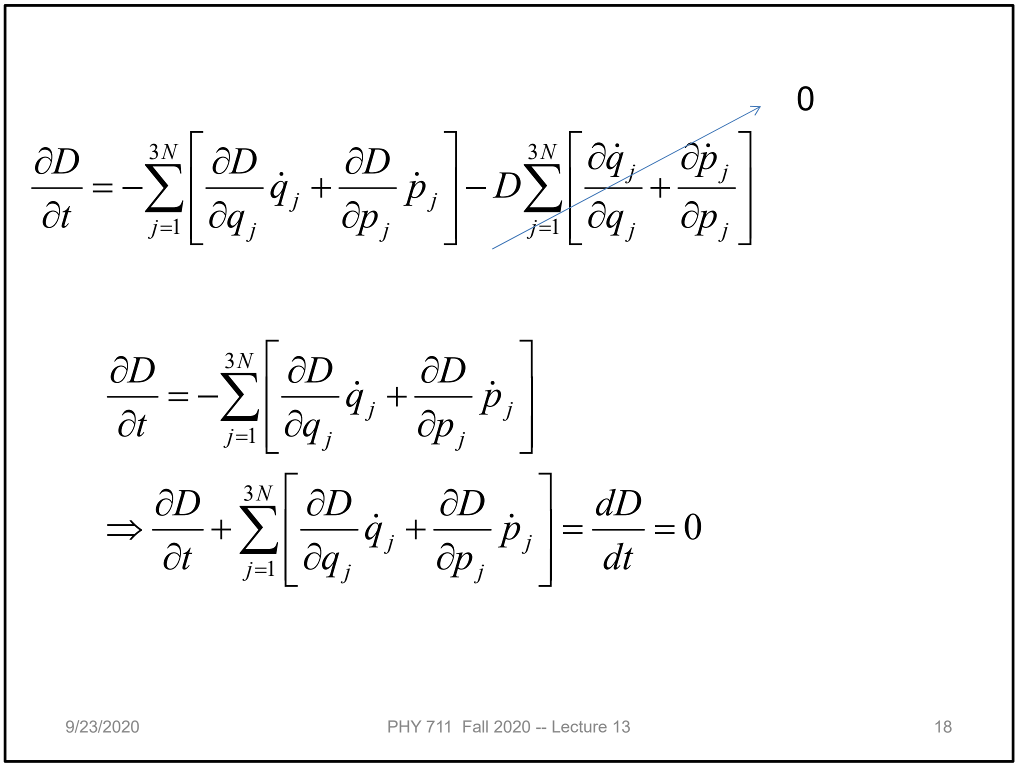
$$\frac{\partial D}{\partial t} = -\nabla \cdot (\mathbf{v}D)$$

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

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

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

More details.

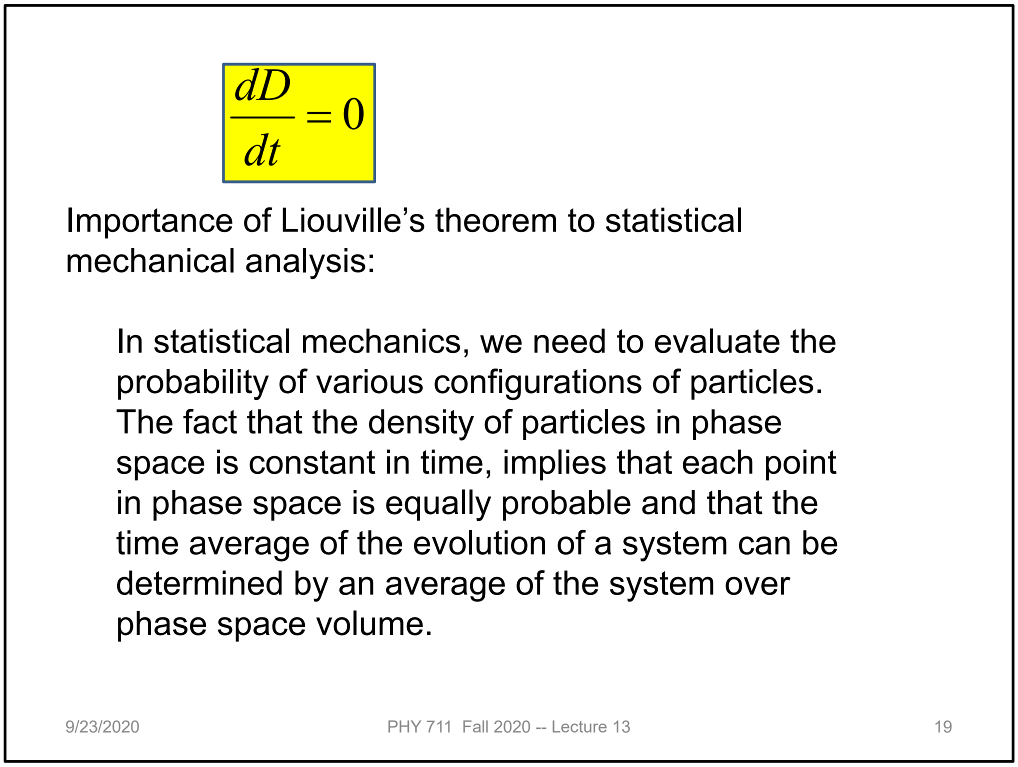


$$\frac{\partial D}{\partial t} = -\sum_{j=1}^{3N}\left[\frac{\partial D}{\partial q_j}\dot{q}_j + \frac{\partial D}{\partial p_j}\dot{p}_j\right] - \cancelto{0}{D\sum_{j=1}^{3N}\left[\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j}\right]}$$

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

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

Derivation of Liouville theorem



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

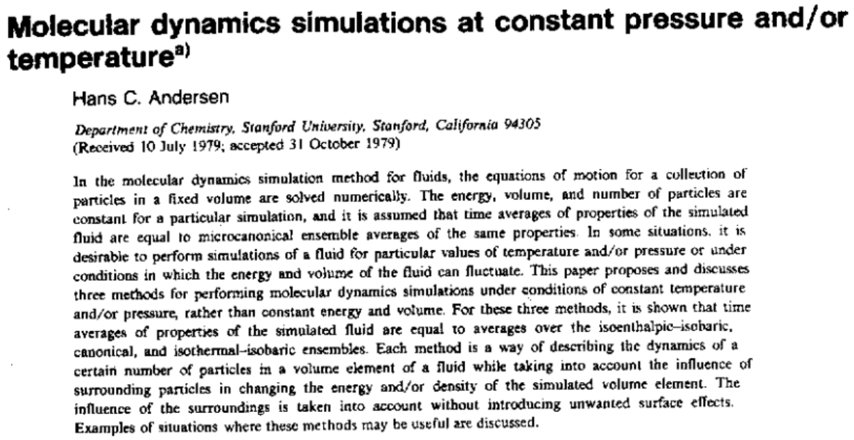
Importance of Liouville’s theorem to statistical mechanical analysis:

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.

Comment.

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.

This paper shows an example of Lagrangian and Hamiltonian mechanics use to make realistic simulations of real materials.

"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.

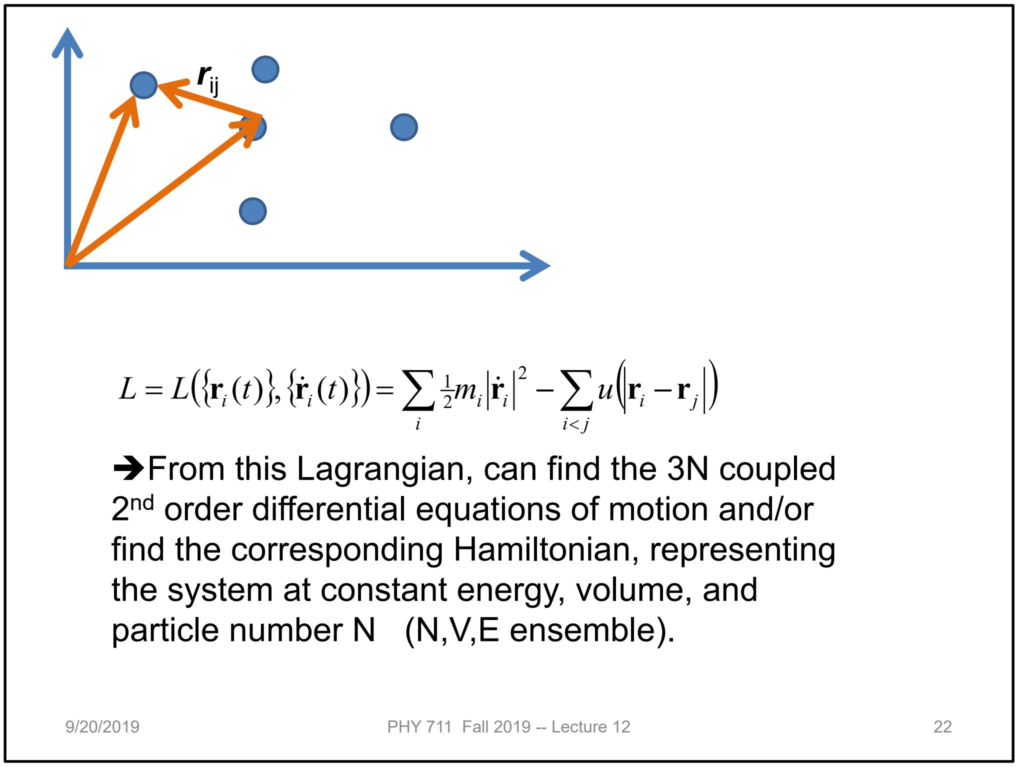
Imagine that the generalized coordinates $\{q_\sigma(t)\}$ represent N atoms, each with 3 spacial coordinates:

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

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

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

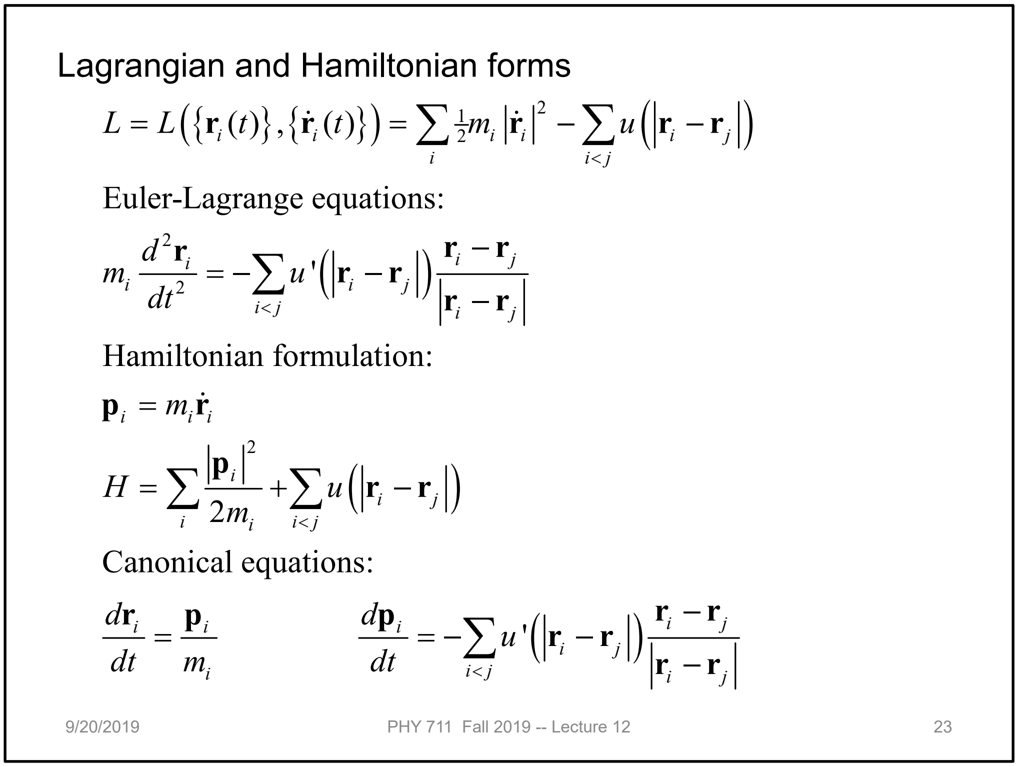
Brief introduction to the approach of H. C. Andersen



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

➔From this Lagrangian, can find the 3N coupled 2^{nd} 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).

Schematic drawing of system modeled.



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:

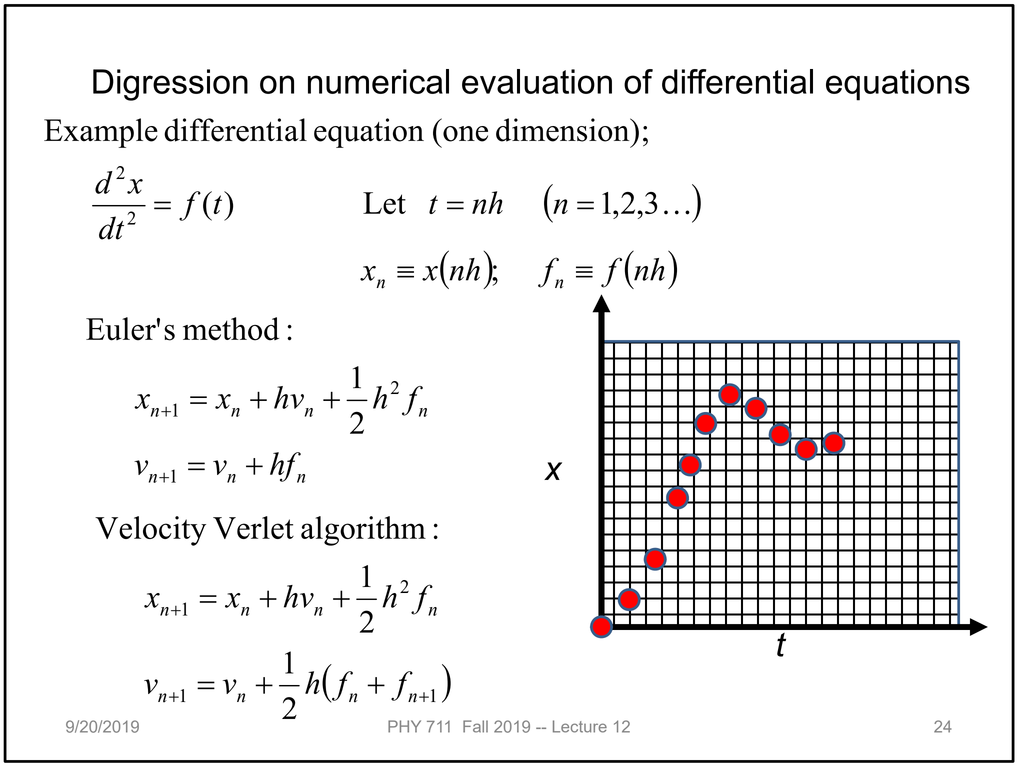
$$\mathbf{p}_i = m_i \dot{\mathbf{r}}_i$$

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

Canonical equations:

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

Lagrangian and Hamiltonian of particle system.



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:

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

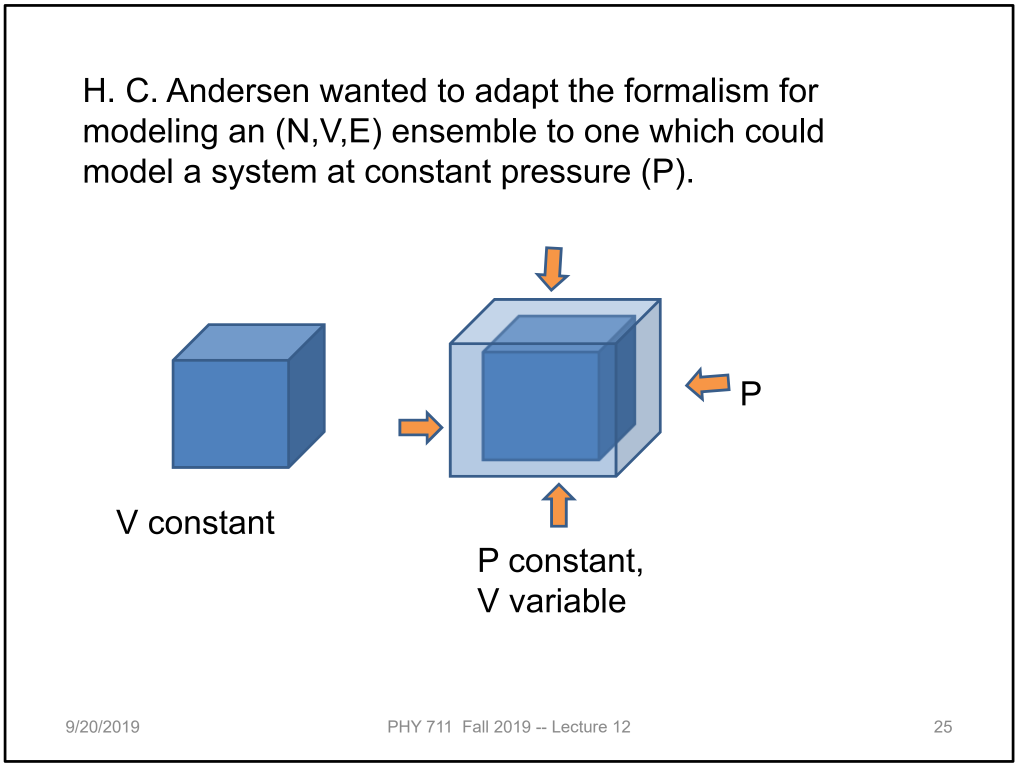
$$v_{n+1} = v_n + hf_n$$

Velocity Verlet algorithm:

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

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

The equations cannot generally be solved analystically so that numerical methods must be used. This slide shows some of the ideas for numerical devaluations.



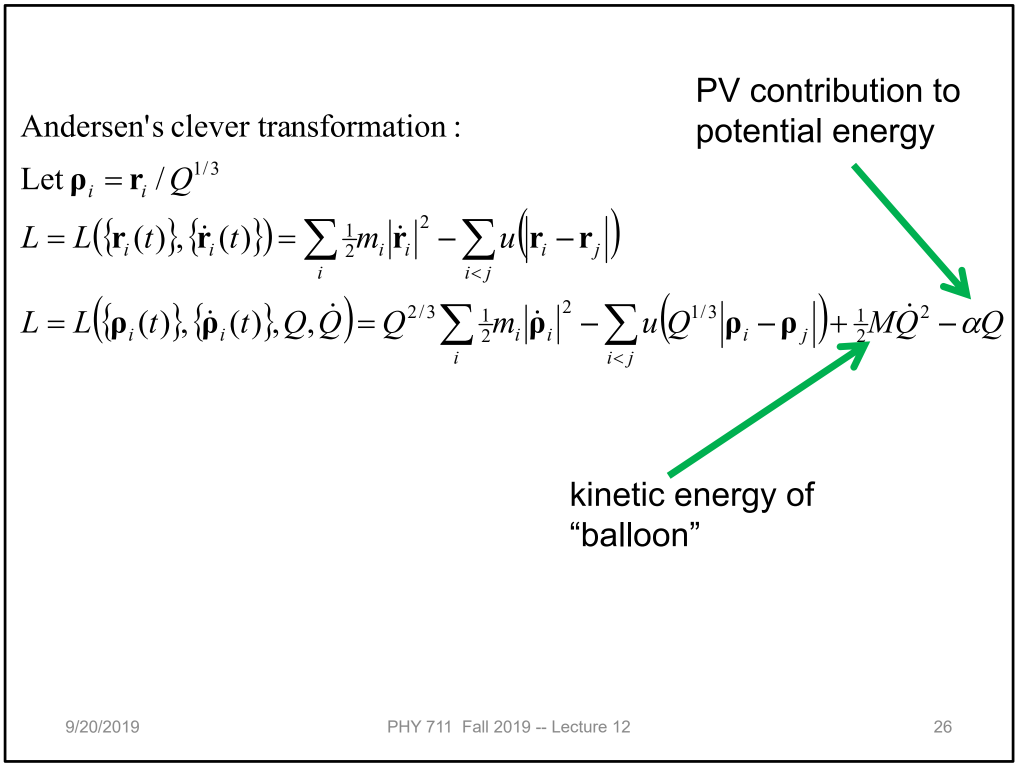
H. C. Andersen wanted to adapt the formalism for modeling an (N,V,E) ensemble to one which could model a system at constant pressure (P).

V constant

P

P constant,
V variable

Back to the ideas of H. C. Andersen.



PV contribution to potential energy

Andersen's clever transformation :

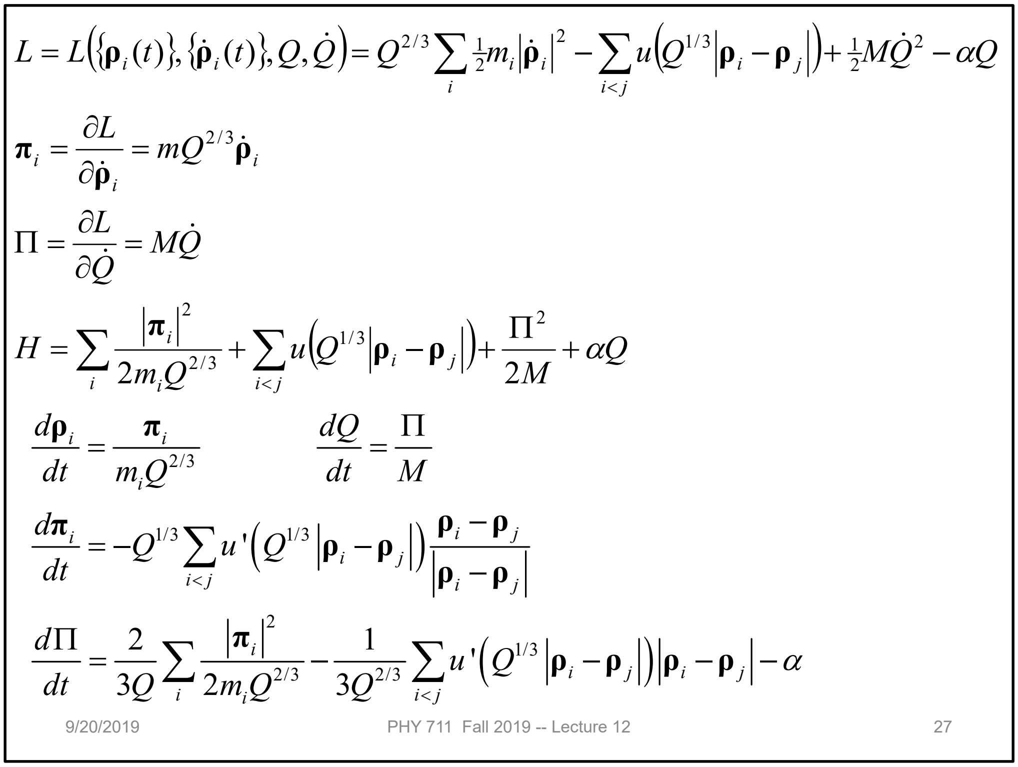
Let $\boldsymbol{\rho}_i = \mathbf{r}_i / Q^{1/3}$

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

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

kinetic energy of “balloon”

Andersen’s approach of “extending the Lagrangian to include pressure effects.



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

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

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

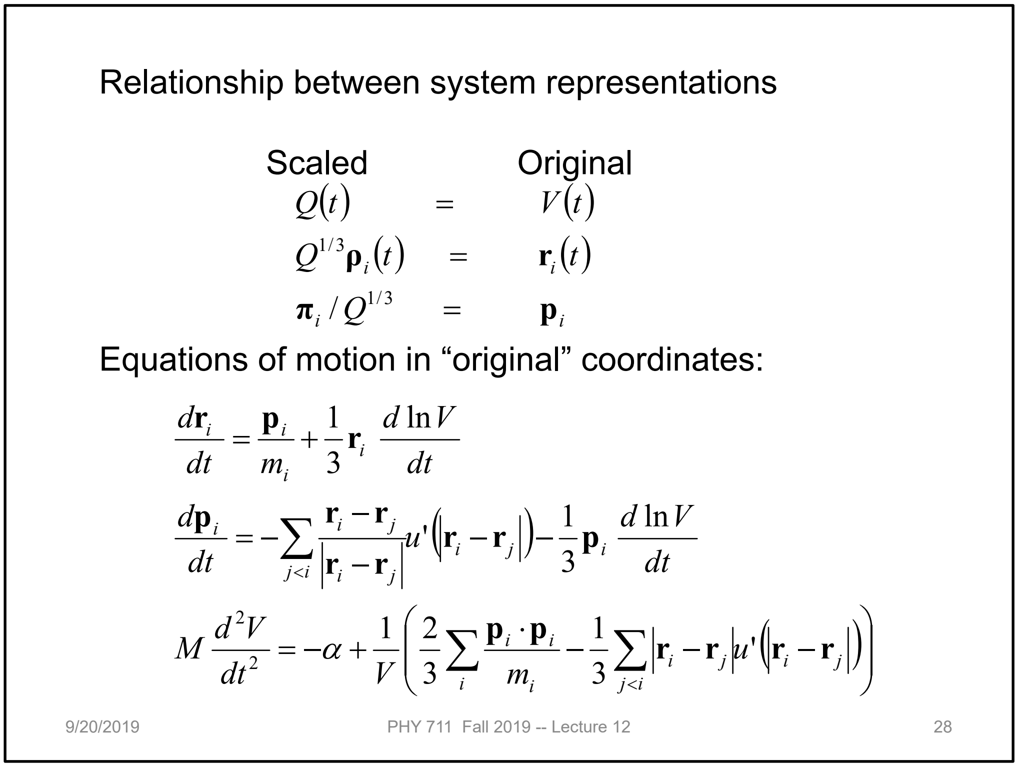
$$H = \sum_i \frac{\left|\boldsymbol{\pi}_i\right|^2}{2m_iQ^{2/3}} + \sum_{i<j} u\left(Q^{1/3}\left|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j\right|\right) + \frac{\Pi^2}{2M} + \alpha Q$$

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

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

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

Some details.



Relationship between system representations

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

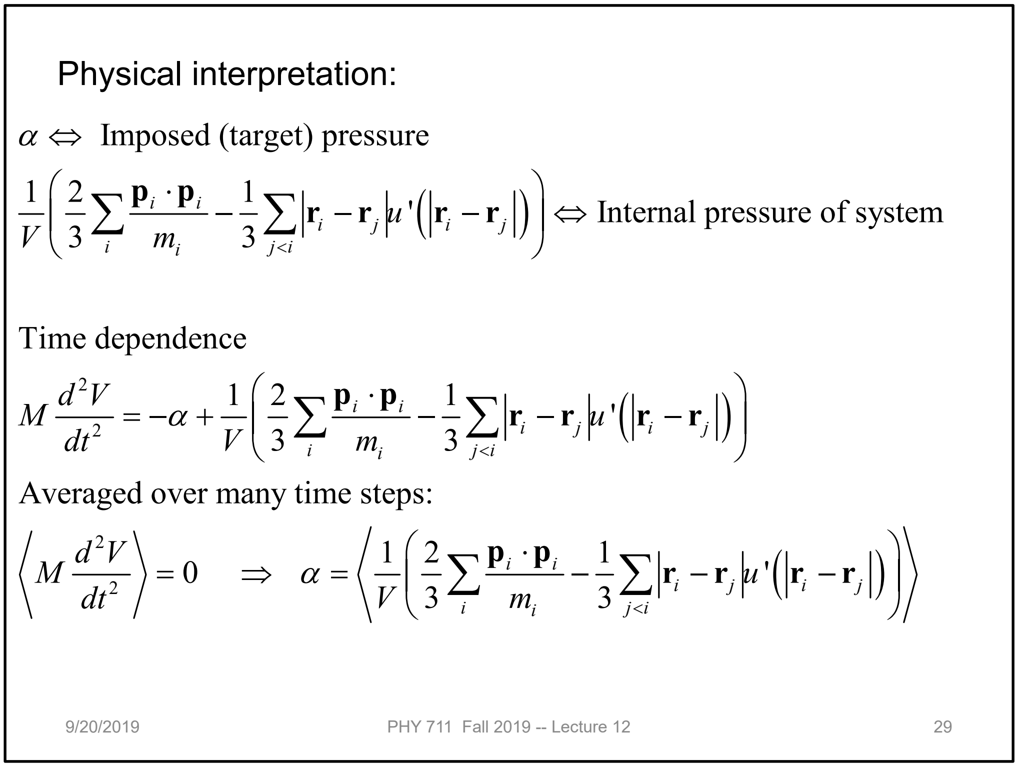
Equations of motion in “original” coordinates:

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

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

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

More details.



Physical interpretation:

$\alpha \Leftrightarrow$ Imposed (target) pressure

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

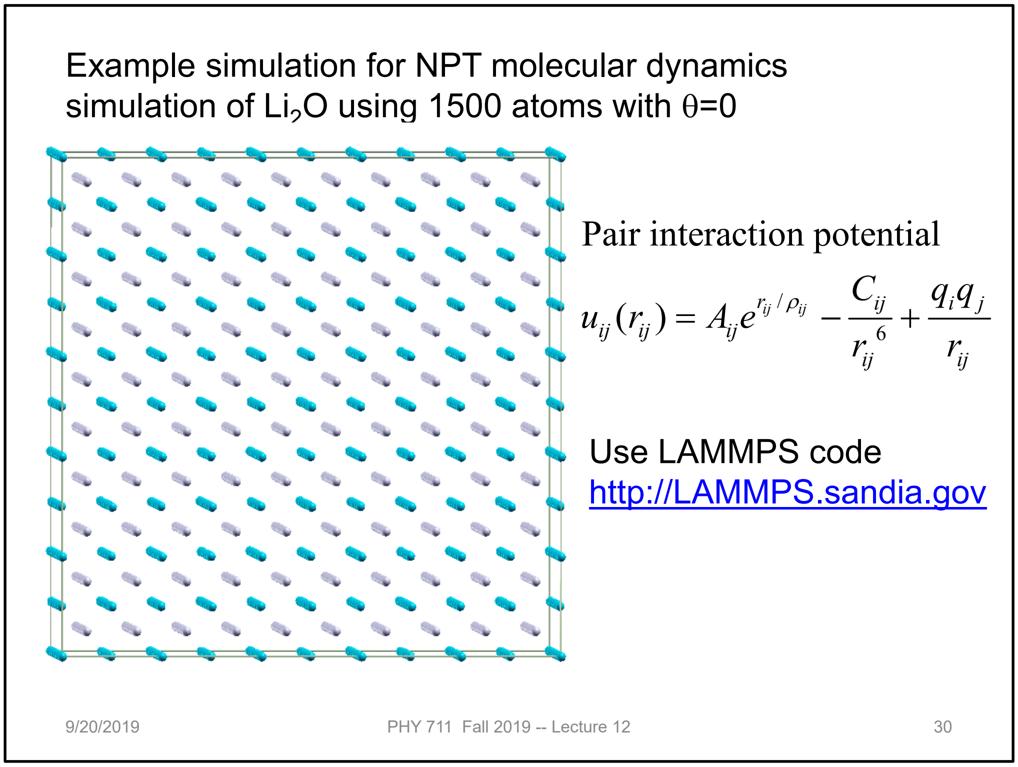
Time dependence

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

Averaged over many time steps:

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

Here alpha represents the controlling pressure.



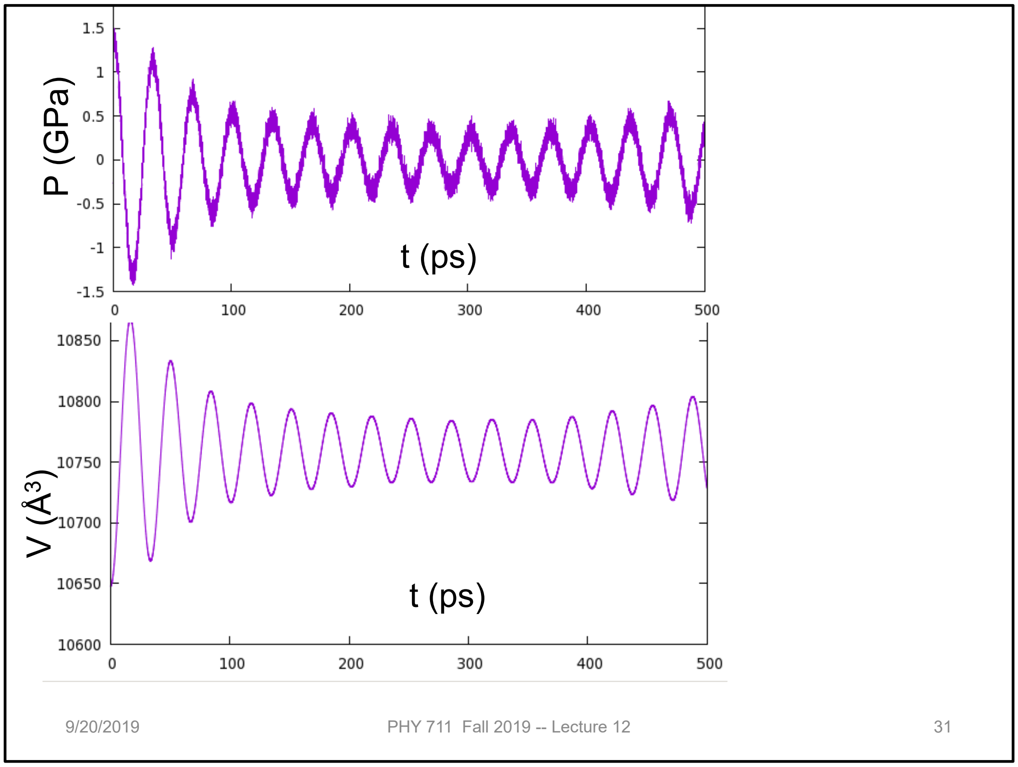
Example simulation for NPT molecular dynamics simulation of Li_2O using 1500 atoms with $\theta=0$

Pair interaction potential

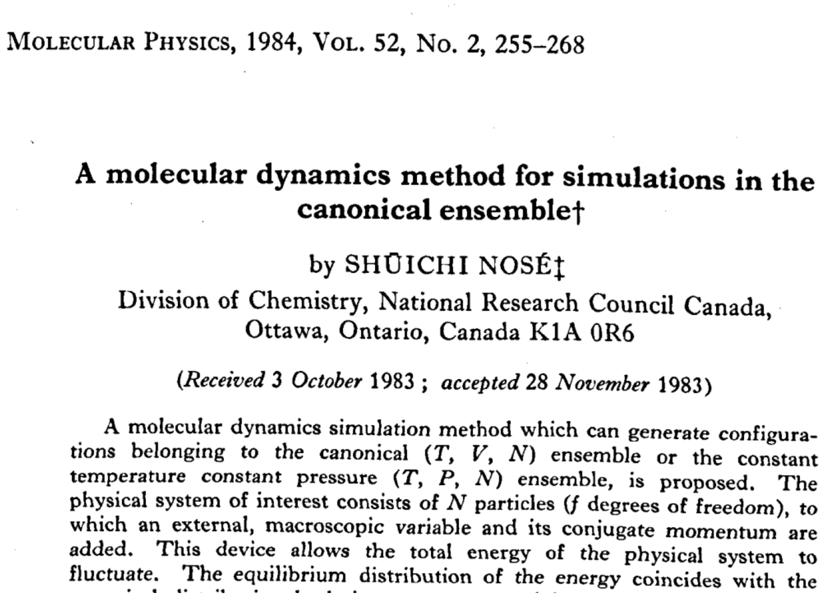
$$u_{ij}(r_{ij}) = A_{ij}e^{r_{ij}/\rho_{ij}} - \frac{C_{ij}}{r_{ij}^{\,6}} + \frac{q_i q_j}{r_{ij}}$$

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

An illustration of simulation for a particular system.



Plot of volume and pressure variation for a particular simulation.



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A molecular dynamics method for simulations in the canonical ensemble†

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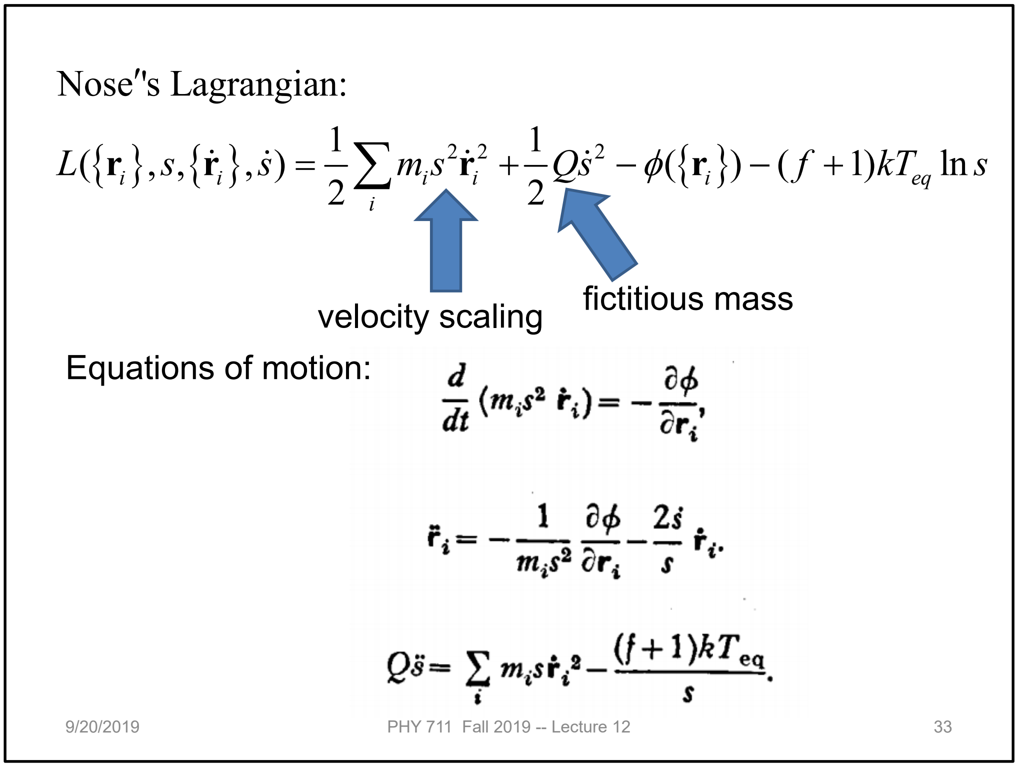
A molecular dynamics simulation method which can generate configurations belonging to the canonical (T, V, N) ensemble or the constant temperature constant pressure (T, P, N) ensemble, is proposed. The physical system of interest consists of N particles (f degrees of freedom), to which an external, macroscopic 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

Another famous paper controlling the temperature rather than the pressure.



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:

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

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

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

Nose’’s idea to control the temperature using an “extended” Lagrangian.

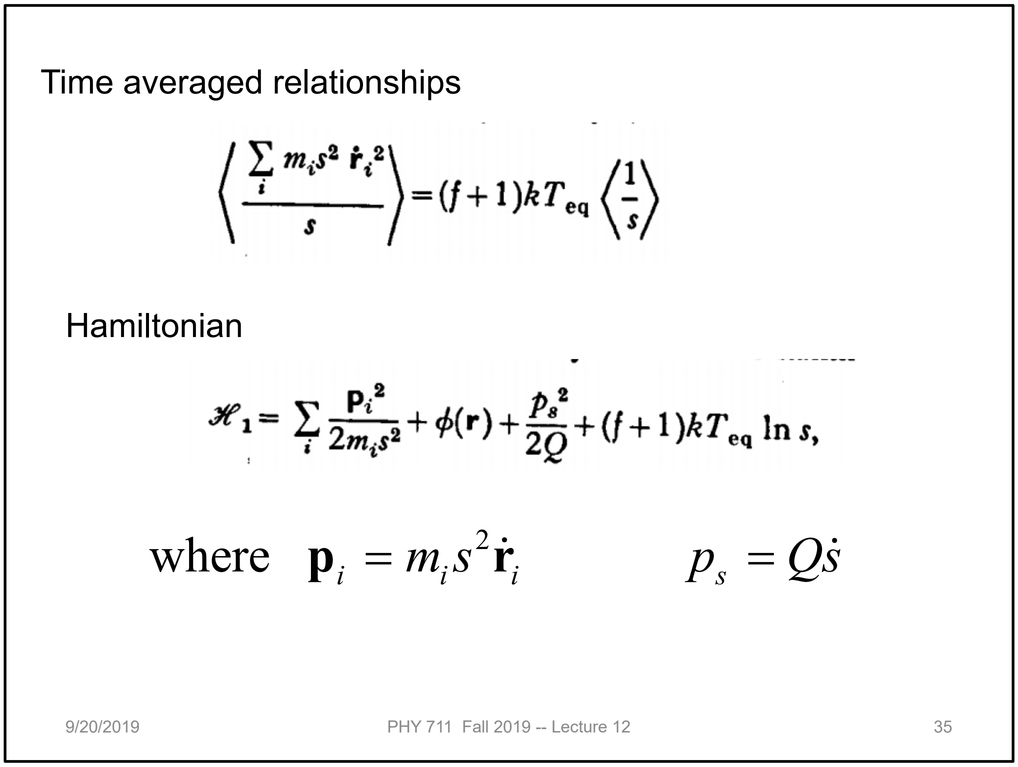
Time averaged relationships

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

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

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

Showing how the scale factor s behaves on averate.



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

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

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

More details.

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:

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

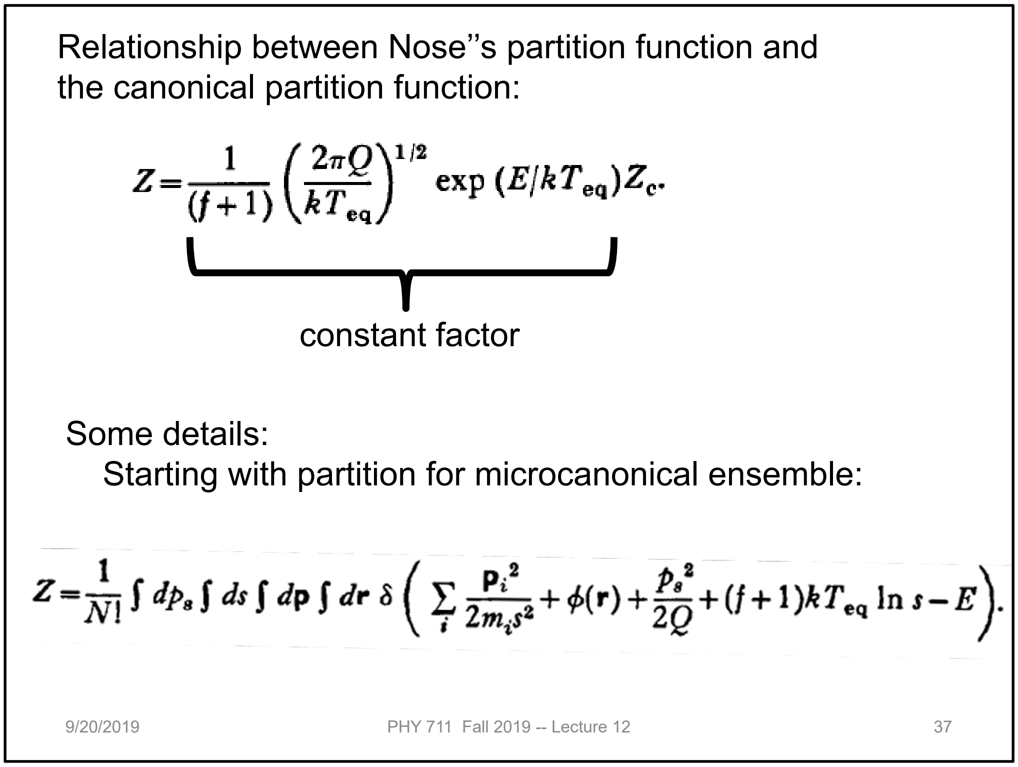
where $\mathscr{H}(\{\bar{\mathbf{r}}_i\},\{\bar{\mathbf{p}}_i\}) \equiv \sum_i \frac{\bar{\mathbf{p}}_i^2}{2m_i} + \phi(\{\bar{\mathbf{r}}_i\})$

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

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

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

Some references to the related statistical mechanics developments.



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

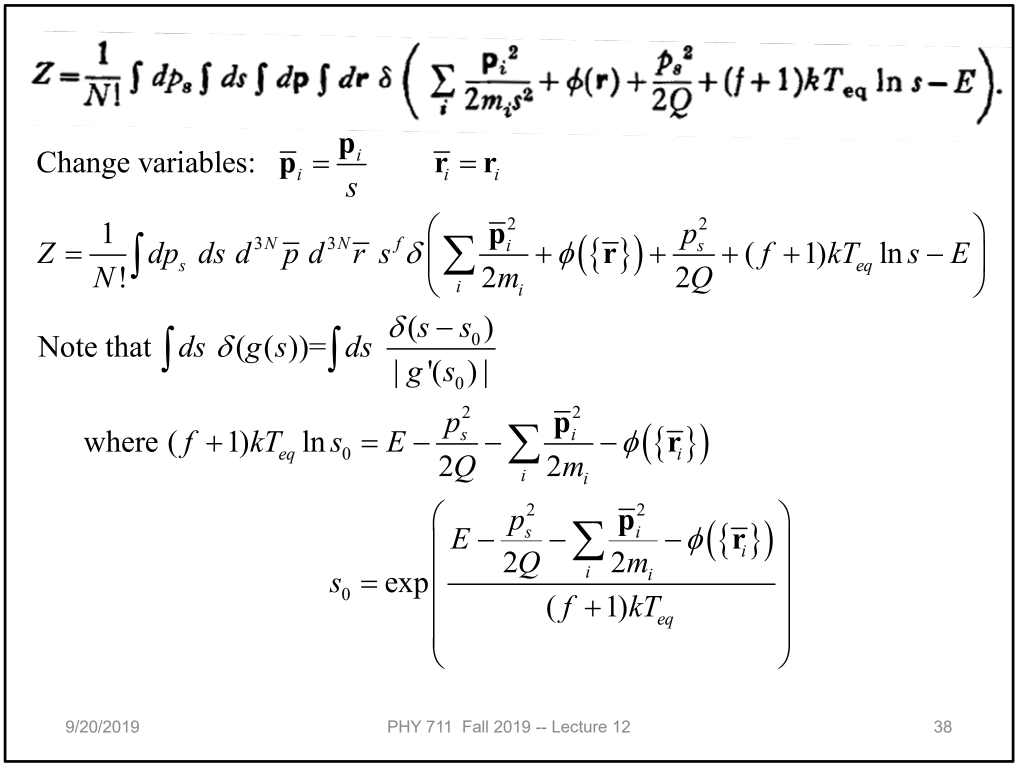
$$Z=\underbrace{\frac{1}{(f+1)}\left(\frac{2\pi Q}{kT_{\mathrm{eq}}}\right)^{1/2}\exp\left(E/kT_{\mathrm{eq}}\right)}_{\text{constant factor}}Z_{\mathrm{c}}.$$

Some details:

Starting with partition for microcanonical ensemble:

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

More statistical mechanics.



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

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

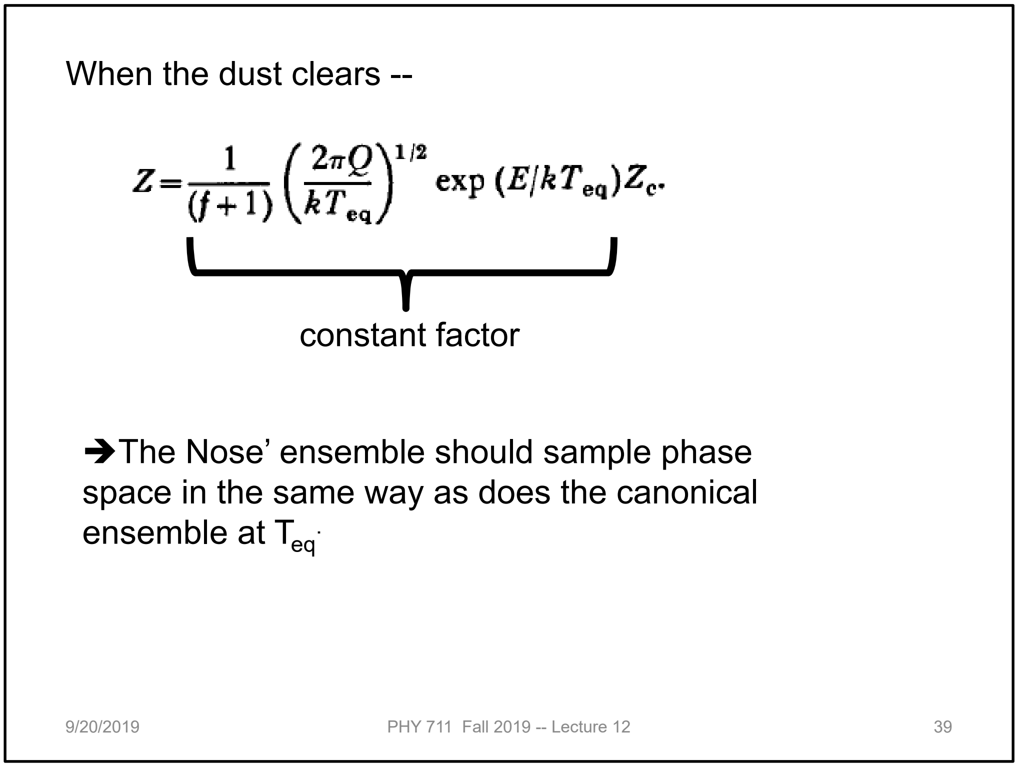
$$Z=\frac{1}{N!}\int dp_s\;ds\;d^{3N}\overline{p}\;d^{3N}\overline{r}\;s^f\delta\left(\sum_i\frac{\overline{\mathbf{p}}_i^2}{2m_i}+\phi\left(\{\overline{\mathbf{r}}\}\right)+\frac{p_s^2}{2Q}+(f+1)kT_{eq}\ln s-E\right)$$

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

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

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

Details.

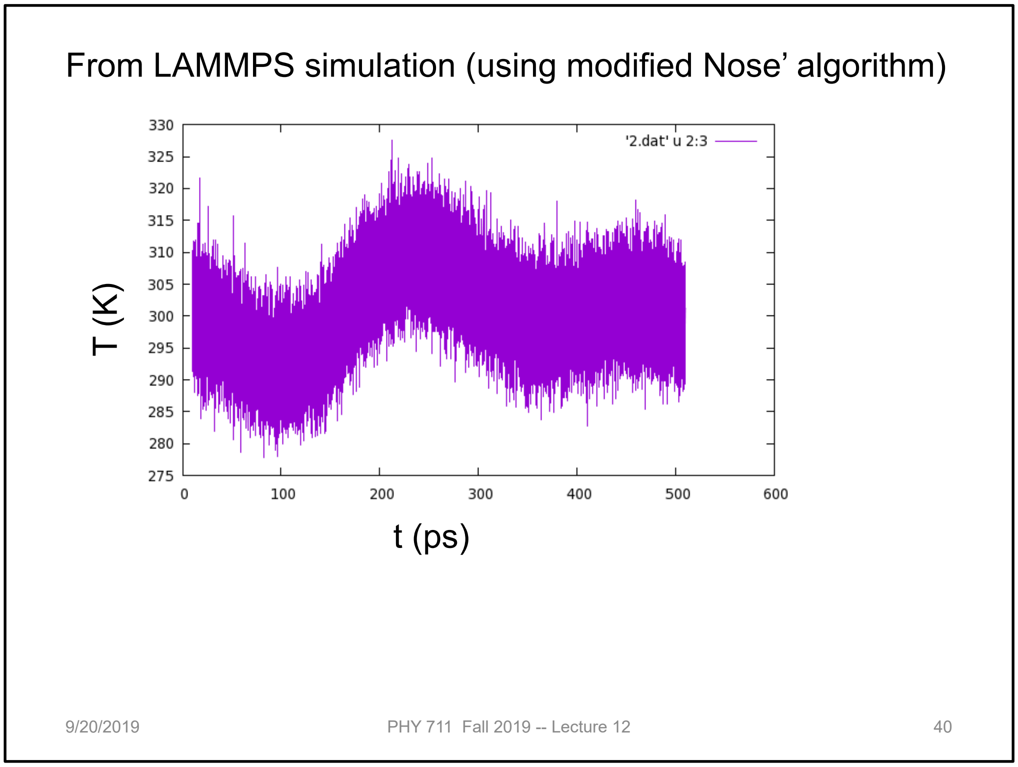


When the dust clears --

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

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

More details.



From LAMMPS simulation (using modified Nose' algorithm)

How does this really work? We see that the approach allows fluctuations in the temperature, but the average is apparently controlled.