Principles

Notes on Statistical Mechanics for Molecular Simulation

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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 normal examples, I won't number the equations.

Table of Contents

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:

$$\boldsymbol{F} = m\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} = m\ddot{\boldsymbol{r}} \tag{1.1}$$

And Newton's third law:

$$\boldsymbol{F}_{AB} = -\boldsymbol{F}_{BA} \tag{1.2}$$

The definition of work:

$$W_{AB} = \int_A^B \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{l} \tag{1.3}$$

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

$$\boldsymbol{F} = \frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} \tag{1.4}$$

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*:

$$x_t = (\boldsymbol{r}_1(t), \ldots, \boldsymbol{r}_N(t), \boldsymbol{p}_1(t), \ldots, \boldsymbol{p}_N(t)) \tag{1.5}$$

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*

$$\boldsymbol{F} = -\nabla U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \tag{1.6}$$

where $\nabla = \dfrac{\partial}{\partial \boldsymbol{r}}$. Or for each particle i

$$\boldsymbol{F}_i = -\frac{\partial U}{\partial \boldsymbol{r}_i} \tag{1.7}$$

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

$$K(\dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2, \ldots, \dot{\boldsymbol{r}}_N) = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i^2 \tag{1.8}$$

1.4.2 Formulation

Here we introduce the *Lagrangian* of a system

$$\mathcal{L} = K(\dot{\boldsymbol{r}}_1, \ldots, \dot{\boldsymbol{r}}_N) - U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \tag{1.9}$$

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

$$E = K(\dot{\boldsymbol{r}}_1, \ldots, \dot{\boldsymbol{r}}_N) + U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \tag{1.10}$$

The Euler-Lagrangian equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{r}}_i} = \frac{\partial \mathcal{L}}{\partial \boldsymbol{r}_i} \tag{1.11}$$

which can be verified with the substitution of eqn. 1.7 and 1.8 (poco).

This equation helps generate the equations of motion. 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

$$q_\alpha = f_\alpha(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \qquad \alpha = 1, 2, \ldots, 3N \tag{1.12}$$

It is assumed that the transformation has a unique inverse

$$\boldsymbol{r}_i = \boldsymbol{g}_i(q_1, \ldots, q_{3N}) \qquad i = 1, 2, \ldots, N \tag{1.13}$$

Thus, through the chain rule, we have

$$\dot{\boldsymbol{r}}_i = \sum_{\alpha=1}^{3N} \frac{\partial \boldsymbol{r}_i}{\partial q_\alpha}\dot{q_\alpha} \tag{1.14}$$

The kinetic energy can then be written as[(1)]

$$\begin{aligned}
K(\boldsymbol{q},\dot{\boldsymbol{q}}) &= \frac{1}{2}\sum_{i=1}^{N} m_i \sum_{\alpha=1}^{3N}\frac{\partial \boldsymbol{r}_i}{\partial q_\alpha}\dot{q}_\alpha \sum_{\beta=1}^{3N}\frac{\partial \boldsymbol{r}_i}{\partial q_\beta}\dot{q}_\beta \\
&= \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}\sum_{i=1}^{N} m_i \frac{\partial \boldsymbol{r}_i}{\partial q_\alpha}\frac{\partial \boldsymbol{r}_i}{\partial q_\beta}\dot{q}_\alpha\dot{q}_\beta \\
&= \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N} G_{\alpha\beta}\dot{q}_\alpha\dot{q}_\beta
\end{aligned} \tag{1.15}$$

where

$$G_{\alpha\beta}(\boldsymbol{q}) = \sum_{i=1}^{N} m_i \frac{\partial \boldsymbol{r}_i}{\partial q_\alpha}\cdot\frac{\partial \boldsymbol{r}_i}{\partial q_\beta} \tag{1.16}$$

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-Lagrangian equation, considering q_γ as q_α:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{\beta=1}^{3N} G_{\gamma\beta}\dot{q}_\beta\right) = \sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N}\frac{\partial G_{\alpha\beta}}{\partial q_\gamma}\dot{q}_\alpha\dot{q}_\beta - \frac{\partial U}{\partial q_\gamma} \tag{1.17}$$

1.4.4 Example: two-particle system

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

$$\mathcal{L} = \frac{1}{2}m_1\dot{\boldsymbol{r}}_1^2 + \frac{1}{2}m_2\dot{\boldsymbol{r}}_2^2 - U(|\boldsymbol{r}_1-\boldsymbol{r}_2|) \tag{1.18}$$

And knowing that (not important)

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

[(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 1.11, we can get

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

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

$$
\begin{aligned}
\boldsymbol{R} &= \frac{m_1\boldsymbol{r}_1+m_2\boldsymbol{r}_2}{m_1+m_2} \\
\boldsymbol{r} &= \boldsymbol{r}_1-\boldsymbol{r}_2
\end{aligned}
$$

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

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

Substituted into eqn 1.18, 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

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

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

§ 1.5 Legendre transforms

§ 1.6 Hamiltonian formulation

Recall our mass metric matrix G

$$
G_{\alpha\beta}(\boldsymbol{q}) = \sum_{i=1}^{N} m_i \frac{\partial\boldsymbol{r}_i}{\partial q_\alpha}\frac{\partial\boldsymbol{r}_i}{\partial q_\beta} \tag{1.19}
$$

§ 1.7 Summary of chapter

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。

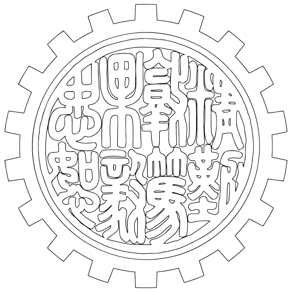

Fig. 2.1 V2 版本的封面图片

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：

$$ax^2 + bx + c = 0 \tag{2.1}$$

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 (2.1) 之解为

$$x = -\frac{b}{2a} \pm \sqrt{\frac{b^2}{4a^2} - \frac{c}{a}} \tag{2.2}$$

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 [1, 2]：

- ……
- ……
- ……

References

[1] KNUTH D E. The TEXbook [M]. Addison-Wesley: Reading, 1986.

[2] 刘海洋. LATEX 入门 [M]. 人民邮电出版社: 北京, 2013.