

Multiscale methods for soft matter physics

Maurizio Gilioli

Contents

1	Questions	2
2	Definition of soft matter	4
2.1	Classical mechanics	5
2.1.1	Time intervals and time evolution	5
2.1.2	Lagrangian mechanics	6
2.1.3	Statistical mechanics	6
2.2	Nature is not quantum	7
2.2.1	Born-Oppenheimer approximation	7

Chapter 1

Questions

All in notes if not specified

Legend:

- tuckerman: Tuckerman book
- not notes
- demonstrate: make the demonstration

Lessons questions

- Lesson 1
 1. What is soft matter?
 2. Is active moving matter soft material?
 3. What is the definition of soft matter?: Soft matter or soft condensed matter is a subfield of condensed matter comprising a variety of physical systems that are deformed or structurally altered by thermal or mechanical stress of the magnitude of thermal fluctuations.
 4. What does it mean to define soft matter as mesoscopic? what are the consequences?
 5. How should be defined the bigger compounds? what happens to time and space scale when those are utilized?
 6. Will have the force to be specific?
 7. What is the approximation that allow to simplify quantum mechanical problems with classical mechanics?
 8. How are thermal systems driven?
 9. What is the Helmholtz free energy? Which system is described? How is it obtained? (Tuckerman)
 10. What is the critical point? (See tuckerman) What happens?
 11. What is the Ising model? How can you describe with it the critical point?
 12. What is necessary to make Multiscale methods relevant? (hierarchy)
 13. What procedure allows the coarse-graining?
- Lesson 2
 1. Where are defined experimental observations?
 2. What is the Newton principle of determinacy

-
3. What elements are defined in your experimental space?
 4. What is Galilean invariance? In which conditions it is maintained?
 5. What is a model? and what allows to build?
 6. Is invariance maintained in case of isolated systems? and in the case of systems with several bodies?
 7. When are forces conservative?
 8. What is the action integral? What does it tell? What does satisfy a path called stationary? (demonstrate) (tuckerman)
 9. What does the action integral concept suggest? (tuckerman)
 10. What is the formula of the Lagrangian?
 11. What is the Legendre transformation (tuckerman)
 12. What is the Hamiltonian? how is it obtained? (tuckerman)
 13. Which are the Hamilton equations?
 14. What happens to the Hamiltonian when the Lagrangian is conserved?
 15. What is an ensemble?
 16. How is the value of a macroscopic observable normally obtained? (through a time average ...)
 17. To what a time average can be converted? what is a phase space average?
 18. When is a stochastic process called ergodic?
 19. How do we obtain a microcanonical ensemble?
 20. What are Poisson brackets? When is a quantity conserved? (tuckerman)
 21. What does the Liouville theorem say?
 22. When is the average of a quantity constant in time?
 23. How can you write the average of that quantity?
 24. What is a partition function? what type of coefficient it has?
 25. Formula for entropy in the microcanonical ensemble
- Lesson 3
 - Describe the canonical partition function, what is the related coefficient?
 - What is a Boltzmann weight?
 - Write the Hamiltonian formulation for a quantum problem
 - What type of ansatz you assume to simplify your work? What is the diabatic approximation?
 - Describe the Born-Oppenheimer approximation
 - What is meant by separability when talking about the potential energy? and additivity?
 - What is a multi-body potential? What type of truncation you can perform?
 - What is the difference between bonded and non-bonded interactions?

Chapter 2

Definition of soft matter

Soft matter is plastic (polymers), water (liquids), air (gas), liquid crystals and colloidal suspensions (particles in liquid), gels, sand (granular materials). Also active matter (such as bacteria and fishes and birds are soft matters in some sense).

What is not soft matter: graphite is a dense matter, but graphene is a soft matter. metals functionalized with proteins or nanoparticles could be considered as soft matter.

Poor definition:

Definition 1. *Soft matter systems SM systems are deformable upon stresses of the order of magnitude of thermal fluctuations*

This is an anthropocentric definition! as in fact you are referring to our body temperature. Some elements become soft matter with the Temperature.

Soft matter is **mesoscopic**: RELEVANT STRUCTURES ARE MUCH LARGER THAN THE CONSTITUENTS BUT MUCH SMALLER THAN THE WHOLE \rightarrow you don't need very profound analysis to define and characterize your system. By coarse graining, you have to select space and time scales that are good for your system.

In general, you generate a coarse-grained system whenever you consider as independent compounds groups of atoms. The larger the size of the phenomena you are trying to observe, the less are the important details you have to consider!

The first level of approximation is done through the Born-Oppenheimer approximation, in fact through that method you can consider the electrons and the nuclei separately (at first by solving the so called the electronic problem, after by solving the motion of nuclei through Newton mechanics).

To go from a scale to another, you need a mapping function $\underline{R}_I = M(\underline{r})$. This determines

- loss of degrees of freedom (loss of information). in fact, several high resolution can produce the same low resolution arrangement.
- substantial increase of entropy in the system: you gain an effective entropy that you have to take into account, although you lose some simplifying.

Machine L. can be used to extract features useful for the coarse graining.

2.1 Classical mechanics

the space is expressed in 3 dimensions, while the time is expressed in a single independent dimension. From the point of view of classical mechanics, it is sufficient to know the S0 state of the system

$$(q_0, p_0) \rightarrow (q, p)$$

where q represents the positions and p the momenta.
three mathematical objects are fundamental

- Universe: affine space with 4D, no origin, everything is defined in there
- Time: if $t_a = t_b$ then a and b are simultaneous
- Distance: separation between simultaneous events

$$P(a, b) = \sqrt{(a - b)(a - b)} = ||a - b||$$

The Gallilean space has to remain invariant after the following transformations:

- Uniform motion: $g_1(t, \underline{x}) = (t, \underline{x} + vt) \forall t \in R$ where v is a constant velocity
- Invariance under translation: $g_2(t, \underline{x}) = (t + s, \underline{x} + s) \forall s \in R^3$ where s is a shift in time and space
- Invariance under spatial rotation: $g_3(t, \underline{x}) = (t, R\underline{x})$ where R is a rotation matrix applied to \underline{x} such that $R : R^3 \rightarrow R^3$ consequently, the distances are maintained between points

2.1.1 Time intervals and time evolution

the evolution of the motion of a system is defined as mapping:

$$\underline{x} : I \rightarrow R^n$$

where n is the number of coordinates in the system. At each time point in the interval of time I , you can obtain the coordinates of the points. You can also obtain the speed and the acceleration by computing the derivatives.

The image of \underline{x} in the interval of time I is defined as the trajectory, which is a collection of points in all the point of I . a law of motion can describe the time evolution of a system.

In classical mechanics, by defining a model for computing the forces, you define the system

$$\underline{F}(\underline{x}, \dot{\underline{x}}, t) \propto \dot{\underline{x}}$$

In the case of isolated systems, dependence on time should not be present to allow the invariances written above. Also, since after a translation of the form $\underline{x} = \underline{x} + \underline{s}$ shouldn't change the description of the system (there are not objective coordinates but only relative positions). consequently, you can write that the acceleration of a system at a particular time point in a Gallilean system is in the form:

$$\dot{\underline{x}}_i = \phi_i \left((\underline{x}_j - \underline{x}_i), (\dot{\underline{x}}_j - \dot{\underline{x}}_i) \right)$$

but also, because of rotational invariance

$$\phi(R\underline{x}, R\dot{\underline{x}}) = R\phi(\underline{x}, \dot{\underline{x}})$$

The invariance laws are true until a force acts, and it performs a work on the system

$$\begin{aligned}
 W(A \rightarrow B) &= \int_A^B \phi d\underline{x} \\
 W(A \rightarrow B \rightarrow A) &= \oint \phi d\underline{x} = \int_A^B \phi d\underline{x} + \int_B^A \phi d\underline{x} \\
 &= \int_{\Sigma} \nabla \times \phi d\sigma \quad \text{Gauss theorem, sigma is the surface enclosed by path} \\
 &= - \int (\nabla \times \nabla U) d\sigma
 \end{aligned}$$

in the equation, if the quantity is 0, then the integral computed on the right and on the left are equal. This is real when the forces in the system are all conservative.

2.1.2 Lagrangian mechanics

it relies on the action

$$\begin{aligned}
 S : \text{action} &= \int [\underline{x}, \underline{x}_a, \underline{x}_b, T] \\
 &= \int_a^b dt L(\underline{x}, \dot{\underline{x}}, t)
 \end{aligned}$$

where a and b are respectively starting and ending position. T is the time interval. The Lagrangian is calculated as $L = K - U$, where K is the kinetic energy and U the potential. Interestingly, the action has a minimum value when it is considered the real path.

$$\frac{\partial S}{\partial \underline{x}}(\alpha^*) = 0$$

where α^* is the real path

The correct path is obtained through the Euler-Lagrange equation:

$$\frac{\partial}{\partial t} \left(\frac{\partial L}{\partial \dot{\underline{x}}} \right) = \frac{\partial L}{\partial \underline{x}} \quad (2.1)$$

if $\frac{\partial L}{\partial t} = 0$, then the associated conserved quantity

$$\sum q_i p_i - L = H$$

where H is the Hamiltonian, if it is conserved, the energy of the system is conserved. There are the so called Hamilton's equations.

2.1.3 Statistical mechanics

Lagrangian mechanics is for single trajectories, but not for more complicated systems, with higher degrees of freedom (N atoms in our). We want to define a phase space, where points are defined as \underline{pq} . The calculation of a quantity A is as follows:

$$A = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} a(\underline{q}, \underline{p}) dt$$

In the limit of $\tau \rightarrow \infty$, you define the value of the macroquantity A by taking into consideration volumes.

$$A = \int d\underline{q} d\underline{p} \rho(\underline{q}, \underline{p}) a(\underline{q}, \underline{p})$$

2.2. NATURE IS NOT QUANTUM

Definition 2. A stochastic process is said to be in an ergodic regime if an observable's ensemble average is equal to the time average.

An ensemble is a set of systems identical in terms of some fundamental parameters but with different initial values

In the case in which N , V , E are the conserved macroquantities, then you are in a microcanonical system.

2.2 Nature is not quantum

Nature is quantum, but in many cases, you need classical mechanics to allow the production of simulations. A classical representation is wrong in principle, but allows to address the task. An Hamiltonian can be written like this:

$$\begin{aligned}\hat{H} &= -\sum_i \frac{\hbar^2}{2} \Delta_i^2 - \sum_I \frac{\hbar^2}{2M_I} \Delta_I^2 + \sum_{i,j} \frac{1}{|r_{ij}|} + \sum_{i,j} \frac{Z_i Z_j}{r_{ij}} - \sum_{i,I} \frac{Z_I}{r_{iI}} \\ &= \hat{T}_r + \hat{T}_n + \hat{U}_{en} + \hat{U}_{ee} + \hat{U}_{nn}\end{aligned}$$

This Hamiltonian can be used to compute and solve the Schrodinger equation.

2.2.1 Born-Oppenheimer approximation

it starts with defining the following ansatz:

$$\psi = \phi(\underline{r})\chi(\underline{R})$$

where ϕ represents the function related to the electrons and χ the function related to nuclei. According to the adiabatic approximation, you can estimate the nuclei to move much slower than the electrons. Since the mass of an electron $m_e \sim \frac{1}{1836} M_n$, then you can assume as true that approximation, and neglect nucleus kinetics. Consequently, you can solve the dynamical problem through the following steps:

1. Solve problem with the electrons, given that the nuclei are considered fixed
2. Solve the problem for the nuclei.

Because of the previous named approximations, you can say that \hat{T}_n and U_{nn} are approximately $= 0$, since you assume that in a time interval the nuclei don't move. Consequently,

$$\hat{H} = T_e(\underline{r}) + U_{ee}(\underline{r}) + U_{en}(\underline{r}, \underline{R})$$

also, you can say that

$$\phi(\underline{r}, \underline{R}) = \sum_k \phi_k(\underline{r}, \underline{R}) \chi_k(\underline{R})$$

then

$$\begin{aligned}\hat{H}\psi &= E\psi \\ \sum_{k'} \hat{H} \phi_{k'} \chi_{k'} &= E \sum_{k'} \phi_{k'} \chi_{k'} \\ \sum_{k'} \langle \phi_{k'} | \hat{H} | \phi_{k'} \rangle | \chi_{k'} \rangle &= E \sum_{k'} \langle \phi_{k'} | \phi_{k'} \rangle | \chi_{k'} \rangle && \text{From which Kronecker delta} \\ \sum_{k'} \langle \phi_{k'} | \hat{H} | \phi_{k'} \rangle | \chi_{k'} \rangle &= E | \chi_k \rangle\end{aligned}$$