

PHY 337/637 Analytical Mechanics

12:30-1:45 PM TR in Olin 103

Notes for Lecture 13

Comments on “modern” uses of methodologies of analytical mechanics

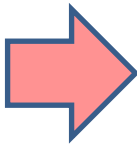
- 1. Atomistic viewpoint of materials**
- 2. Computer simulation to analyze effects of atomic scale phenomena on macroscopic scale**
- 3. Concept of phase space and the Liouville theorem**
- 4. Examples**

Course schedule

In the table below, **Reading** refers to the chapters in the [Cline textbook](#), **PP** refers to textbook section listing practice problems to be discussed at the course tutorials, and **Assign** is a link to the graded homework for the lecture. The graded homeworks are due each Tuesday following the associated lecture.

(Preliminary schedule -- subject to frequent adjustment.)

	Date	Reading	Topic	PP	Assign
1	Tu, 8/29/2023	Ch. 1 & 2	Introduction, history, and motivation	2E	#1
2	Th, 8/31/2023	Ch. 5	Introduction to Calculus of variation	5E	#2
3	Tu, 9/05/2023	Ch. 5	More examples of the calculus of variation	5E	#3
4	Th, 9/07/2023	Ch. 6	Lagrangian mechanics	6E	#4
5	Tu, 9/12/2023	Ch. 7 & 8	Hamiltonian mechanics	8E	#5
6	Th, 9/14/2023	Ch. 7 & 8	Hamiltonian mechanics	8E	
7	Tu, 9/19/2023	Ch. 13	Dynamics of rigid bodies	13E	#6
8	Th, 9/21/2023	Ch. 13	Dynamics of rigid bodies	13E	#7
9	Tu, 9/26/2023	Ch. 13 & 11	Review of rigid bodies and intro to scattering	11E	#8
10	Th, 9/28/2023	Ch. 11	Scattering theory	11E	#9
11	Tu, 10/3/2023	Ch. 11	Scattering theory	11E	
12	Th, 10/5/2023		Summary and examples		Take home exam start
13	Tu, 10/10/2023		Comments on more modern uses of analytical mechanics		Take home exam due
	Th, 10/12/2023	Fall Break			
14	Tu, 10/17/2023		Course summary		



Some of the contributors to basic physics principles

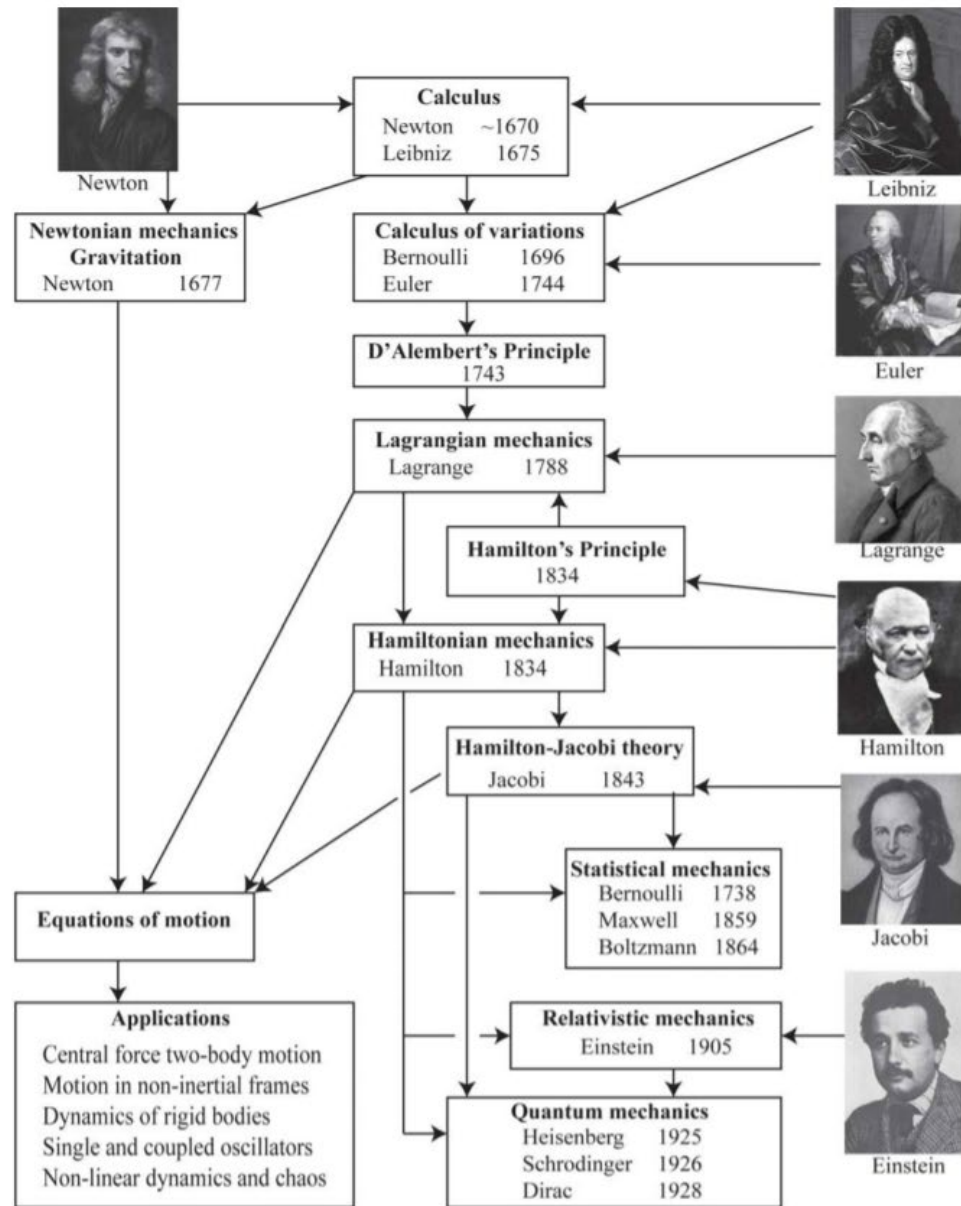


Figure 1.4.1: Chronological roadmap of the parallel development of the Newtonian and Variational-principles approaches to classical mechanics.

Is analytical mechanics too old to be useful?

Possible advantages

- Lagrangian mechanics → systematic scheme for treating large system of particles
- Hamiltonian mechanics → notion of phase space

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

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

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

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

Special property for H :

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

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

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

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

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

Short and notation -- Poisson brackets

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

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

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:

$$\begin{aligned} [x, x]_{PB} &= 0 & [x, p_x]_{PB} &= 1 & [x, p_y]_{PB} &= 0 \\ [L_x, L_y]_{PB} &= L_z \end{aligned}$$

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

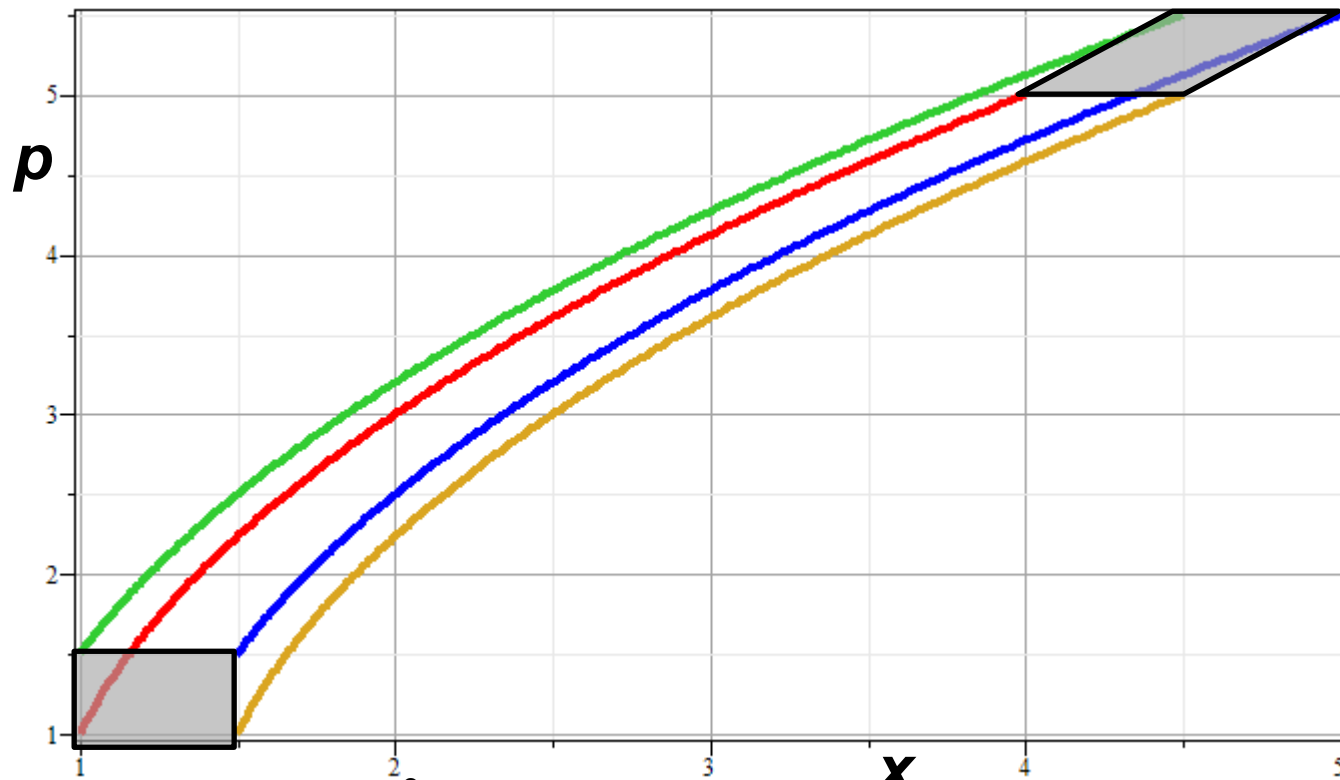
Phase space is defined as the set of all coordinates and momenta of a system:

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

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.

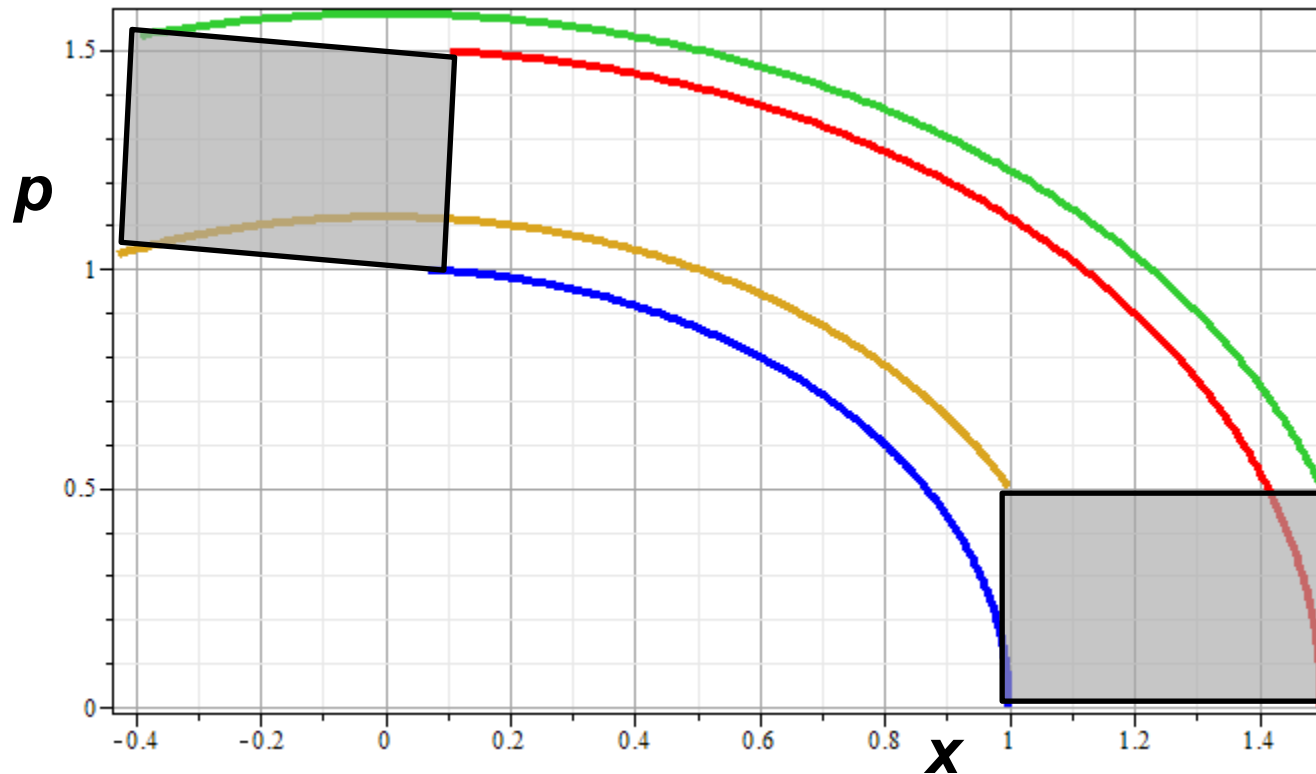
Phase space diagram for one-dimensional motion due to constant force



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

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

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



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

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

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.



Joseph Liouville

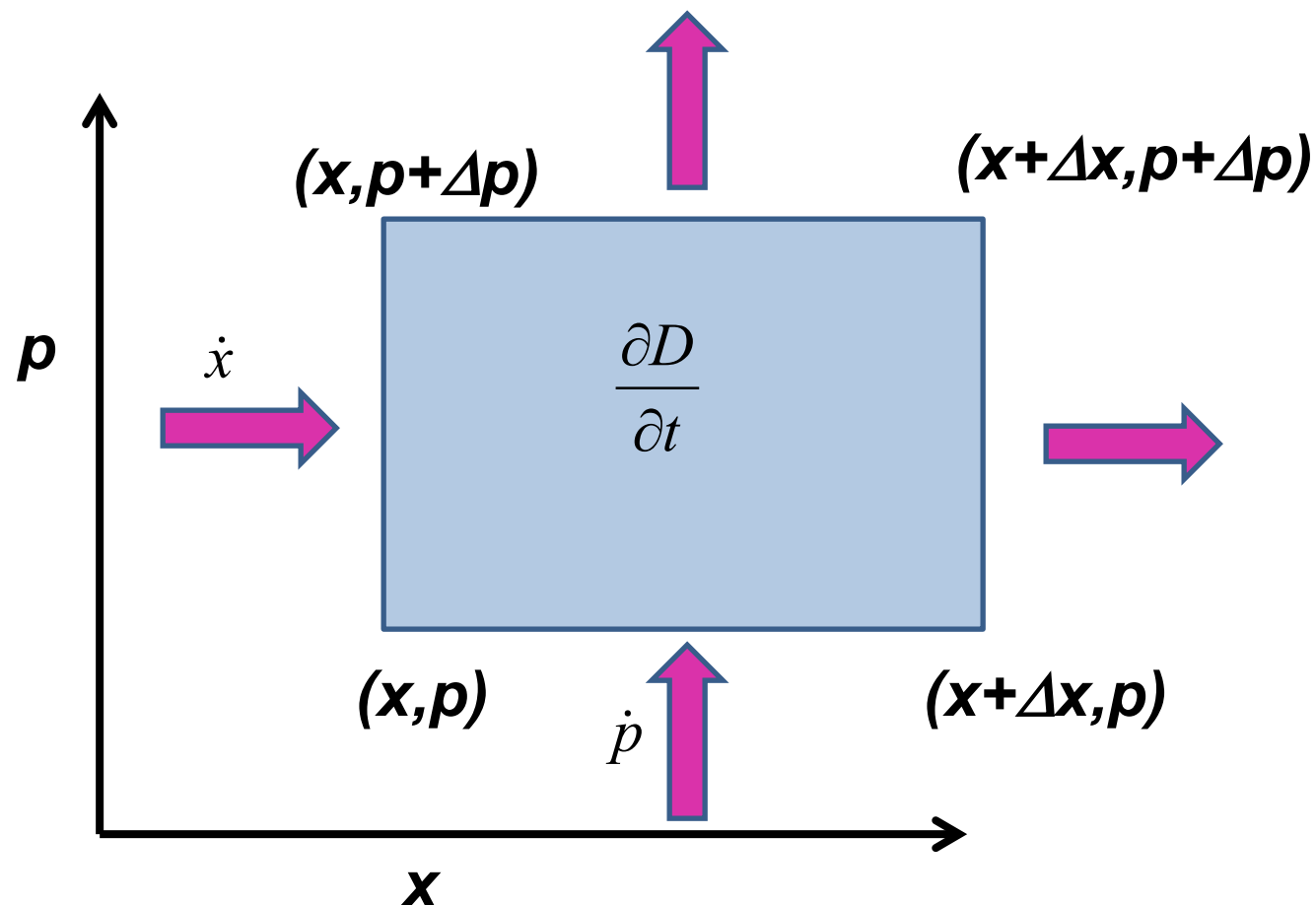
lived from 1809 to 1882

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

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

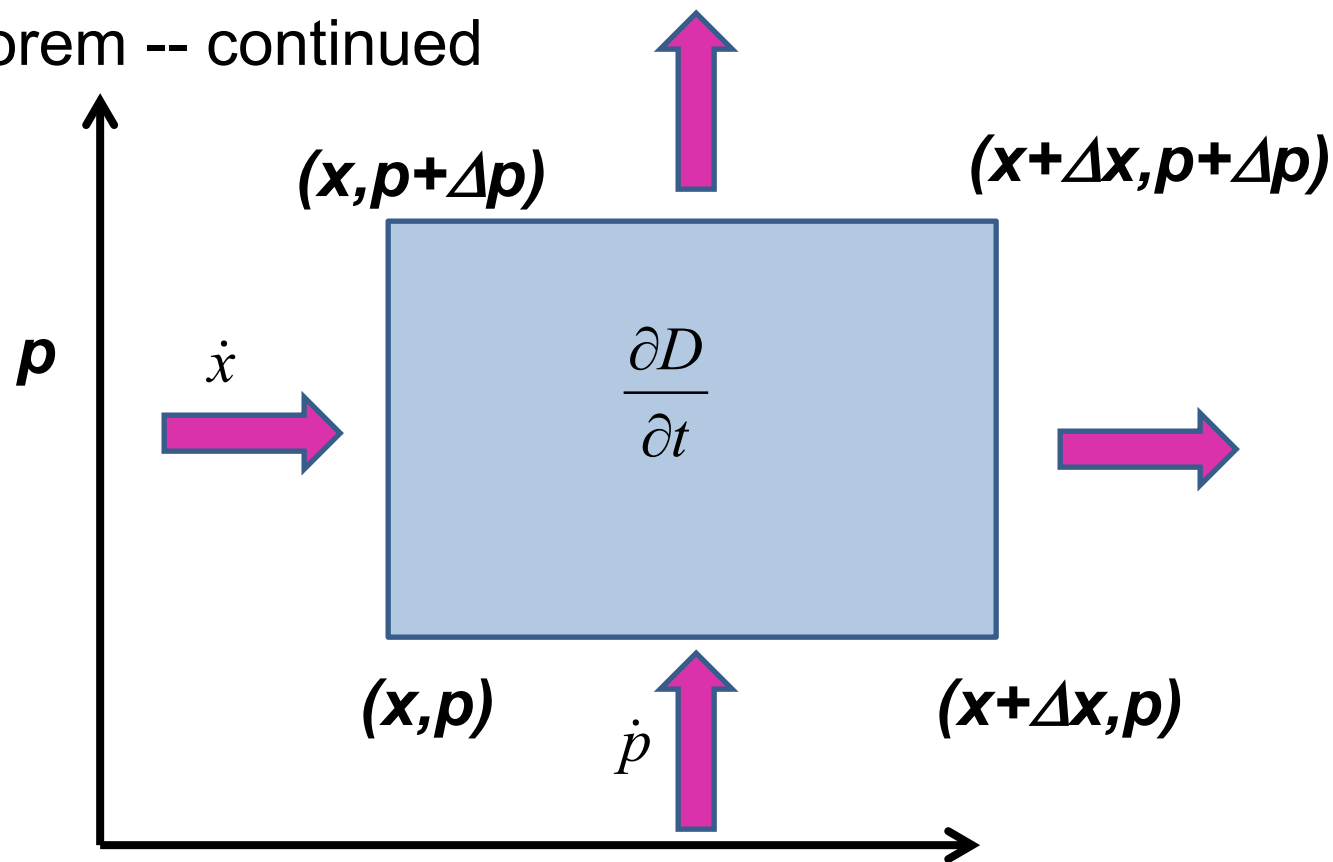
According to Liouville's theorem: $\frac{dD}{dt} = 0$

Liouville's theorem





Liouville's theorem -- continued



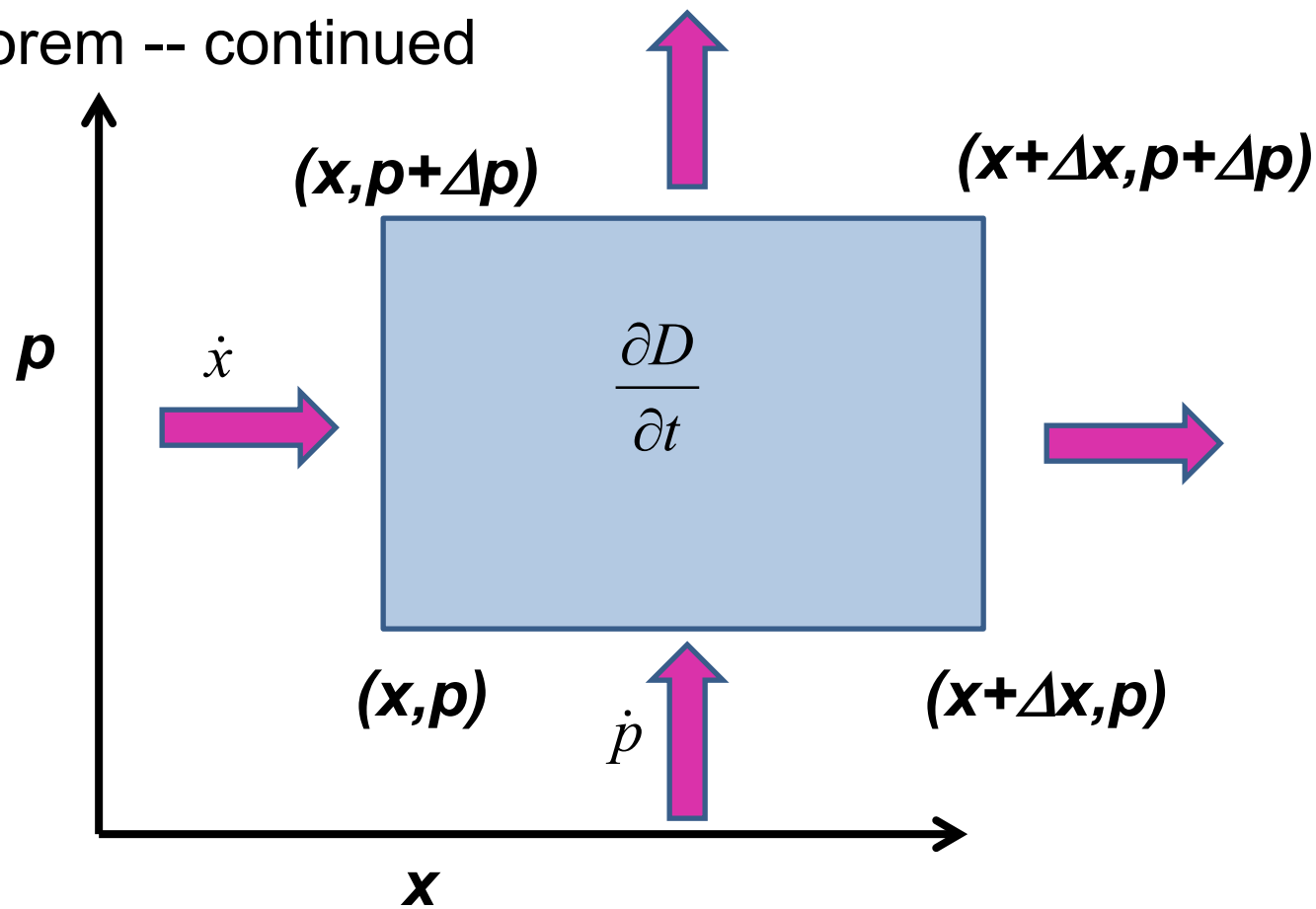
$\frac{\partial D}{\partial t} \Rightarrow$ time rate of change of particles within volume

= 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 :

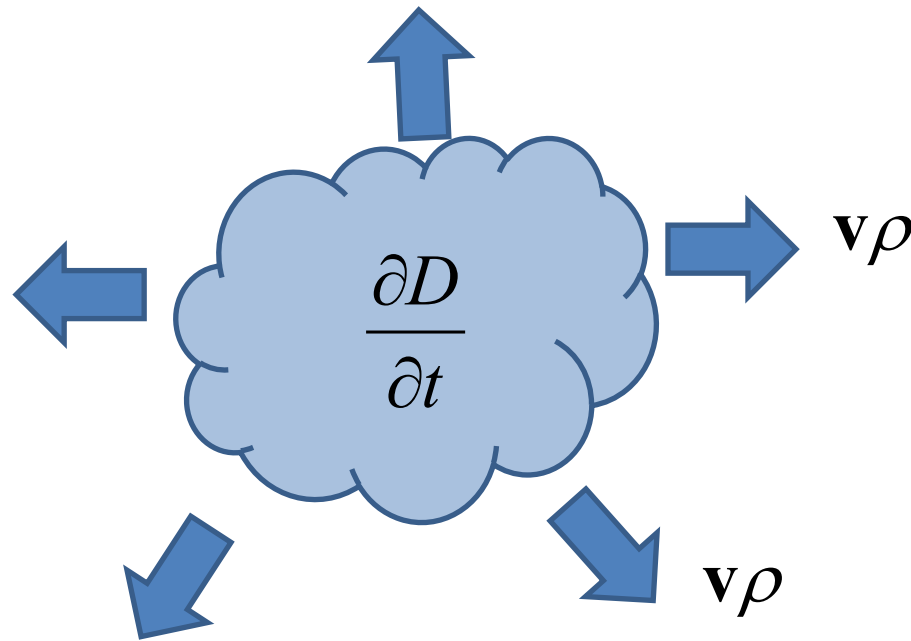
$$D = D(\{q_1 \cdots q_{3N}\}, \{p_1 \cdots p_{3N}\}, t)$$

Liouville's theorem shows that :

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

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:

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

We also have a $6N$ dimensional gradient:

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


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

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

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

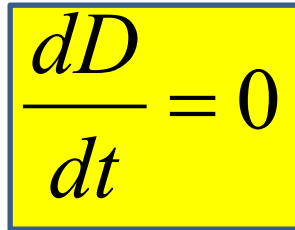
$$\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} = \frac{\partial^2 H}{\partial q_j \partial p_j} + \left(-\frac{\partial^2 H}{\partial p_j \partial q_j} \right) = 0$$



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

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

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


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

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. **Computationally this can be approximated using molecular dynamics or sampling methods.**

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

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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.



Hans Andersen

David Mulvane Ehram and Edward Curtis
Franklin Professor in Chemistry, Emeritus

$$\begin{aligned} \mathcal{H}_2(\rho^N, \pi^N, Q, \Pi) &= \sum_{i=1}^N \dot{\rho}_i \cdot \pi_i + \dot{Q}\Pi - \mathcal{L}_2(\rho^N, \dot{\rho}^N, Q, \dot{Q}) \\ &= (2mQ^{2/3})^{-1} \sum_{i=1}^N \pi_i \cdot \pi_i + \sum_{i < j=1}^N u(Q^{1/3} \rho_{ij}) + (2M)^{-1} \Pi^2 + \alpha Q. \end{aligned} \quad (3.6)$$

The Hamiltonian equations of motion are:

$$\frac{d\mathbf{p}_i}{dt} = \frac{\partial \mathcal{H}_2}{\partial \mathbf{r}_i} = \frac{\pi_i}{mQ^{2/3}} \quad (3.7a)$$

$$\frac{d\pi_i}{dt} = -\frac{\partial \mathcal{H}_2}{\partial \rho_i} = -Q^{1/3} \sum_{j(\neq i)=1}^N \frac{\rho_{ij} u'(Q^{1/3} \rho_{ij})}{|\rho_{ij}|} \quad (3.7b)$$

$$\frac{dQ}{dt} = \frac{\partial \mathcal{H}_2}{\partial \Pi} = \frac{\Pi}{M} \quad (3.7c)$$

$$\begin{aligned} \frac{d\Pi}{dt} &= -\frac{\partial \mathcal{H}_2}{\partial Q} = -(3Q)^{-1} \left(-2(2mQ^{2/3})^{-1} \sum_{i=1}^N \pi_i \cdot \pi_i \right. \\ &\quad \left. + Q^{1/3} \sum_{i < j} \rho_{ij} u'(Q^{1/3} \rho_{ij}) + 3\alpha Q \right). \end{aligned} \quad (3.7d)$$

These equations of motion for the scaled system can be solved numerically to give the coordinates and momenta as a function of time. Such molecular dynamics calculations give trajectory for the scaled system: $\rho^N(t)$, $\pi^N(t)$, $Q(t)$, and $\Pi(t)$.

The trajectory average of any function, $G(\rho^N, \pi^N, Q, \Pi)$, of the coordinates and momenta of the scaled system is defined as in Eq. (2.15).

$$\bar{G} = \lim_{T \rightarrow \infty} T^{-1} \int_0^T dt G(\rho^N(t), \pi^N(t), Q(t), \Pi(t)). \quad (3.8)$$

We assume that this time average exists.

$$\bar{G} = \int \rho^N \pi^N Q \Pi G(\rho^N, \pi^N, Q, \Pi) \Omega \quad (3.12c)$$

Every state of the scaled system corresponds to a unique value of V and a unique point in the phase space of the original system for that volume V . (Note that Π does not appear in these equations, so each V and phase-space point in the original system corresponds to a manifold of states of the scaled system.)

Using this correspondence, the calculated trajectory for the scaled system can be used to generate a trajectory for the original system. Along this latter trajectory, the volume varies with time.

$$V(t) = Q(t), \quad (3.13a)$$

$$\mathbf{r}_i(t) = Q(t)^{1/3} \rho_i(t), \quad (3.13b)$$

$$\mathbf{p}_i(t) = \pi_i(t) / Q(t)^{1/3}. \quad (3.13c)$$


The equations of motion for this trajectory can be derived from (3.13) and (3.7).

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m} + \frac{1}{3} \mathbf{r}_i \frac{d \ln V}{dt}, \quad (3.14a)$$

$$\frac{d\mathbf{p}_i}{dt} = - \sum_{j(\neq i)=1}^N \rho_{ij} u'(r_{ij}) - \frac{1}{3} \mathbf{p}_i \frac{d \ln V}{dt}, \quad (3.14b)$$

$$\frac{Md^2V}{dt^2} = -\alpha + \left(\frac{2}{3} \sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} - \frac{1}{3} \sum_{i < j=1}^N r_{ij} u'(r_{ij}) \right) / V. \quad (3.14c)$$

These equations are not the same as Hamilton's equations for the original system. Compare Eqs. (2.6). In the limit, however, that the mass of the piston, M , becomes infinitely large and M/V approaches a constant,



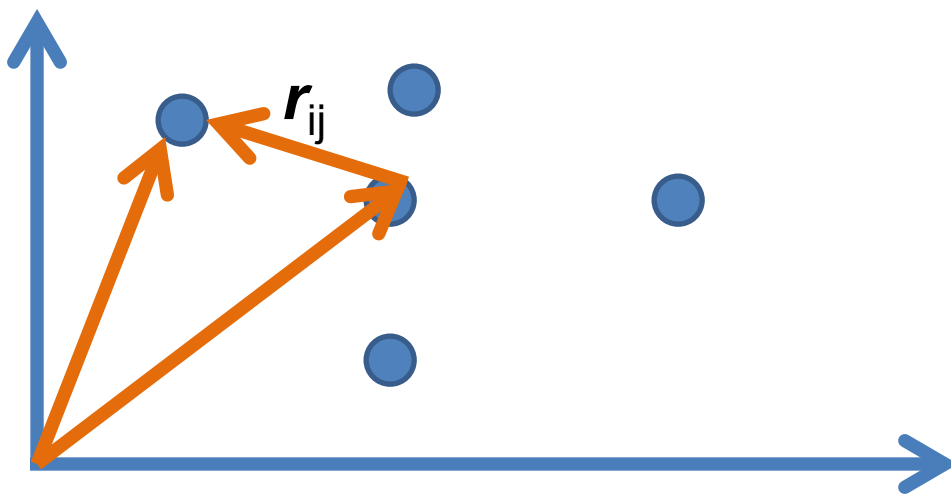
“Molecular dynamics” is a subfield of computational physics focused on analyzing the motions of atoms in fluids and solids with the goal of relating the atomistic and macroscopic properties of materials. Ideally molecular dynamics calculations can numerically realize the statistical mechanics viewpoint.

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:

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



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

→ 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).

Lagrangian and Hamiltonian forms

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

Euler-Lagrange equations:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = - \sum_{i < j} u'(|\mathbf{r}_i - \mathbf{r}_j|) \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Hamiltonian formulation:

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

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

Canonical equations:

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



Digression on numerical evaluation of differential equations

Example differential equation (one dimension);

$$\frac{d^2 x}{dt^2} = f(t)$$

Let $t = nh$ ($n = 1, 2, 3, \dots$)

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

Euler's method :

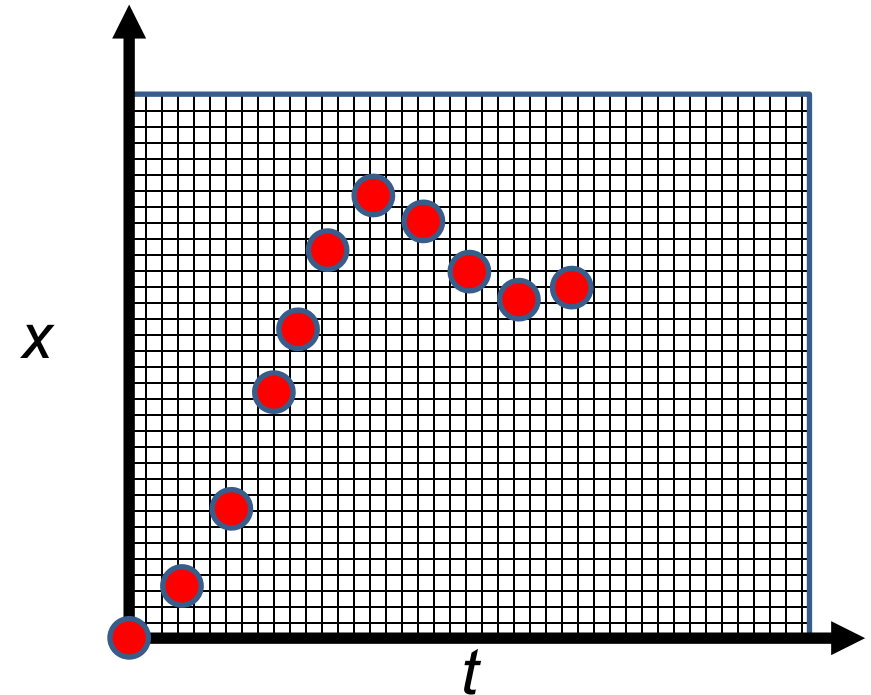
$$x_{n+1} = x_n + hv_n + \frac{1}{2}h^2 f_n$$

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

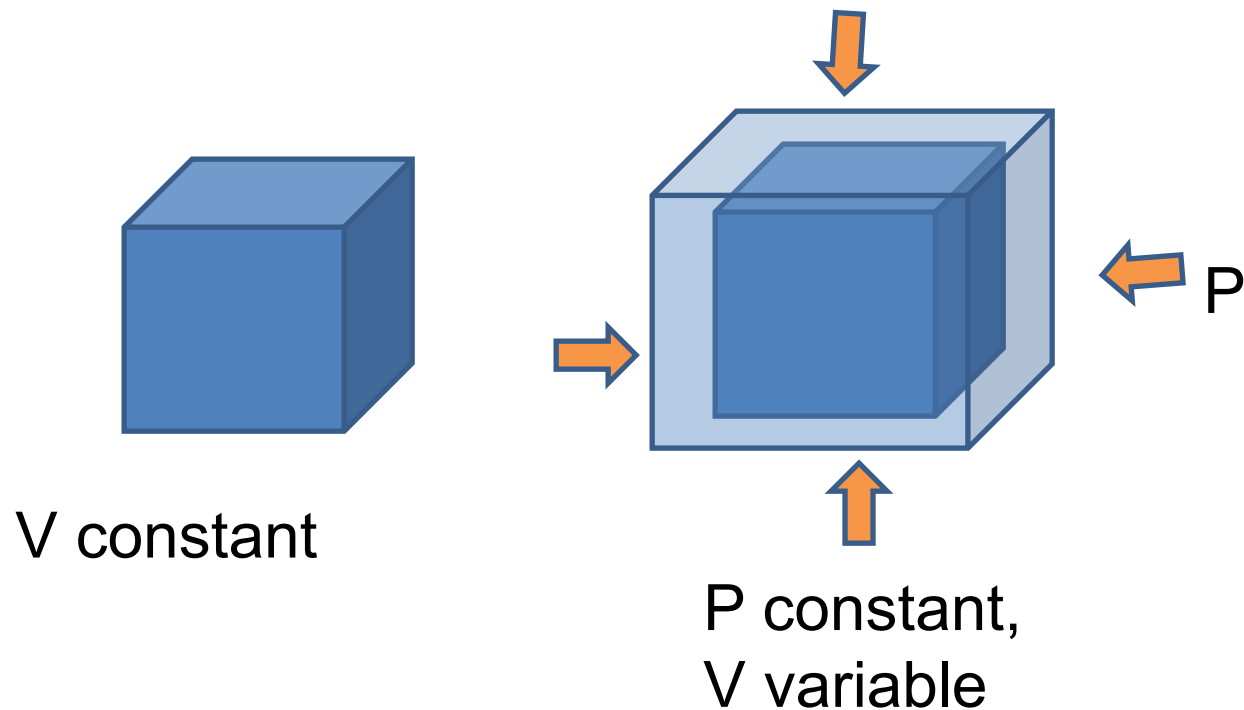
Velocity Verlet algorithm :

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

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



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 (N,P,E) .





PV contribution to potential energy

Andersen's clever transformation:

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

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

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

kinetic energy of “balloon”

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

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

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

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

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

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

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

Relationship between system representations

$$\begin{array}{rcl} \text{Scaled} & & \text{Original} \\ Q(t) & = & V(t) \\ Q^{1/3} \mathbf{p}_i(t) & = & \mathbf{r}_i(t) \\ \boldsymbol{\pi}_i / Q^{1/3} & = & \mathbf{p}_i \end{array}$$

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

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

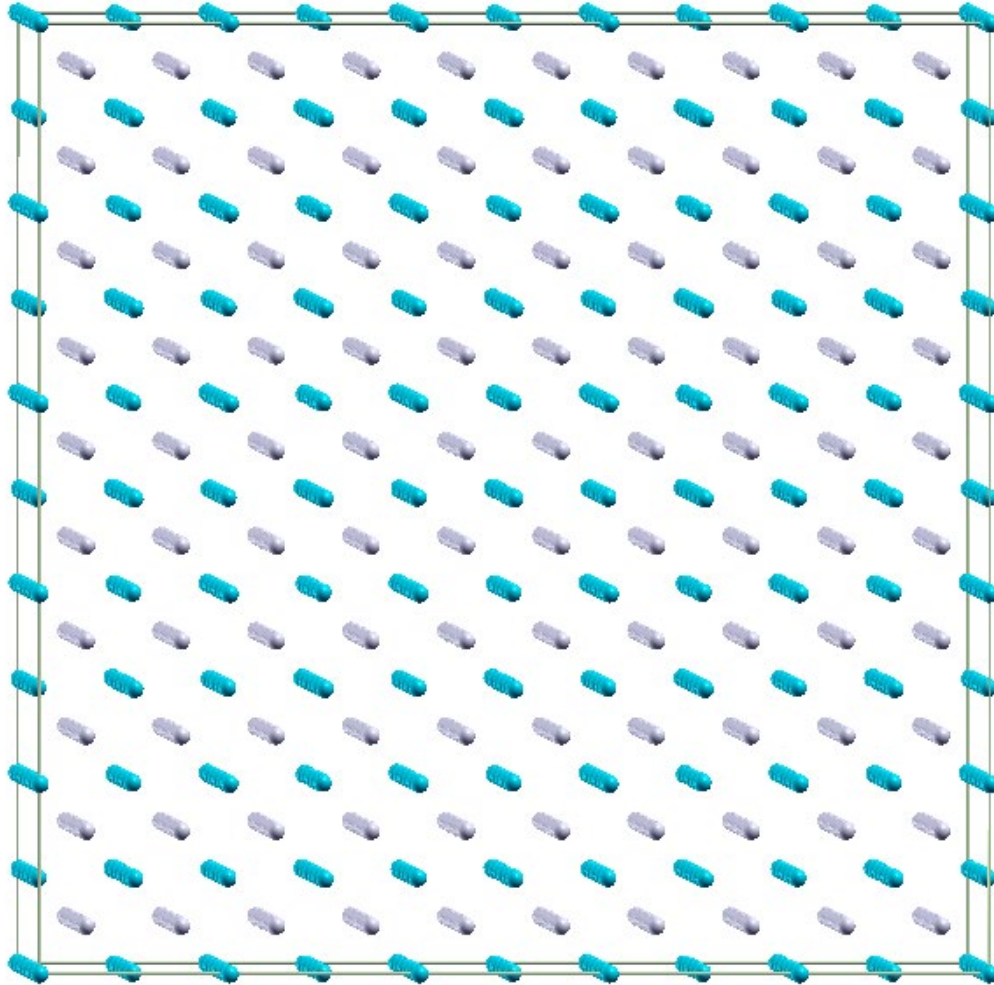
Time dependence

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

Averaged over many time steps:

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

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

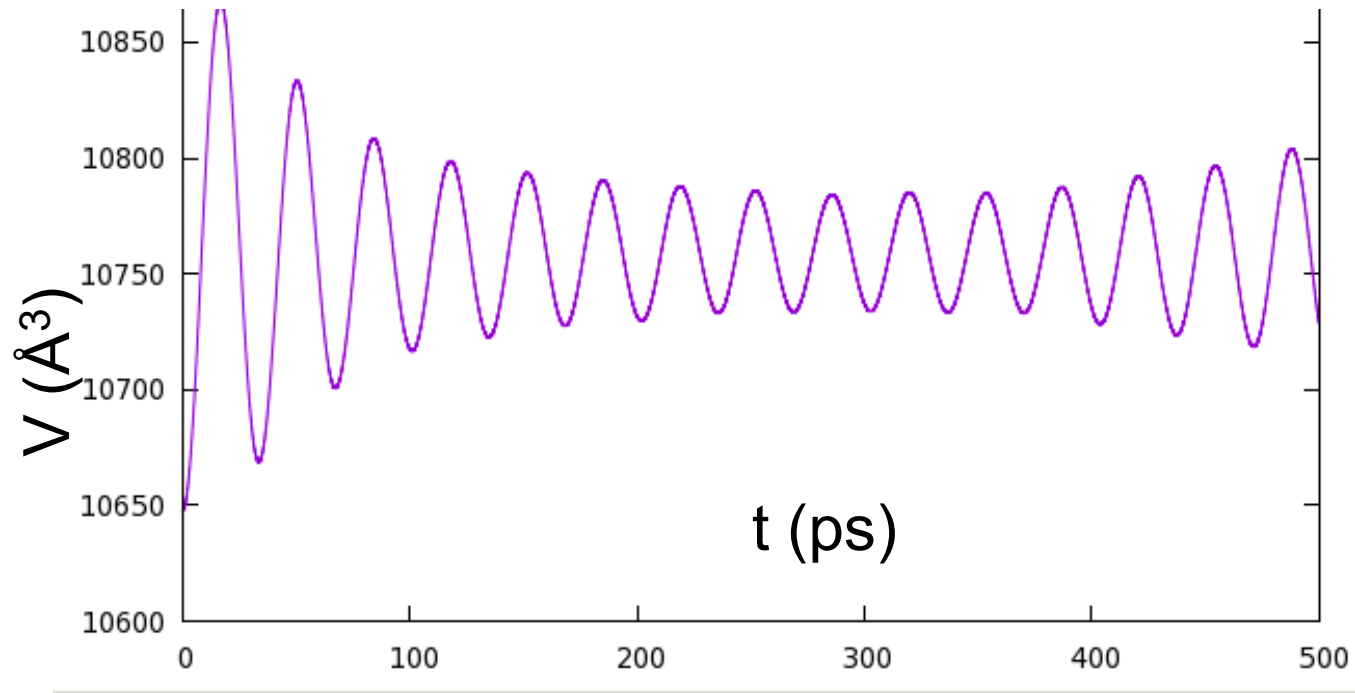
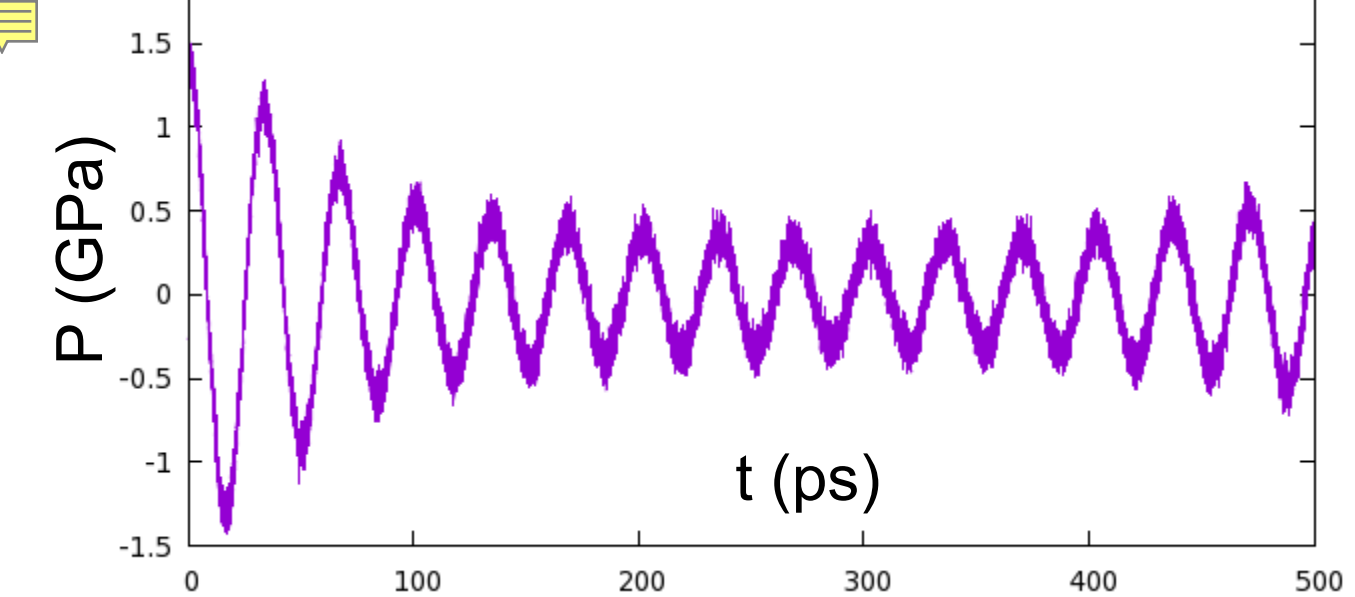


Pair interaction potential

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

Use LAMMPS code

<http://LAMMPS.sandia.gov>



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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

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

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

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

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



Time averaged relationships

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

Hamiltonian

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

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

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:

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

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

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

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

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

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

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

Some details:

Starting with partition for microcanonical ensemble:

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

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

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

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

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

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

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

When the dust clears --

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

→ 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)

