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Introduction to Modeling and Simulation (IM/S)

Spring 2006

Intro 2 (2/10/06) – Diffusion at the Particle Level

Before starting the series of lectures on Continuum Methods, we take a class period (this lecture) to introduce some basic notions of describing a physical phenomenon using a model of particles, and then follow this in the next class (Intro 3) with a discussion of the description in the continuum limit of the same phenomenon. The idea is to show how *the same* phenomenon can be studied at two levels, one involving the particles explicitly and the other where the particles have been averaged out. At the continuum level, whatever it is that the particles do is now represented by systems for which one can write down equations. We hope that once the student understands the connection between these two levels, he can appreciate more broadly the description of any physical phenomenon, whether it is from the standpoint of particles or the continuum.

The phenomenon we choose to discuss is *mass transport* or *diffusion*. Diffusion is a term commonly used in connection with the flow of matter (or concentration). Imagine a drop of dye in water gradually spreading out in a persistent but apparently random manner. What is going on at the particle level is that the dye molecules start to move away from each other by bumping into each other as well as colliding with the surrounding water molecules. By recording the individual motion of each dye molecule, one can collect, in principle, a massive amount of data from which a description can be constructed of how the dye concentration redistributes itself in time. This then would be the particle-method approach to study the diffusion of dye molecules in water.

“If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence is passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the *atomic hypothesis* (or the *atomic fact*, whatever you wish to call it) that *all things are made of atoms – little particles that move around in perpetual motion, attracting*

each other when they are a little distance apart, but repelling upon squeezed into one another. In that one sentence, you will see, there is enormous amount of information about the world, if just a little imagination and thinking are applied.”

Richard P. Feynman, *Six Easy Pieces*, (Addison-Wesley, Reading, 1963), p.4.

This widely quoted statement by a very well-known and respected physicist calls attention to the rich information contained in the apparently chaotic motions of atoms in matter. It sets the tone for this introductory lecture, namely, there is much one can learn about physical phenomena through *particle tracking*, the underlying concept in the particle methods of modeling and simulation.

The motion of dye molecules in water is just about the simplest example of diffusion one can imagine from the standpoint of everyday experience. There is another example which is often mentioned in connection with diffusion. In 1827 the botanist Robert Brown discovered that small pollen grains immersed in a fluid seemed to move in a perpetual, irregular manner. This characteristic movement has come to be called Brownian motion and is now known to be due to the incessant collisions of the pollen particle with molecules of the surrounding fluid. For our purposes the terms of diffusion and Brownian motion will be used interchangeably. So, what Brown observed was the diffusion of grain pollens in water. What does it mean to say that we can describe this phenomenon? Since the grain pollens never stand still, the only meaningful measure of diffusion is to determine how far the grains spread out per unit time. As we will see, the quantity we are after turns out to be the diffusion coefficient, which is something that the particle method can determine and which is an input to the continuum equation.

The Atomic Trajectory $\{\underline{R}^N(t)\}$

Since the concept underlying all particle methods is *particle tracking*, we begin with the consideration of labeling particles in order that particle movement can be followed as precisely we desire. We assign to each particle a position vector \underline{R} , or a set of coordinates such as R_x, R_y, R_z . Because all the particles are allowed to move in time, the position vector will be time-dependent, $\underline{R}(t)$. For a system with N particles, we then have a set of N such positions,

$$\{\underline{R}^N(t)\} \equiv (\underline{R}_1(t), \underline{R}_2(t), \dots, \underline{R}_N(t)) \quad (1)$$

We will call the set of particle positions the *atomic trajectory* from here on. If we know the positions of all the particles at all times, then we have the maximum information possible from our simulation.

How do the particles move in a simulation?

The answer is at the heart of understanding particle tracking. What does it mean to track (follow) the particles as they move about? The implication is that we know enough about how the particles interact among themselves as well as with the molecules in their surrounding. If that is the case, then if we are given a set of particle positions at one instant in time, say $t = t_0$, we can use this knowledge to calculate (predict) the particle positions a short time later, at $t = t_0 + \Delta t$. Repeating this again we can find the particle positions at $t = t_0 + 2\Delta t$, etc. In this way a sequence of particle positions over a large number of time steps is generated. So moving particles in a simulation amounts to calculating the incremental particle positions over a small time interval Δt .

How can one do this simply? Consider writing a Taylor series expansion,

$$R(t_0 + \Delta t) \cong R(t_0) + v(t_0)\Delta t + \frac{1}{2}a(t_0)(\Delta t)^2 \quad (2)$$

where $v(t)$ is the particle velocity at time t , and $a(t)$ is its acceleration. Knowing the original position of the particle, $R(t_0)$, velocity and acceleration one can apply Eq.(2) to obtain the particle new position. Notice that we can use Newton's law, $F = ma$, where F is the force on a particle, m the mass, and a is the acceleration, to rewrite the third term in Eq.(2) as $F(t_0)(\Delta t)^2/2m$. The force on a given particle depends on the positions of all the nearby neighbors. For this reason one needs to know the positions of the neighbors before one knows how to move a given particle. This means that because the particles interact with each other they are coupled in their motions which can be quite complicated. This is the reason why particle simulation can treat highly nonlinear

interaction effects (albeit numerically). We will come back and say more about calculating particle trajectories later when we discuss the simulation method of molecular dynamics. For now the point is that with Eq.(2) we can calculate the force on each particle for all the particles and move every particle forward by the time step Δt together. This may sound tedious if there are many particles in the system, but it is very straightforward and well suited for the computer. In essence one is just numerically solving the set of Newton's equations of motion for the N particle system. Since no assumption is made about the forces being linear, very complex dynamics, such as the apparently chaotic motions of grain pollens in water, can be treated accurately using this approach.

The Meaning of Atomic Diffusion

What does it mean to say that we know how to describe the motion of something that is undergoing diffusion? Suppose we leave out diffusion for the moment and ask how do we describe any motion of an object. This is simple enough so that we are all comfortable with asking this question. Given that we have already labeled or 'tagged' the particles in our model system, we can imagine making a plot of these particle positions over a short period of time, like taking a sequence of snapshots. In Fig. 1 we

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Fig. 1. Atomic trajectories of a two-dimensional crystal (top), liquid (middle), and gas (bottom) simulated by molecular dynamics [J. A. Barker and D. Henderson, *Scientific American*, Nov. 1981].

show what these snapshots would look like for particles in three simple physical systems, a crystal, a liquid, and a gas. These are the atomic trajectories, $\{\underline{R}^N(t)\}$, introduced above, and they are the results of an atomistic simulation (to be discussed in the Particle Methods part of the course). It is no surprise that particles do not move much in a crystal, where each particle is bound a lattice site and all it can do is to vibrate about its equilibrium position. The vibrations allow each particle to wander around a small local region, but none of the particles can travel very far no matter how long one waits. This is of course an idealization since we know that even in a solid there are atomic jumps which allow particles to ‘diffuse’ (although this diffusion is very slow by comparison with similar motions in a liquid).

Looking at the liquid part of Fig. 1 we see much longer trajectories and the possibility of particles moving far from its original position. This is then the major difference between the crystal and the liquid, the onset of diffusive motion. The reason a particle in a liquid can undergo diffusion is because its immediate environment changes over time, unlike that in a crystal. It is as if the particles in the solid are trapped in cages which maintain its structure for very long times (compared to what we are looking at in Fig. 1), whereas in the liquid such cages fluctuate strongly and can open up from time to time to allow the particles to move away. Taking this picture to the extreme, we can say that in a gas the cages are practically nonexistent so that most of the particle motions are straight ahead movements interrupted only by collisions with some of the neighbors. If one still wants to speak of diffusive motions, then it must be concluded that diffusion in a gas is much more rapid than that in a liquid. Talking about particle motions as in Fig. 1 is one way to begin to describe atomic diffusion. Another way is to consider the diffusivity of the motions which can be quantified as a property of the medium in which the motions occur as well as a property of the object which is undergoing the diffusive motion. Thus, diffusivity is a property to which we can assign a numerical value, it can be calculated using simulation as we will show here, and also measured by experiment.

While results like Fig. 1 contain a lot of information about particle motions, we need a way to analyze all this data that will tell us about the diffusivity property. Since the major difference between motions in the three states of matter lies in how far a particle move away from its initial position over a period of time, we define a quantity called the mean square displacement function (MSD),

$$\langle \Delta^2 r(t) \rangle \equiv \langle [R(t) - R(0)]^2 \rangle \quad (3)$$

where the meaning of the angular brackets $\langle \rangle$ is an average over all the particles undergoing diffusion in the model. In the example of grain pollens in water, we would apply Eq.(2) to each grain pollen but not to the water molecules. The water molecules certainly will influence pollen diffusion since they are ‘obstacles’ with which the pollens will collide (in addition, the pollens will collide among themselves). What would a typical MSD look like? This is sketched in Fig. 2 for the three cases we have already considered in Fig. 1. Notice that MSD for a solid grows to a certain and then just oscillates, whereas for a liquid the long-time behavior is a linear growth with time. The slope of the MSD for a liquid is defined as $6D$, where D is the diffusion coefficient. For a gas MSD grows like t^2 in time, and at some point later the curve will turn over like the liquid case (not shown in Fig. 2).

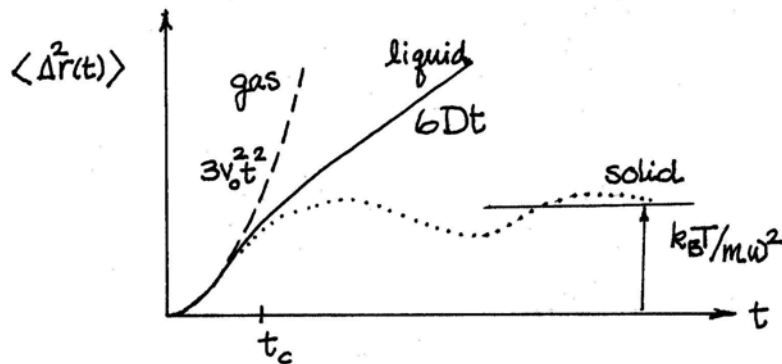


Fig. 2. Schematic sketch of the mean squared displacement function of solid, liquid, and gas. The behavior of MSD at long times, t large compared to a characteristic time t_c ,

defines the diffusion coefficient D , as seen in the case of the liquid. In this illustration, D would be zero for the solid and ‘infinite’ for the gas.

We have now seen that particle tracking gives us plenty of information about the atomic structure of simple states of matter – solid, liquid, and gas, as well as the motions that occur in these systems. The basic information lies in the particle positions, or more generally, their atomic trajectories. If one has this kind of data, then one can use the data to calculate the MSD and from its behavior at sufficiently long times we can determine the diffusion coefficient of the model,

$$D = \langle \Delta^2 r(t) \rangle / 6t, \quad t \gg t_c \quad (4)$$

One connection between the particle model approach and the continuum description is D . Whereas we have shown here that D can be determined from the atomic trajectory information, in the continuum description D is typically a parameter of the equation, a quantity that needs to be determined separately. In the continuum description one is concerned with solving certain equations which will contain physical parameters like the diffusivity. The emphasis there will be on how to solve these equations subject to various boundary and initial value conditions, and not so much on how to determine the physical parameters. Later on when we introduce the particle methods it will be seen that part of the emphasis is to determine physical properties of interest.

How well can we predict the Diffusion Coefficient?

The question is how accurately can we use the above method to predict the diffusion coefficient of a liquid. The answer is in two parts, if the liquid is simple our prediction is quite good (10% or better), whereas if the liquid is complex then our prediction may be only qualitative (to within a factor of 2) which is sometimes still useful. To back up what we are saying here we show in Fig. 3 the MSD of liquid argon which was simulated using the method of molecular dynamics (which we will discuss later) forty years ago. One can compare the actual simulation results with the schematic sketch in Fig. 2. The solid line in Fig. 3 is the best result, an average of some 64 independent trajectories, and from it one obtains $D = 2.43 \times 10^{-5} \text{ cm}^2/\text{sec}$.

Experimentally one measured the same value of D at a slightly different temperature. Both simulation and experiment were carried out at the same density, but the experiment was conducted at 90°K whereas the simulation temperature was 94.4°K . This is therefore an example of accurate prediction of diffusion in a simple liquid.

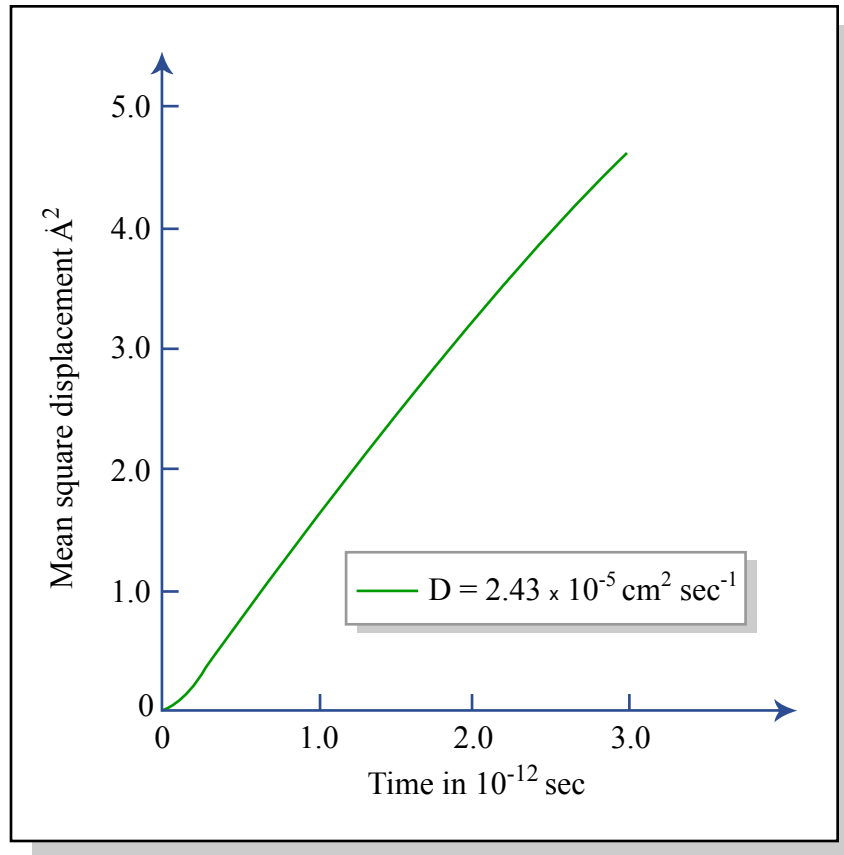


Figure by MIT OCW.

Fig. 3. Mean squared displacement function obtained for liquid argon by molecular dynamics simulation [A. Rahman, Phys. Rev. **136**, a405 (1964)]. From the long-time behavior one can determine the diffusion coefficient D .