Principles

Notes on Statistical Mechanics for Molecular Simulation

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April 19, 2022

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作品信息

- 标题：Principles: *Notes on Statistical Mechanics for Molecular Simulation*
- 作者：Xufan Gao
- 校对排版：Xufan Gao
- 出品时间：April 19, 2022
- 总页数：18

Preface

Oxford Graduate Texts

Tuckerman, M. E. (2010). Statistical mechanics: Theory and molecular simulation. Oxford: Oxford University Press.

As a freshman in college physics, there must be errors.

For non-essential examples, I won't number the equations.

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Chapter 1 Classical Mechanics

§ 1.1 Math recap

Take the derivative with respect to vectors

§ 1.2 Newton's laws of motion

Review basic laws.

Newton's second law:

$$\boldsymbol{F} = m\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} = m\ddot{\boldsymbol{r}} \tag{1.2.1}$$

And Newton's third law:

$$\boldsymbol{F}_{AB} = -\boldsymbol{F}_{BA} \tag{1.2.2}$$

The definition of work:

$$W_{AB} = \int_A^B \boldsymbol{F}\cdot\mathrm{d}\boldsymbol{l} \tag{1.2.3}$$

In statistical mechanics, a particle i will experience a force $\boldsymbol{F}_i(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, \dot{\boldsymbol{r}}_i)$, which is determined by the positions of all other particles and its velocity.

§ 1.3 Phase space: visualization

We use position and momentum in the phase space because

$$\boldsymbol{F} = \frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} \tag{1.3.1}$$

Phase space: $3N$ position variables and $3N$ momentum variables constitute the microscopic state of the system at time t, if the dimensionality is 3. These variables forms a so-called *phase space vector* x. And by solving the Newton's second law, we obtain a *trajectory*:

$$x_t = (\boldsymbol{r}_1(t), \ldots, \boldsymbol{r}_N(t), \boldsymbol{p}_1(t), \ldots, \boldsymbol{p}_N(t)) \tag{1.3.2}$$

We can visualize the trajectory for a single one-dimensional particle. Some examples are (not explained here):

- a free particle with momentum p.
- a harmonic oscillator, with an elliptical phase space.
- a particle crossing a "hill" potential

Visualizing a many-particle system is hard. Maybe we can consider a particular cut or surface representing a set of variables of interest, known as a *Poincaré section*.

§ 1.4 Lagrangian formulation of classical mechanics

1.4.1 Conservative forces

Conservative forces, means **energy conservation**. Defined as the negative gradient of U, the *potential energy function*, Or for each particle i

$$\boldsymbol{F}_i = -\nabla_i U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \tag{1.4.1}$$

where $\nabla = \dfrac{\partial}{\partial \boldsymbol{r}}$.

An important property is that, the work done by conservative forces only depends on the difference of U of the start and end state, i.e. independent of the path taken.

$$W_{AB} = U_B - U_A$$

The kinetic energy of the system is given by

$$K(\dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2, \ldots, \dot{\boldsymbol{r}}_N) = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i^2 \tag{1.4.2}$$

1.4.2 Formulation

Here we introduce the *Lagrangian* of a system

$$\mathcal{L} = K(\dot{\boldsymbol{r}}_1, \ldots, \dot{\boldsymbol{r}}_N) - U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \tag{1.4.3}$$

which is the difference between the kinetic energy and potential energy. In contrast, the total energy is the sum of the two:

$$E = K(\dot{\boldsymbol{r}}_1, \ldots, \dot{\boldsymbol{r}}_N) + U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \tag{1.4.4}$$

The Euler-Lagrange equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{r}}_i} = \frac{\partial \mathcal{L}}{\partial \boldsymbol{r}_i} \tag{1.4.5}$$

For any one of position coordinates, taking the partial derivative with respect to the velocity and then time, is equal to that with respect to the position directly.

which can be verified with the substitution of eqn. 1.4.1 and 1.4.2 (poco).

This equation helps generate the equations of motion.

Example Take the example of the one-dimensional harmonic oscillator, where

$$\begin{aligned} U(x) &= \frac{1}{2}kx^2 \\ K(\dot{x}) &= \frac{1}{2}m\dot{x}^2 \\ \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{x}} = \frac{\mathrm{d}(m\dot{x})}{\mathrm{d}t} &= m\ddot{x} \\ \frac{\partial \mathcal{L}}{\partial x} &= -kx \end{aligned}$$

It also helps to verify conservation of the energy.

$$\begin{aligned} \frac{\mathrm{d}E}{\mathrm{d}t} &= \sum_{i=1}^{N} m\dot{\boldsymbol{r}}_i\ddot{\boldsymbol{r}}_i + \sum_{i=1}^{N}\frac{\partial U}{\partial \boldsymbol{r}_i}\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} \\ &= \sum_{i=1}^{N} m\dot{\boldsymbol{r}}_i\ddot{\boldsymbol{r}}_i - \sum_{i=1}^{N}\boldsymbol{F}_i\dot{\boldsymbol{r}}_i \\ &= \sum_{i=1}^{N} m\dot{\boldsymbol{r}}_i\ddot{\boldsymbol{r}}_i - m\ddot{\boldsymbol{r}}_i\dot{\boldsymbol{r}}_i \\ &= 0 \end{aligned}$$

1.4.3 Generalized coordinates

The power of Lagrangian formulation lies in the fact that the equations in an arbitrary coordinate system can be derived easily in order to address a particular problem. A set of $3N$ *generalized coordinates* are related to the original Cartesian coordinate via

$$q_\alpha = f_\alpha(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \qquad \alpha = 1, 2, \ldots, 3N \tag{1.4.6}$$

It is assumed that the transformation has a unique inverse

$$\boldsymbol{r}_i = \boldsymbol{g}_i(q_1, \ldots, q_{3N}) \qquad i = 1, 2, \ldots, N \tag{1.4.7}$$

Thus, through the chain rule, we have

$$\dot{\boldsymbol{r}}_i = \sum_{\alpha=1}^{3N}\frac{\partial \boldsymbol{r}_i}{\partial q_\alpha}\dot{q}_\alpha \tag{1.4.8}$$

The kinetic energy can then be written as[1]

$$\begin{aligned} K(\boldsymbol{q},\dot{\boldsymbol{q}}) &= \frac{1}{2}\sum_{i=1}^{N} m_i \sum_{\alpha=1}^{3N} \frac{\partial \boldsymbol{r}_i}{\partial q_\alpha}\dot{q}_\alpha \sum_{\beta=1}^{3N} \frac{\partial \boldsymbol{r}_i}{\partial q_\beta}\dot{q}_\beta \\ &= \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}\sum_{i=1}^{N} m_i \frac{\partial \boldsymbol{r}_i}{\partial q_\alpha}\frac{\partial \boldsymbol{r}_i}{\partial q_\beta}\dot{q}_\alpha\dot{q}_\beta \\ &= \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N} G_{\alpha\beta}\dot{q}_\alpha\dot{q}_\beta \end{aligned} \tag{1.4.9}$$

where

$$G_{\alpha\beta}(\boldsymbol{q}) = \sum_{i=1}^{N} m_i \frac{\partial \boldsymbol{r}_i}{\partial q_\alpha}\cdot\frac{\partial \boldsymbol{r}_i}{\partial q_\beta} \tag{1.4.10}$$

is the function of q (so is $U(\boldsymbol{q})$). α and β as indices, these elements forms a matrix G, the *mass metric matrix*.

Then the Lagrangian is expressed as a function of $\boldsymbol{q}$ and $\dot{\boldsymbol{q}}$. Adopting the Euler-Lagrange equation, considering q_γ as q_α:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{\beta=1}^{3N} G_{\gamma\beta}\dot{q}_\beta\right) = \sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}\frac{\partial G_{\alpha\beta}}{\partial q_\gamma}\dot{q}_\alpha\dot{q}_\beta - \frac{\partial U}{\partial q_\gamma} \tag{1.4.11}$$

where $\gamma = 1,\ldots,3N$. These are the $3N$ equations of motion of the system.

1.4.4 An example: two-particle system

A two particle system subject to a potential U which only depends on the distance between them. We can write:

$$\mathcal{L} = \frac{1}{2}m_1\dot{\boldsymbol{r}}_1^2 + \frac{1}{2}m_2\dot{\boldsymbol{r}}_2^2 - U(|\boldsymbol{r}_1-\boldsymbol{r}_2|) \tag{1.4.12}$$

And knowing that (not important)

$$\begin{gathered} |\boldsymbol{r}_1-\boldsymbol{r}_2| = \sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2} \\ \frac{\partial|\boldsymbol{r}_1-\boldsymbol{r}_2|}{\partial x_1} = \frac{2x_1}{2\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}} = \frac{x_1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \\ \frac{\partial U(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}{\partial \boldsymbol{r}_1} = \frac{\mathrm{d}U(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}{\mathrm{d}(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}\frac{\partial|\boldsymbol{r}_1-\boldsymbol{r}_2|}{\partial \boldsymbol{r}_1} = \frac{\mathrm{d}U(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}{\mathrm{d}(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}\frac{\boldsymbol{r}_1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \\ \frac{\partial U(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}{\partial \boldsymbol{r}_2} = -\frac{\mathrm{d}U(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}{\mathrm{d}(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}\frac{\boldsymbol{r}_2}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \end{gathered}$$

[1] separate everything containing q (i) and the $\dot{q}$ velocities, by summing over i first. Imagina a 3D cube, the z-axis is m_i, while on the x-y plane sits pairs of q terms...

, using eqn 1.4.5, we can get

$$m_1\ddot{\boldsymbol{r}}_1 = -\frac{\mathrm{d}U(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}{\mathrm{d}(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}\frac{\boldsymbol{r}_1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$
$$m_2\ddot{\boldsymbol{r}}_2 = \frac{\mathrm{d}U(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}{\mathrm{d}(|\boldsymbol{r}_1-\boldsymbol{r}_2|)}\frac{\boldsymbol{r}_1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$

We now want to introduce a more natural set of general coordinates: *center of mass* and *relative position*:

$$\boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1+m_2}$$
$$\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$$

Let $M = m_1 + m_2$. The inverse of this transformation is

$$\boldsymbol{r}_1 = \boldsymbol{R} + \frac{m_2}{M}\boldsymbol{r}$$
$$\boldsymbol{r}_2 = \boldsymbol{R} - \frac{m_1}{M}\boldsymbol{r}$$

Substituted into eqn 1.4.12, the Lagrangian becomes

$$\begin{aligned}\mathcal{L} &= \frac{1}{2}m_1\left(\dot{\boldsymbol{R}} + \frac{m_2}{M}\dot{\boldsymbol{r}}\right)^2 + \frac{1}{2}m_2\left(\dot{\boldsymbol{R}} - \frac{m_1}{M}\dot{\boldsymbol{r}}\right)^2 - U(|\boldsymbol{r}|)\\ &= \frac{1}{2}M\dot{\boldsymbol{R}}^2 + \frac{1}{2}\mu\dot{\boldsymbol{r}}^2 - U(|\boldsymbol{r}|)\end{aligned}$$

where *reduced mass* $\mu = \dfrac{m_1m_2}{M}$.

Since the energy does not change as the center of mass moves, $\dfrac{\partial\mathcal{L}}{\partial\boldsymbol{R}} = 0$. Then the equation of motion will be

$$M\ddot{\boldsymbol{R}} = 0$$
$$\mu\ddot{\boldsymbol{r}} = -\frac{\mathrm{d}U}{\mathrm{d}|\boldsymbol{r}|}\frac{\boldsymbol{r}}{|\boldsymbol{r}|}$$

We can also transform $\boldsymbol{r}$ further into spherical coordinates to obtain the one-dimensional equation of motion.

§ 1.5 Legendre transforms

Consider a derivable function $f(x)$. Define

$$s = f'(x) = g(x) \tag{1.5.1}$$

and assume $s = g(x)$ is a one-to-one mapping (i.e. $x = g^{-1}(s)$ exists).

For all $x = x_0$,

$$f(x_0) = f'(x_0)x_0 + b(x_0)$$

holds, where $b(x_0)$ is the y-intercept. Thus, for all x

$$f(x) = f'(x)x + b(x) \tag{1.5.2}$$

We now express the relation in the function of s, i.e. find the equivalent expression. Let $\tilde{f} = b$, then

$$\tilde{f} = b(g^{-1}(s)) = f(x(s)) - sx(s) \tag{1.5.3}$$

This is called a *Legendre transform*.

For multiple variables $x_1, \ldots, x_n$, there will be corresponding $s_1, \ldots, s_n$, and the generalized form is

$$\tilde{f}(s_1, \ldots, s_n) = f(x_1(s_1, \ldots, s_n), \ldots, x_n(s_1, \ldots, s_n)) - \sum_{i=1}^{n} s_i x_i(s_1, \ldots, s_n) \tag{1.5.4}$$

f is constituted of n pairs of variable $\times$ its derivative, plus a bias term $\tilde{f}$.

§ 1.6 Hamiltonian formulation

1.6.1 the Hamiltionian under Cartesian coordinates

Before the derivation, An interesting fact is worth noting:

$$\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{r}}_i} = \frac{\partial}{\partial \dot{\boldsymbol{r}}_i}\left[\sum_{i=1} \frac{1}{2} m_i \dot{\boldsymbol{r}}_i^2 - U(\boldsymbol{r}_i, \ldots, \boldsymbol{r}_N)\right] = m_i \dot{\boldsymbol{r}}_i = \boldsymbol{p}_i \tag{1.6.1}$$

$$K = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{\boldsymbol{r}}_i^2 = \frac{1}{2} \sum_{i=1}^{N} \boldsymbol{p}_i \dot{\boldsymbol{r}}_i \left(= \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i}\right) \tag{1.6.2}$$

$\dot{\boldsymbol{r}}_i$ is a function of $\boldsymbol{p}_i$ ($\dot{\boldsymbol{r}}_i(\boldsymbol{p}_i) = \boldsymbol{p}_i/m_i$; s_i is $\boldsymbol{p}_i$; x_i is $\dot{\boldsymbol{r}}_i$).

The reason we introduce the Hamiltionian is to replace $\dot{\boldsymbol{r}}_i$ in $\mathcal{L}$ into $\boldsymbol{p}_i$. Do the Leg-

endre transform with $\boldsymbol{r}_i$ fixed, plugging in the two equaitons above:

$$\begin{aligned}\tilde{\mathcal{L}} &= \mathcal{L}(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N,\dot{\boldsymbol{r}}_1(\boldsymbol{p}_1),\dots,\dot{\boldsymbol{r}}_N(\boldsymbol{p}_N)) - \sum_{i=1}^{N}\boldsymbol{p}_i\dot{\boldsymbol{r}}_i(\boldsymbol{p}_i)\\ &= \sum_{i=1}^{N}\frac{1}{2}\frac{\boldsymbol{p}_i^2}{m_i} - U(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) - \sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{m_i}\\ &= -\left(\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{2m_i} + U(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N)\right) \qquad (1.6.3)\end{aligned}$$

Thus, the Hamilitonian is just the negative Legandre transformation of the Lagrangian:

$$\mathcal{H}(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N,\boldsymbol{p}_1,\dots,\boldsymbol{p}_N) = K(\boldsymbol{p}_1,\dots,\boldsymbol{p}_N) + U(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) \qquad (1.6.4)$$

which is the **total energy** of the system.

1.6.2 Equations of motion under generalized coordinates

Likewise, we can define the *generalized momentum* p_α as

$$p_\alpha = \frac{\partial\mathcal{L}}{\partial\dot{q}_\alpha} \qquad (1.6.5)$$

$$K(\boldsymbol{p},\dot{\boldsymbol{q}}) = \frac{1}{2}\sum_{\alpha=1}^{3N}p_\alpha\dot{q}_\alpha = \frac{1}{2}\boldsymbol{p}\cdot\dot{\boldsymbol{q}} \qquad (1.6.6)$$

for every set of generalized coordinates, where $\boldsymbol{p} = (p_1,\dots,p_{3N})$ and $\dot{\boldsymbol{q}} = (\dot{q}_1,\dots,\dot{q}_{3N})$.. These momenta are referred to as *conjugated* to the coordinates. But why is there a $1/2$? Becuase $\dot{q}_\alpha$ is a function of p_α.

Recall eqn 1.4.9:

$$K = \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}G_{\alpha\beta}\dot{q}_\alpha\dot{q}_\beta$$

Comparing with eqn. 1.6.6, we can infer that

$$p_\alpha = \sum_{\beta=1}^{3N}G_{\alpha\beta}\dot{q}_\beta \qquad (1.6.7)$$

In the form of matrix multiplication, it's $\boldsymbol{p} = G\dot{\boldsymbol{q}}$, or reversely

$$\dot{\boldsymbol{q}} = G^{-1}\boldsymbol{p} \qquad (1.6.8)$$

which implies that $\dot{\boldsymbol{q}}$ is a function of $\boldsymbol{p}$. Though our mass metric matrix G is a function of $\boldsymbol{q}$, once the generalized coordinates are defined, G remains unchanged. The value of $\boldsymbol{r}$ and $\boldsymbol{q}$ vary along the trajectory, but the direvatives do not.

For any set of generalized coordinates, the Hamiltionian is given similarly:

$$\mathcal{H}(\boldsymbol{q},\boldsymbol{p}) = K(\boldsymbol{p},\dot{\boldsymbol{q}}(\boldsymbol{p})) + U(\boldsymbol{q}) \tag{1.6.9}$$

where K is only the function of $\boldsymbol{p}$ (m_i as constants) and U is only the function of $\boldsymbol{q}$.

From eqn. 1.6.9, we can obtain by referring to eqn. 1.6.6 and 1.4.1:

Hamiltonian's equations of motion

$$\frac{\partial \mathcal{H}}{\partial p_\alpha} = \dot{q}_\alpha \qquad \frac{\partial \mathcal{H}}{\partial q_\alpha} = -\dot{p}_\alpha \tag{1.6.10}$$

for $\alpha = 1, \dots, 3N$.

Example You may verify it in the example of harmonic oscillation:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2$$
$$m\ddot{x} = \dot{p} = -\frac{\partial \mathcal{H}}{\partial x} = -kx$$

Notes on the Hamiltonian equations of motion:

- It's equivalent to Newton's second law of motion (eqn. 1.2.1, with eqn. 1.6.5)
- It's equivalent to the Lagrangian equations of motion (eqn. 1.4.11), which is a set of $3N$ second-order DEs. Eqn. 1.6.10 is a set of $6N$ first-order DEs and thus looks simpler.

Supplement I can't explain the $1/2$ yet...

1.6.3 Properties

Energy conservation

$$\begin{aligned}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} &= \sum_{\alpha=1}^{3N} \frac{\partial \mathcal{H}}{\partial q_\alpha}\dot{q}_\alpha + \frac{\partial \mathcal{H}}{\partial p_\alpha}\dot{p}_\alpha \\ &= \sum_{\alpha=1}^{3N} \frac{\partial \mathcal{H}}{\partial q_\alpha}\frac{\partial \mathcal{H}}{\partial p_\alpha} + \frac{\partial \mathcal{H}}{\partial p_\alpha}(-\frac{\partial \mathcal{H}}{\partial q_\alpha}) = 0\end{aligned}$$

For a trajectory under constant energy, the phase space vectors (eqn. 1.3.2) remain in a surface known as *constant-energy (hyper)surface*.

Work-energy theroem writes:

$$K_A + U_A = K_B + U_B$$
$$U_B - U_A = W_{AB} = K_A - K_B \tag{1.6.11}$$

Consider any arbitrary phase space function $a(x)$, a function of positions and momentums. To study its time evolution:

$$\begin{aligned}\frac{\mathrm{d}a}{\mathrm{d}t} &= \sum_{\alpha=1}^{3N} \frac{\partial a}{\partial p_\alpha}\dot{p}_\alpha + \frac{\partial a}{\partial q_\alpha}\dot{q}_\alpha \\ &= \sum_{\alpha=1}^{3N} \frac{\partial a}{\partial p_\alpha}\frac{\partial \mathcal{H}}{\partial q} - \frac{\partial a}{\partial q_\alpha}\frac{\partial \mathcal{H}}{\partial p_\alpha} \qquad (1.6.12)\\ &= \{a, \mathcal{H}\} \qquad (1.6.13)\end{aligned}$$

where the last line is known as the *Poisson bracket*.

Example Suppose a system without external forces acting on it, which implies $\sum_{i=1}^{N} \boldsymbol{F}_i = 0$, then consider the total momentum $\boldsymbol{P} = \sum_{i=1}^{N} \boldsymbol{p}_i$

$$\begin{aligned}\{\boldsymbol{P}, \mathcal{H}\} &= \sum_{\alpha=1}^{3N} \{p_\alpha, \mathcal{H}\} \\ &= \sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}\left[\frac{\mathrm{d}p_\alpha}{\mathrm{d}r_\beta}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}p_\beta} - \frac{\mathrm{d}p_\alpha}{\mathrm{d}p_\beta}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}r_\beta}\right] \qquad (p \text{ and } q \text{ are independent}) \\ &= \sum_{\beta=1}^{3N}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}r_\beta} = \sum_{i=1}^{N}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}\boldsymbol{r}_i} = \sum_{i=1}^{N}\frac{\mathrm{d}U}{\mathrm{d}\boldsymbol{r}_i} = \sum_{i=1}^{N}\boldsymbol{F}_i = 0\end{aligned}$$

which inplies that without external forces, the total momentum is conserved.

The Hamiltonian is invariant with respect to simply a translation transformation $\boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{a}$.

Phase space incompressibility

The derivative of the phase space vector $\boldsymbol{x}$, η is a function of $\boldsymbol{x}$

$$\begin{aligned}\dot{\boldsymbol{x}}(t) &= (\dot{q_1}, \ldots, \dot{q_{3N}}, \dot{p_1}, \ldots, \dot{p_{3N}}) \\ \eta(\boldsymbol{x}) &= (\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}p_1}, \ldots, \frac{\mathrm{d}\mathcal{H}}{\mathrm{d}p_{3N}}, -\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}q_1}, \ldots, \frac{\mathrm{d}\mathcal{H}}{\mathrm{d}q_{3N}}) \qquad (1.6.14)\end{aligned}$$

Divergence (散度) is defined as $\nabla_x = \dfrac{\partial}{\partial \boldsymbol{x}}$, then

$$\begin{aligned}\nabla_x \cdot \dot{\boldsymbol{x}} &= \sum_{\alpha=1}^{3N}\frac{\partial \dot{q_\alpha}}{\partial q\alpha} + \frac{\partial \dot{p_\alpha}}{\partial p_\alpha} \\ &= \sum_{\alpha=1}^{3N}\frac{\partial^2 \mathcal{H}}{\partial p_\alpha \partial q_\alpha} + \frac{\partial^2 \mathcal{H}}{\partial(-q_\alpha)\partial p_\alpha} = 0\end{aligned}$$

which means there is no sources and sinks, called an incompressible flow in hydrodynamics.

Symplectic structure

As eqn. 1.6.14 indicated

$$\dot{\boldsymbol{x}} = M\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}\boldsymbol{x}} \tag{1.6.15}$$

where M is a matrix

$$M = \begin{pmatrix} \mathbf{0} & \boldsymbol{I} \\ -\boldsymbol{I} & \mathbf{0} \end{pmatrix} \tag{1.6.16}$$

where $\mathbf{0}$ and $\boldsymbol{I}$ are $3N \times 3N$ zero and identity matrices respectively.

Consider a solution $\boldsymbol{x}_t$ to eqn. 1.6.15 starting from an initial condition $\boldsymbol{x}_0$, $\boldsymbol{x}_t$ is a unique function of $\boldsymbol{x}_0$. This dependence can be viewed as a transformation from the beginning $6N$ variables to the end $6N$ variables[(2)], whose Jacobian matrix is

$$J_{kl} = \frac{\partial x_t^k}{\partial x_0^l} \tag{1.6.17}$$

which is known as *symplectic property*[(3)], and satisfies

$$M = J^T M J \tag{1.6.18}$$

Example the one-dimensional harmonic oscillator

$$x(t) = x_0 \cos\omega t + \frac{p(0)}{m\omega}\sin\omega t$$
$$p(t) = p_0 \cos\omega t - m\omega x_0 \sin\omega t$$

Thus,

$$J = \begin{pmatrix} \cos\omega t & -m\omega\sin\omega t \\ \dfrac{1}{m\omega}\sin\omega t & \cos\omega t \end{pmatrix}$$

and M is just

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

then

$$\begin{aligned} J^T M J &= \begin{pmatrix} -\dfrac{1}{m\omega}\sin\omega t & \cos\omega t \\ -\cos\omega t & -m\omega\sin\omega t \end{pmatrix}\begin{pmatrix} \cos\omega t & -m\omega\sin\omega t \\ \dfrac{1}{m\omega}\sin\omega t & \cos\omega t \end{pmatrix} \\ &= \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = M \end{aligned}$$

(2) multivariate vector function, 多元向量值函数

(3) 辛性质

§ 1.7 A simple classic polymer model

变分法是处理泛函的数学领域，和处理函数的普通微积分相对。譬如，这样的泛函可以通过未知函数的积分和它的导数来构造。变分法最终寻求的是极值函数：它们使得泛函取得极大或极小值。有些曲线上的经典问题采用这种形式表达：一个例子是最速降线，在重力作用下一个粒子沿着该路径可以在最短时间从点 A 到达不直接在它底下的一点 B。

§ 1.8 The action integral

The action integral emerges naturally from quantum mechanics. It is defined as

$$A = \int_{t_1}^{t_2} \mathcal{L}\left(\boldsymbol{q}(t), \dot{\boldsymbol{q}}(t)\right) \mathrm{d}t \tag{1.8.1}$$

where $\boldsymbol{q} = (q_1, \ldots, q_{3N})$. A is trajectory-dependent because it counts every value of $\boldsymbol{q}$ and $\dot{\boldsymbol{q}}$ from t_1 to t_2. Since a trajectory is a function of t, then the action integral is a *functional*, usually denoted as $A[\boldsymbol{q}]$.

Definitions:

- A functional[(4)] is a quantity that depends on all values of a function between two points of its domain.
- A stationary point[(5)] is where the first order derivative of a function is zero.
- The variational principle[(6)]. The variational method is to find an extremal function[(7)] for a functional, just like to find an extreme value for a function.

A detailed introduction of the variational method is here. A relevant example is to find the ground state wave function of a H_2^+, where we use a linear combination of basis functions as the trial function, get the derivative of the total energy, let them equal to zero and calculate the coefficients. Then we obtain the wave function that may make the energy the lowest.

Here we will do similar things to the action integral. First of all, such a trajectory must satisfy the endpoint conditions:

$$\boldsymbol{q}(t_1) = \boldsymbol{q}_1, \qquad \dot{\boldsymbol{q}}(t_1) = \dot{\boldsymbol{q}}_1, \qquad \boldsymbol{q}(t_2) = \boldsymbol{q}_2, \qquad \dot{\boldsymbol{q}}(t_2) = \dot{\boldsymbol{q}}_2 \tag{1.8.2}$$

(4) 泛函
(5) 驻点
(6) 变分原理
(7) 极值函数

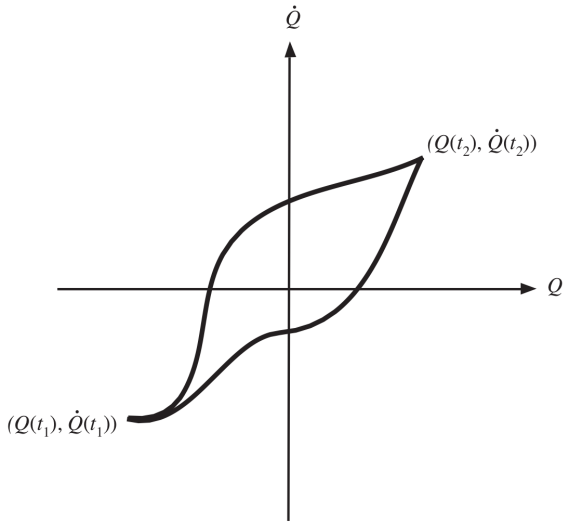

Fig. 1.1 Two proposed paths joining the fixed endpoints.

Second, for a slightly changed trajectory $\boldsymbol{q}(t) + \delta\boldsymbol{q}(t)$ that also satisfies the endpoint conditions, i.e.

$$\delta\boldsymbol{q}(t_1) = \delta\boldsymbol{q}(t_2) = 0, \qquad \delta\dot{\boldsymbol{q}}(t_1) = \delta\dot{\boldsymbol{q}}(t_2) = 0 \tag{1.8.3}$$

where $\delta\boldsymbol{q}$ is called the variation of $\boldsymbol{q}$[8], the variation of A must be zero, which means

$$\delta A = \int_{t_1}^{t_2} \mathcal{L}\left(\boldsymbol{q}(t) + \delta\boldsymbol{q}(t), \dot{\boldsymbol{q}}(t) + \delta\dot{\boldsymbol{q}}(t)\right) \mathrm{d}t - \int_{t_1}^{t_2} \mathcal{L}\left(\boldsymbol{q}(t), \dot{\boldsymbol{q}}(t)\right) \mathrm{d}t = 0$$

Perform a first-order Taylor expansion to the first term, we get

$$A = \int_{t_1}^{t_2} \left[\frac{\partial \mathcal{L}}{\partial \boldsymbol{q}(t)}\delta\boldsymbol{q}(t) + \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{q}}}\delta\dot{\boldsymbol{q}}(t)\right] \mathrm{d}t$$

Knowing that $\delta\dot{\boldsymbol{q}}(t) = \dfrac{\mathrm{d}\left[\delta\boldsymbol{q}(t)\right]}{\mathrm{d}t}$, and hoping to merge the two δ terms, we integrate the second term by parts[9]

$$\begin{aligned} A &= \int_{t_1}^{t_2} \frac{\partial \mathcal{L}}{\partial \boldsymbol{q}(t)}\delta\boldsymbol{q}(t)\mathrm{d}t + \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{q}}}\mathrm{d}\left[\delta\boldsymbol{q}(t)\right] \\ &= \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{q}}}\delta\boldsymbol{q}(t)\Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} \left[\frac{\partial \mathcal{L}}{\partial \boldsymbol{q}(t)} - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{q}}(t)}\right)\right] \delta\boldsymbol{q}(t)\mathrm{d}t = 0 \end{aligned}$$

Since $\delta\boldsymbol{q}(t) = 0$ at t_1 and t_2, the first term is 0; for any $\delta\boldsymbol{q}$ the above equation holds, then there must be

$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{q}} - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{q}}}\right) = 0 \tag{1.8.4}$$

[8] $\delta\boldsymbol{q}$ 是 $\boldsymbol{q}$ 的变分

[9] integrate ... by parts: 分部积分法

which is exactly the Euler-Lagrange equation (eqn. 1.4.5).

In statistical mechanics, we care more about endpoint problems than initial-value problems, though the solution to the "endpoint problem"[10] is not guaranteed to be a "stationary function". We are interested in the behaviors of large numbers of trajectories all seeded differently. Initial conditions for Hamilton's equations are generally chosen at random (e.g. random velocities). And we are interested in paths that evolve from one region of phase space to another, but not one point to another.

§ 1.9 Lagrangian mechanics and systems with constraints

It is often necessary to impose constraints to a system.

- high-frequency (rigid) chemical bonds
- thermal or barostatic control mechanisms

A system with N_c constraints have $3N - N_c$ degrees of freedom, and must satisfy N_c equations of the coordinates and velocities.

Holonomic constraints[11]: all relationships are functions of only the coordinates and time:

$$\sigma_k(q_1, \ldots, q_{3N}, t) = 0 \quad \text{for } k = 1, 2, \ldots, N_c \tag{1.9.1}$$

If not, the constraints are said to be *nonholonomic constraints*. For example, to keep the kinetic energy (temperature) constant, the system must satisfy

$$\sum_{i=1}^{N} \frac{1}{2} m_i \dot{\boldsymbol{r}}_i^2 - C = 0$$

where C is a constant.

Constraints will reduce the degrees of freedom, which is good, but it is not always convienent to write new equations particularly when there is a large number of coupled constraints. Then we try to incorporate them into the framework of classical mechanics. We apply the method of *Lagrangian undetermined multiplier*[12], but the constraint conditions must satisfy

$$\sum_{\alpha=1}^{3N} a_{k\alpha} \mathrm{d}q_\alpha + a_{kt} \mathrm{d}t = 0 \tag{1.9.2}$$

[10] comparing with the the initial-value problem, there are two conditions.

[11] 完整约束，相对地有非完整约束

[12] 拉格朗日不定乘子

where $a_{k\alpha}$ is a set of coefficients for the displacements $\mathrm{d}q_\alpha$. For a holonomic constraint, they can be obtained by

$$a_{k\alpha} = \frac{\partial \sigma_k}{\partial q_\alpha} a_{kt} = \frac{\partial \sigma_k}{\partial t} \tag{1.9.3}$$

while nonholonomic constraints can not always be expressed in the form of eqn. 1.9.2, but

§ 1.10 Gauss's priniciple of least constraint

§ 1.11

§ 1.12 Summary of chapter

-
- the Hamiltonian is a Legandre transform of the Lagrangian.

Chapter 2　内容示例

§2.1　用户环境示例

GRE 备考指南
https://qyxf.site/latest/GRE备考指南-v2.0.pdf
军事理论教程
https://qyxf.site/latest/军事理论教程.pdf
分析力学笔记
https://qyxf.site/latest/分析力学笔记-v1.0.pdf
大学物理题解
https://qyxf.site/latest/大物题解（上）.pdf
实变函数习题解答
https://qyxf.site/latest/实变函数习题解答.pdf
计算方法撷英
https://qyxf.site/latest/计算方法撷英-v1.1.pdf
计算机程序设计指南
https://qyxf.site/latest/计算机设计程序指南.pdf

Equation 1 *Euler-Lagrangian equation*

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{r}}_i} =$$

定义 1 极限就是超越自我。

定理 1 任何极限都可以直接观察得出。

引理 2 以上内容，纯属扯淡。

推论 3 这是一个推论。

注记

好好学习，天天向上。

警告

今天你学习了吗？

§2.2 列表样式

- 这是第一层
- 这也是第一层
  - 这是第二层
    - 这是第三层

1. 这是第一层
2. 这也是第一层
   1. 这是第二层
      (1) 这是第三层

§2.3 正文示例

微分学（*differential calculus*）是微积分的一部分，是通过导数和微分来研究曲线斜率、加速度、最大值和最小值的一门学科，也是探讨特定数量变化速率的学科。微分学是微积分的两个主要分支之一，另一个分支则是**积分学**，探讨曲线下的面积。

Tab. 2.1 常用导数

原函数	导函数	原函数	导函数
C	0	$\ln x$	$\frac{1}{x}$
x^{μ}	$\mu x^{\mu-1}$	$\sin x$	$\cos x$
e^{x}	e^{x}	$\cos x$	$-\sin x$

……几乎所有量化的学科中都有**微分**的应用。例如在物理学中，运动物体其位移对时间的导数即为其速度，速度对时间的导数就是加速度、物体动量对时间的导数即为物体所受的力，重新整理后可以得到牛顿第二运动定律 $F = ma$ 。化学反

应的化学反应速率也是导数。在运筹学中，会透过导数决定在运输或是设计上最有效率的做法。

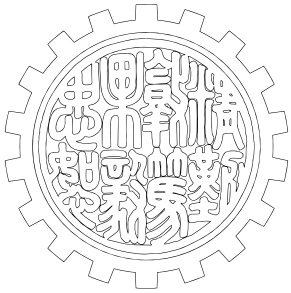

Fig. 2.1 V2 版本的封面图片

导数常用来找函数的极值。含有微分项的方程式称为**微分方程**，是自然现象描述的基础。微分以及其广义概念出现在许多数学领域中，例如复分析、泛函分析、微分几何、测度及抽象代数[1]。

§2.4 引导命令示例

练习 1 试用配方法求解方程：

$$ax^2 + bx + c = 0 \tag{2.4.1}$$

解 首先，方程左右两侧同除以 a，得到

$$x^2 + \frac{b}{a}x + \frac{c}{a} = 0$$

根据一次项来配方，按公式 $(x + A)^2 = x^2 + 2Ax + A^2$ 配出常数项：

$$x^2 + \frac{b}{a}x + \left(\frac{b}{2a}\right)^2 + \frac{c}{a} - \left(\frac{b}{2a}\right)^2 = 0$$

配方并移项得到

$$\left(x + \frac{b}{2a}\right)^2 = \frac{b^2}{4a^2} - \frac{c}{a}$$

方程左右开方，得

$$x + \frac{b}{2a} = \pm\sqrt{\frac{b^2}{4a^2} - \frac{c}{a}}$$

[1] 以上内容摘自维基百科中文词条 — 微分学：https://zh.wikipedia.org/wiki/微分学。

从而得到方程 (2.4.1) 之解为

$$x = -\frac{b}{2a} \pm \sqrt{\frac{b^2}{4a^2} - \frac{c}{a}} \tag{2.4.2}$$

该式即为一元二次方程的**通用求根公式**。

分析 在这一问题中，需要注意以下几点 [**? ?**]：

- ……
- ……
- ……