

ASSIGNMENT 7: MOLECULAR DYNAMICS

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MOLECULAR DYNAMICS

INTRODUCTION

It is a common task to need to model the time evolution of a set of particles. In surface physics, the conceptual interpretation of this is simple; a set of molecules can be individually tracked as they interact with the surface, and with each other. Of course, with the involvement of so many entities, the reality is much less straightforward. Providing a computational model requires a great many ideas, and significant processing power: gradually learning this skill, the reader should exert significant caution - it is very difficult to write a fast script, especially without errors!

PREREQUISITES

From the *Theory Handbook*, the chapters on:

- The Fourier transform,
- Verlet integration,
- Langevin mechanics.

Ensuring that you understand the above before starting is vital. This document does not cover them in detail. We recommend that the reader understands the relation between the van Hove pair correlation function and the intermediate scattering function before starting this tutorial, allowing them to make links to direct measurements with spin echo techniques.

THEORY: LANGEVINS

There is a surprisingly simple equation that dictates the motion of an adsorbate on a substrate. Known as the *Langevin*, this equation has been extensively studied in the literature. The simplified form of the Langevin equation, applying under a particular set of assumptions, is:

$$m_i \ddot{\mathbf{r}}_i = -\eta m_i \dot{\mathbf{r}}_i + \boldsymbol{\xi}(t),$$

where:

1. \mathbf{r}_i is the position of the i th adsorbate,

2. m_i is the mass of the i th adsorbate ,
3. η is a friction coefficient,
4. ξ is a stochastic force, described by a vector quantity.

What does this equation represent? As you may reasonably expect, the motion of a particle on a surface is *not* uniform. The most simple interpretation of this is that the particle experiences a force: consequently causing it to accelerate, and change direction.

Assumptions

When can we use this form of the Langevin equation? Noting the fuller form of the Langevin given in the *Theory Handbook*, we notice that two terms have disappeared: the gradient of the potential, and the adsorbate-adsorbate interactions. We can easily justify removing these terms, in suitable contexts. For weakly corrugated surfaces, the potential will change very little around the surface (thus justifying the removal of the gradient). For sparsely populated adsorbates, they are simply too far away to strongly affect each other - and so feel a very small force.

The Stochastic Force

The stochastic force ξ is a more abstract term in the Langevin. For a detailed discussion of its origin, see the *Theory Handbook*. For the purposes of this document, we will repeat what has already been mentioned: the stochastic force is normally distributed in each direction, and independent in each direction. In a small time interval δt , the impulse it exerts (in each direction) has a standard deviation

$$\sigma = \sqrt{2k_B T_s m \eta \delta t}.$$

This is the impulse! Do not get it mixed up with the force.

There is one further comment to make. Why does the stochastic force take this value? This standard deviation is the precise value that allows the system to maintain thermal equilibrium. If it were any different, thermal equilibrium would not be maintained. This would not resemble a steady state for the system!

THEORY: THE EQUIPARTITION THEOREM

This section includes additional theory required to complete this task. For a system with n quadratic modes, all of which are degrees of freedom, the expectation value of the energy of the system is:

$$\langle E \rangle = \frac{n}{2} k_B T,$$

where k_B is the Boltzmann constant, and T is the temperature of the heat bath to which the system is connected.

What do “degrees of freedom” mean? Simply put, if a system has n quadratic degrees of freedom, then we can write the energy of the system in the form:

$$E = \sum_{i=1}^n \alpha_i x_i^2,$$

where each x_i is a distinct variable. Consider how many degrees there are, for a particle moving on a surface. Is it the same for both atoms and molecules (consider the form of the potential function of a covalent bond)?

OBJECTIVE OF THIS TUTORIAL

In this tutorial, we will attempt to build a primitive model of atoms moving on a surface. This surface will have very weak corrugation, allowing us to massively simplify the system. We will also neglect forces between molecules, thus simplifying the Langevin further. The result of these assumptions is the form of the Langevin given above. We will numerically solve the system using Verlet integration.

Doing Molecular dynamics is a little more involved than the other tasks set so far. Don’t worry if it takes several attempts to get it working properly! This is entirely normal.

TASK

1. The main task set by this tutorial is straightforward to describe. Given a single particle was at rest at the origin at $t = 0$, solve the Langevin equation, using Verlet integration. Plot the two dimensional time evolution of the position of the particle on the surface.
2. Repeat the simulation above, except for an ensemble of 50 particles. Plot each particle on the same graph, in a different colour.
3. State how many quadratic degrees of freedom there are for a diffusing particle on this surface. Using the equipartition theorem, state what the equation for the total energy of the adsorbate is, as a function of temperature.
4. Find the root mean square kinetic energy of the particles in this ensemble, as a function of time. Plot this as a graph. Confirm that this corresponds to the temperature of the substrate surface. Provide a physical interpretation of this correspondence.

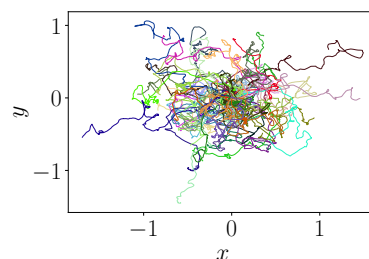


Figure 1 | An ensemble of 50 particles moving on a surface, using the model in this document. The units on the axis are arbitrary

Parameters

Throughout this tutorial, we advise that you set the parameters as below.

1. The friction coefficient η as 50ps^{-1} ,
2. The mass of each particle m as 1amu ,
3. The temperature of the substrate T_s as 100K ,
4. The Boltzmann constant k_B as $0.8314\text{\AA}^2\text{amu} \cdot \text{ps}^{-2}\text{K}^{-1}$,
5. The timestep δt from the Verlet algorithm as 0.001ps ,
6. 100 000 steps in the Verlet algorithm.

SUMMARY

This tutorial introduces the skill of how to model the diffusion of particles on a flat surface, using the Langevin equation of motion. This naturally leads on to more advanced simulations.