

**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**
- 3. Liouville's theorem**

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

1

Course schedule

(Preliminary schedule -- subject to frequent adjustment.)

	Date	F&W Reading	Topic	Assignment
1	Wed, 8/26/2015	Chap. 1	Review of basic principles	#1
2	Fri, 8/28/2015	Chap. 1	Scattering theory	#2
3	Mon, 8/31/2015	Chap. 1	Scattering theory continued	#3
4	Wed, 9/02/2015	Chap. 2	Accelerated coordinate systems	#4
5	Fri, 9/04/2015	Chap. 3	Calculus of variations	#5
6	Mon, 9/07/2015	Chap. 3	Calculus of variations	#6
7	Wed, 9/09/2015	Chap. 3	Hamilton's principle	#7
8	Fri, 9/11/2015	Chap. 3 & 6	Hamilton's principle	#8
9	Mon, 9/14/2015	Chap. 3 & 6	Lagrangians with constraints	#9
10	Wed, 9/16/2015	Chap. 3 & 6	Lagrangians and constants of motion	#10
11	Fri, 9/18/2015	Chap. 3 & 6	Hamiltonian formalism	#11
12	Mon, 9/21/2015	Chap. 3 & 6	Hamiltonian formalism	#12
13	Wed, 9/23/2015	Chap. 3 & 6	Hamiltonian Jacobi transformations	
14	Fri, 9/25/2015	Chap. 4	Small oscillations	
15	Mon, 9/28/2015	Chap. 4	Normal modes of motion	
16	Wed, 9/30/2015	Chap. 4	Normal modes of motion	

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

2

Hamiltonian formalism

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

Canonical equations of motion

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

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

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

3

Hamiltonian formalism and time evolution:

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

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

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

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

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

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

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

4

Hamiltonian formalism and time evolution:

Poisson brackets:

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

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

Define :

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

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

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

5

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 :

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

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

Liouville theorem

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

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

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

6

Phase space

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

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

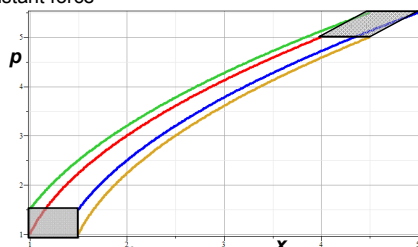
For a d dimensional system with N particles, the phase space corresponds to $2dN$ degrees of freedom.

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

7

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



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

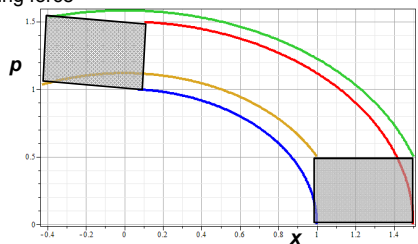
$$p_i(t) = p_{0i} + F_0 t \quad x_i(t) = x_{0i} + \frac{p_{0i}}{m} t + \frac{1}{2} F_0 t^2$$

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

8

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



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

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

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

9

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: $D = D(\{q_\sigma(t)\}, \{p_\sigma(t)\}, t)$

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

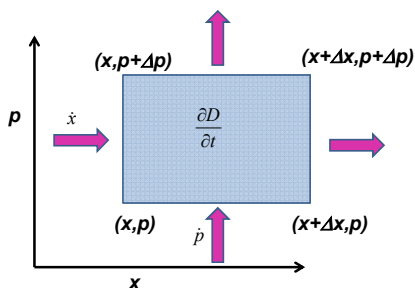
According to Liouville's theorem: $\frac{dD}{dt} = 0$

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

10

Liouville's theorem

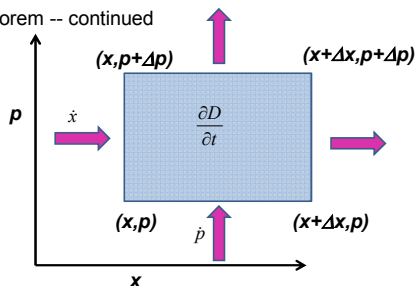


9/21/2015

PHY 711 Fall 2015 -- Lecture 12

11

Liouville's theorem -- continued



$$\begin{aligned} \frac{\partial D}{\partial t} &\Rightarrow \text{time rate of change of particles within volume} \\ &= \text{time rate of particle entering minus particles leaving} \\ &= -\frac{\partial D}{\partial x} \dot{x} - \frac{\partial D}{\partial p} \dot{p} \end{aligned}$$

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

12

Liouville's theorem -- continued

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

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

9/21/2015 PHY 711 Fall 2015 -- Lecture 12 13

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 :

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

Liouville's theorem shows that :

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

9/21/2015 PHY 711 Fall 2015 -- Lecture 12 14

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 :

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

We also have a $6N$ dimensional gradient :

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

9/21/2015 PHY 711 Fall 2015 -- Lecture 12 15

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

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

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

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

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

16

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

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

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

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

17

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

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.

9/21/2015

PHY 711 Fall 2015 -- Lecture 12

18

Modern usage of Lagrangian and Hamiltonian formalisms

J. Chem. Physics **72** 2384-2393 (1980)**Molecular dynamics simulations at constant pressure and/or temperature¹⁾**

Hans C. Andersen

Department of Chemistry, Stanford University, Stanford, California 94305

(Received 10 July 1979; accepted 11 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 isothermal-isobaric, canonical, and isochoric-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.

9/24/2014

PHY 711 Fall 2014 -- Lecture 13

19

"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 :

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

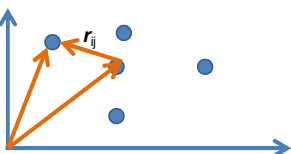
For simplicity, it is assumed that the potential interaction is a sum of pairwise interactions :

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

9/24/2014

PHY 711 Fall 2014 -- Lecture 13

20



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

→ 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).

9/24/2014

PHY 711 Fall 2014 -- Lecture 13

21

Lagrangian and Hamiltonian forms

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

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

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

Canonical equations :

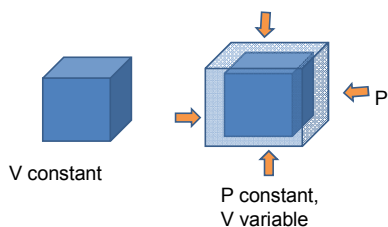
$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} \quad \frac{d\mathbf{p}_i}{dt} = - \sum_{i < j} u'(|\mathbf{r}_i - \mathbf{r}_j|) \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$

9/24/2014

PHY 711 Fall 2014 -- Lecture 13

22

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).



9/24/2014

PHY 711 Fall 2014 -- Lecture 13

23

Andersen's clever transformation :

$$\text{Let } \mathbf{p}_i = \mathbf{r}_i / Q^{1/3}$$

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

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

kinetic energy of
"balloon"

PV contribution to
potential energy

9/24/2014

PHY 711 Fall 2014 -- Lecture 13

24

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

$$\boldsymbol{\pi}_i = \frac{\partial L}{\partial \dot{\mathbf{p}}_i} = m_i Q^{2/3} \dot{\mathbf{p}}_i$$

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

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

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

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

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

9/24/2014 PHY 711 Fall 2014 -- Lecture 13 25

Relationship between system representations

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

Equations of motion in "original" coordinates:

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

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

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

9/24/2014 PHY 711 Fall 2014 -- Lecture 13 26

Physical interpretation:

$\alpha \Leftrightarrow$ Imposed (target) pressure

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

Time dependence

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

9/24/2014 PHY 711 Fall 2014 -- Lecture 13 27

Digression on numerical evaluation of differential equations

Example differential equation (one dimension);

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

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

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 :

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

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

9/24/2014

PHY 711 Fall 2014 -- Lecture 13

28
