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

Plan for Lecture 13:

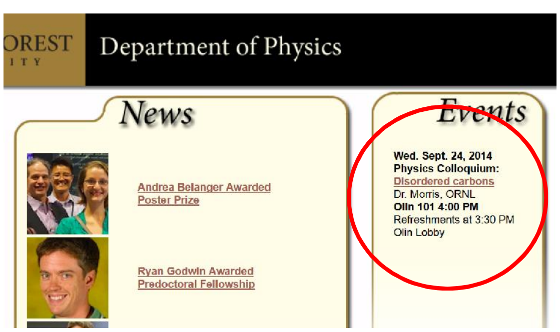
Finish reading Chapter 6

1. Canonical transformations
2. Hamilton-Jacobi formalism
3. Modern applications

Course schedule

(Preliminary schedule -- subject to frequent adjustment.) rrr>

	Date	F&W Reading	Topic	Assignment
1	Wed, 8/27/2014	Chap. 1	Review of basic principles	#1
2	Fri, 8/29/2014	Chap. 1	Scattering theory	#2
3	Mon, 9/01/2014	Chap. 1	Scattering theory continued	#3
4	Wed, 9/03/2014	Chap. 2	Accelerated coordinate systems	#4
5	Fri, 9/05/2014	Chap. 3	Calculus of variations	#5
6	Mon, 9/08/2014	Chap. 3	Calculus of variations	#6
7	Wed, 9/10/2014	Chap. 3	Hamilton's principle	#7
8	Fri, 9/12/2014	Chap. 3 & 6	Hamilton's principle	#8
9	Mon, 9/15/2014	Chap. 3 & 6	Lagrangians with constraints	#9
10	Wed, 9/17/2014	Chap. 3 & 6	Lagrangians and constants of motion	#10
11	Fri, 9/19/2014	Chap. 3 & 6	Hamiltonian formalism	#11
12	Mon, 9/22/2014	Chap. 3 & 6	Hamiltonian formalism	#11
13	Wed, 9/24/2014	Chap. 3 & 6	Hamiltonian Jacobi transformations	
14	Fri, 9/26/2014	Chap. 4	Small oscillations	Begin Take-Home
15	Mon, 9/29/2014	Chap. 4	Normal modes of motion	Continue Take-Home
16	Wed, 10/01/2014	Chap. 4	Normal modes of motion	Continue Take-Home
17	Fri, 10/03/2014	Chap. 4	Normal modes of motion	Take-Home due



WFU Physics Colloquium

TITLE: From Crumpled Sheets to Quantum Fluids

SPEAKER: Dr. James R. Morris,

Oak Ridge National Laboratory,
Oak Ridge, Tennessee

TIME: Wednesday September 24, 2014 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

Carbon materials continue to generate great interest, particularly in graphene-based materials. A number of experimental and theoretical developments have led to a deeper understanding and predictive capabilities in these materials, and their relationship to confined fluids in porous carbon. High-resolution microscopy studies at ORNL show that "disordered" carbon materials are actually much more ordered than previously believed, leading to new models of these materials. Topological defects play an important role, and generate new features: "folds" in graphene that change the three dimensional structure of graphene, and that provide relatively strong physisorption sites for gas molecules. We have connected developments in density functional calculations to continuum thermodynamic modeling of adsorption to make material-specific predictions of gas densification. Small angle neutron scattering provides a key test of these predictions, by probing the strong enhancement of adsorption in particular sizes of pores. At low temperatures, light molecules such as H_2 and D_2 adsorbed in these materials become quantum fluids, leading to novel effects. Quasi-elastic neutron scattering has been used to demonstrate strong "quantum sieving," with D_2 diffusing ~70 times faster than H_2.

Hamiltonian formalism

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

Canonical equations of motion

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

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

Notion of "Canonical" distributions

$$q_\sigma = q_\sigma(\{Q_1 \cdots Q_n\},\{P_1 \cdots P_n\},t) \qquad \text{for each } \sigma$$

$$p_\sigma = p_\sigma(\{Q_1 \cdots Q_n\},\{P_1 \cdots P_n\},t) \qquad \text{for each } \sigma$$

$$\sum_\sigma p_\sigma \dot{q}_\sigma - H(\{q_\sigma\},\{p_\sigma\},t) =$$

$$\sum_\sigma P_\sigma \dot{Q}_\sigma - \widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) + \frac{d}{dt}F(\{q_\sigma\},\{Q_\sigma\},t)$$

Apply Hamilton's principle:

$$\delta \int_{t_i}^{t_f} \left[\sum_\sigma P_\sigma \dot{Q}_\sigma - \widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) + \frac{d}{dt}F(\{q_\sigma\},\{Q_\sigma\},t) \right] dt = 0$$

$$\dot{Q}_\sigma = \frac{\partial \widetilde{H}}{\partial P_\sigma} \qquad \dot{P}_\sigma = -\frac{\partial \widetilde{H}}{\partial Q_\sigma}$$

Note that it is conceivable that if we were extraordinarily clever, we could find all of the constants of the motion!

$$\sum_\sigma p_\sigma \dot{q}_\sigma - H(\{q_\sigma\},\{p_\sigma\},t) =$$

$$\sum_\sigma P_\sigma \dot{Q}_\sigma - \widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) + \frac{d}{dt} F(\{q_\sigma\},\{Q_\sigma\},t)$$

$$\frac{d}{dt} F(\{q_\sigma\},\{Q_\sigma\},t) = \sum_\sigma \left(\left(\frac{\partial F}{\partial q_\sigma} \right) \dot{q}_\sigma + \left(\frac{\partial F}{\partial Q_\sigma} \right) \dot{Q}_\sigma \right) + \frac{\partial F}{\partial t}$$

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

$$\sum_\sigma \left(P_\sigma + \left(\frac{\partial F}{\partial Q_\sigma} \right) \right) \dot{Q}_\sigma - \widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) + \frac{\partial F}{\partial t}$$

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

$$\sum_\sigma \left(P_\sigma + \left(\frac{\partial F}{\partial Q_\sigma} \right) \right) \dot{Q}_\sigma - \widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) + \frac{\partial F}{\partial t}$$

$$\Rightarrow p_\sigma = \left(\frac{\partial F}{\partial q_\sigma} \right) \qquad P_\sigma = -\left(\frac{\partial F}{\partial Q_\sigma} \right)$$

$$\Rightarrow \widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) = H(\{q_\sigma\},\{p_\sigma\},t) + \frac{\partial F}{\partial t}$$

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Note that it is conceivable that if we were extraordinarily clever, we could find all of the constants of the motion!

$$\dot{Q}_\sigma = \frac{\partial \widetilde{H}}{\partial P_\sigma} \qquad \dot{P}_\sigma = -\frac{\partial \widetilde{H}}{\partial Q_\sigma}$$

$$\text{Suppose: } \dot{Q}_\sigma = \frac{\partial \widetilde{H}}{\partial P_\sigma} = 0 \text{ and } \dot{P}_\sigma = -\frac{\partial \widetilde{H}}{\partial Q_\sigma} = 0$$

$\Rightarrow Q_\sigma, P_\sigma$ are constants of the motion

Possible solution – Hamilton-Jacobi theory:

$$\text{Suppose: } F(\{q_\sigma\},\{Q_\sigma\},t) \Rightarrow -\sum_\sigma P_\sigma Q_\sigma + S(\{q_\sigma\},\{P_\sigma\},t)$$

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$$\sum_\sigma p_\sigma \dot{q}_\sigma - H(\{q_\sigma\},\{p_\sigma\},t) =$$

$$\sum_\sigma P_\sigma \dot{Q}_\sigma - \widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) + \frac{d}{dt}\left(-\sum_\sigma P_\sigma Q_\sigma + S(\{q_\sigma\},\{P_\sigma\},t)\right)$$

$$= -\widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) - \sum_\sigma \dot{P}_\sigma Q_\sigma + \sum_\sigma\left(\frac{\partial S}{\partial q_\sigma}\dot{q}_\sigma + \frac{\partial S}{\partial P_\sigma}\dot{P}_\sigma\right) + \frac{\partial S}{\partial t}$$

Solution :

$$p_\sigma = \frac{\partial S}{\partial q_\sigma} \qquad Q_\sigma = \frac{\partial S}{\partial P_\sigma}$$

$$\widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t) = H(\{q_\sigma\},\{p_\sigma\},t) + \frac{\partial S}{\partial t}$$

When the dust clears :

Assume $\{Q_\sigma\},\{P_\sigma\},\widetilde{H}$ are constants; choose $\widetilde{H} = 0$

Need to find $S(\{q_\sigma\},\{P_\sigma\},t)$

$$p_\sigma = \frac{\partial S}{\partial q_\sigma} \qquad Q_\sigma = \frac{\partial S}{\partial P_\sigma}$$

$$\Rightarrow H\left(\{q_\sigma\},\left\{\frac{\partial S}{\partial q_\sigma}\right\},t\right) + \frac{\partial S}{\partial t} = 0$$

Note : S is the "action":

$$\sum_\sigma p_\sigma \dot{q}_\sigma - H(\{q_\sigma\},\{p_\sigma\},t) =$$

$$\cancelto{0}{\sum_\sigma P_\sigma \dot{Q}_\sigma} - \cancelto{0}{\widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t)} + \frac{d}{dt}\left(-\cancelto{0}{\sum_\sigma P_\sigma Q_\sigma} + S(\{q_\sigma\},\{P_\sigma\},t)\right)$$

$$\sum_\sigma p_\sigma \dot{q}_\sigma - H(\{q_\sigma\},\{p_\sigma\},t) =$$

$$\cancelto{0}{\sum_\sigma P_\sigma \dot{Q}_\sigma} - \cancelto{0}{\widetilde{H}(\{Q_\sigma\},\{P_\sigma\},t)} + \frac{d}{dt}\left(-\cancelto{0}{\sum_\sigma P_\sigma Q_\sigma} + S(\{q_\sigma\},\{P_\sigma\},t)\right)$$

$$\int_{t_i}^{t_f}\left(\sum_\sigma p_\sigma \dot{q}_\sigma - H(\{q_\sigma\},\{p_\sigma\},t)\right)dt = \int_{t_i}^{t_f}\left(\frac{d}{dt}\left(S(\{q_\sigma\},\{P_\sigma\},t)\right)\right)dt$$

$$= S(\{q_\sigma\},\{P_\sigma\},t)\Big|_{t_i}^{t_f}$$

Differential equation for ***S***:

$$H\left(\{q_\sigma\},\left\{\frac{\partial S}{\partial q_\sigma}\right\},t\right)+\frac{\partial S}{\partial t}=0$$

$$\text{Example:}\qquad H(\{q\},\{p\},t)=\frac{p^2}{2m}+\frac{1}{2}m\omega^2q^2$$

$$\text{Hamilton - Jacobi Eq:}\quad H\left(\{q\},\left\{\frac{\partial S}{\partial q}\right\},t\right)+\frac{\partial S}{\partial t}=0$$

$$\frac{1}{2m}\left(\frac{\partial S}{\partial q}\right)^2+\frac{1}{2}m\omega^2q^2+\frac{\partial S}{\partial t}=0$$

$$\text{Assume:}\qquad S(q,t)\equiv W(q)-Et\qquad\qquad (E\quad\text{constant})$$

Continued:

$$\frac{1}{2m}\left(\frac{\partial S}{\partial q}\right)^2+\frac{1}{2}m\omega^2q^2+\frac{\partial S}{\partial t}=0$$

$$\text{Assume:}\qquad S(q,t)\equiv W(q)-Et\qquad\qquad (E\quad\text{constant})$$

$$\frac{1}{2m}\left(\frac{dW}{dq}\right)^2+\frac{1}{2}m\omega^2q^2=E$$

$$\frac{dW}{dq}=\sqrt{2mE-(m\omega)^2q^2}$$

$$W(q)=\int\sqrt{2mE-(m\omega)^2q^2}\,dq$$

Continued:

$$W(q)=\int\sqrt{2mE-(m\omega)^2q^2}\,dq$$

$$=\frac{1}{2}q\sqrt{2mE-(m\omega)^2q^2}+\frac{E}{\omega}\sin^{-1}\left(\frac{m\omega q}{\sqrt{2mE}}\right)+C$$

$$S(q,E,t)=\frac{1}{2}q\sqrt{2mE-(m\omega)^2q^2}+\frac{E}{\omega}\sin^{-1}\left(\frac{m\omega q}{\sqrt{2mE}}\right)-Et$$

$$\frac{\partial S}{\partial E}=Q=\frac{1}{\omega}\sin^{-1}\left(\frac{m\omega q}{\sqrt{2mE}}\right)-t$$

$$\Rightarrow q(t)=\frac{\sqrt{2mE}}{m\omega}\sin(\omega(t+Q))$$

Recap --

Lagrangian picture

For independent generalized coordinates $q_\sigma(t)$:

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

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_\sigma} - \frac{\partial L}{\partial q_\sigma} = 0$$

$\Rightarrow$ Second order differential equations for $q_\sigma(t)$

Hamiltonian picture

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

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

$\Rightarrow$ Coupled first order differential equations for

$q_\sigma(t)$ and $p_\sigma(t)$

Modern usage of Lagrangian and Hamiltonian formalisms

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

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

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(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.

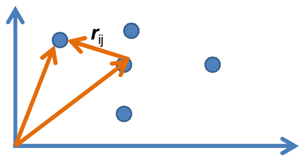
"Molecular dynamics" is a subfield of computational physics focused on analyzing the motions of atoms in fluids and solids with the goal of relating the atomistic and macroscopic properties of materials. Ideally molecular dynamics calculations can numerically realize the statistical mechanics viewpoint.

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:

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



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

➔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

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

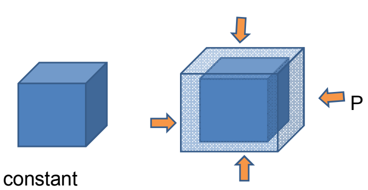
$$\mathbf{p}_i = m_i \dot{\mathbf{r}}_i$$

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

Canonical equations:

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

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

Andersen's clever transformation :

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

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

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

PV contribution to potential energy

kinetic energy of "balloon"

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

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

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

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

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

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

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

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:

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

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

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

Physical interpretation:

$\alpha \Leftrightarrow$ Imposed (target) pressure

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

Time dependence

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

Digression on numerical evaluation of differential equations

Example differential equation (one dimension);

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

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

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 :

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

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