# *Green Kubo Relations:*
# *Macro-properties from micro-fluctuations using MD simulations*

Material for these lecture notes was compiled from the references below

✓ D. Frenkel and B. Smit, *Understanding Molecular Simulations* (Academic) – Also consult case studies related to this textbook here

✓ MIT's 3.320 course notes

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# *Diffusion in a solid*

➤ Let us study diffusion in a solid. Consider a Si crystal that you are doping with Gallium or Phosphorus and you are interested in studying how the impurities in this system move around.

$$\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t)$$

➤ The concentration c(**r**,t) of impurities is a function of space and time.

➤ Fick's law tells us that the flux is proportional to the gradient of the concentration: **J** = - D $\nabla$ c.

➤ The Green-Kubo formalism relates macroscopic properties (e.g. the diffusion coefficient) to microscopic properties (fluctuations of the equilibrium distribution).

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# *Fick's Diffusion Law*

➤ From the continuity equation, the derivative of the concentration with respect to time plus the divergence of your flux needs to be constant (let's say zero).

$$\frac{\partial c}{\partial t} + \nabla \bullet J = 0$$

➤ In an infinitesimal volume, the concentration changes because there is a current going out of that infinitesimal volume. The divergence of the current measures this.

➤ Substituting Fick's diffusion law, we can obtain the PDE for the concentration profile:

$$\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t)$$

# *Connection with microscopic dynamics*

$$\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t)$$

➢ This is our starting macroscopic relationship. We will now see Einstein's derivation to recover a connection with the microscopic dynamics.

➢ Let's multiply the left term and the right hand terms by $r^2$ and integrate over all space.

$$\frac{\partial}{\partial t}\int d\vec{r}\ r^2 c(r,t) = D\int d\vec{r}\ r^2 \nabla^2 c(r,t)$$

➢ By integration by parts and assuming that the concentration is normalized to 1 when integrated in the whole space, we can show that the integral on the right is equal to 2 times the dimensionality *d* of the problem (in *1D, d=1*, in *2D, d=2*, ..).

$$\int d\vec{r}\ r^2 \nabla^2 c(r,t) = 2d$$

# *Connection with microscopic dynamics*

$$\frac{\partial}{\partial t} \int d\vec{r}\, r^2 c(r,t) = 2dD$$

➢ On the left hand side we have the average value $<r^2>$ of $r^2$. What we mean by this bracket is the integral over all space of $r^2$ multiplied with the probability. The concentration is identical to the probability of having a certain particle in a certain position and a certain time.

➢ The integral on the left hand side is just the average value over all space of $r^2$, how much the particles have moved :

$$\frac{\partial}{\partial t} \int d\vec{r}\, r^2 c(r,t) = \frac{\partial}{\partial t} \left\langle r^2(t) \right\rangle = 2dD$$

# *Connection with microscopic dynamics*

➢ Now we have a connection between the diffusion coefficient D (macroscopic property) and the microscopic dynamics (that is, how much the particles are moving once you put them somewhere).

$$\frac{\partial}{\partial t}\left\langle r^2(t) \right\rangle = 2dD$$

➢ We now need to discuss how to calculate the term on the left using an MD simulation.

❑ For example, you put Ga on the surface of Si and you want to see how these atoms will diffuse (move) towards the inside.

# *Micro to Macro*

➤ If you want to calculate this average value of of $r^2$ what is called **the mean square displacement**, you need to do the average of $\Delta r^2$ over all your particles at a certain time. $\Delta r^2$ is really how far all these particles have moved.

$$\left\langle \Delta r(t)^2 \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \Delta r_i(t)^2$$

Iodine atoms sit on a bcc lattice

➤ The example here shows the difference between a liquid and a solid. It's the case of **Silver Iodide** (ionic crystal). For each Iodine atom there is a Silver atom. Above ~420 K this system is in a **superionic state** in which the **iodine atoms oscillate around their equilibrium position exactly as atoms do in a solid state while the Silver atoms (sublattice) move around exactly like a liquid**.
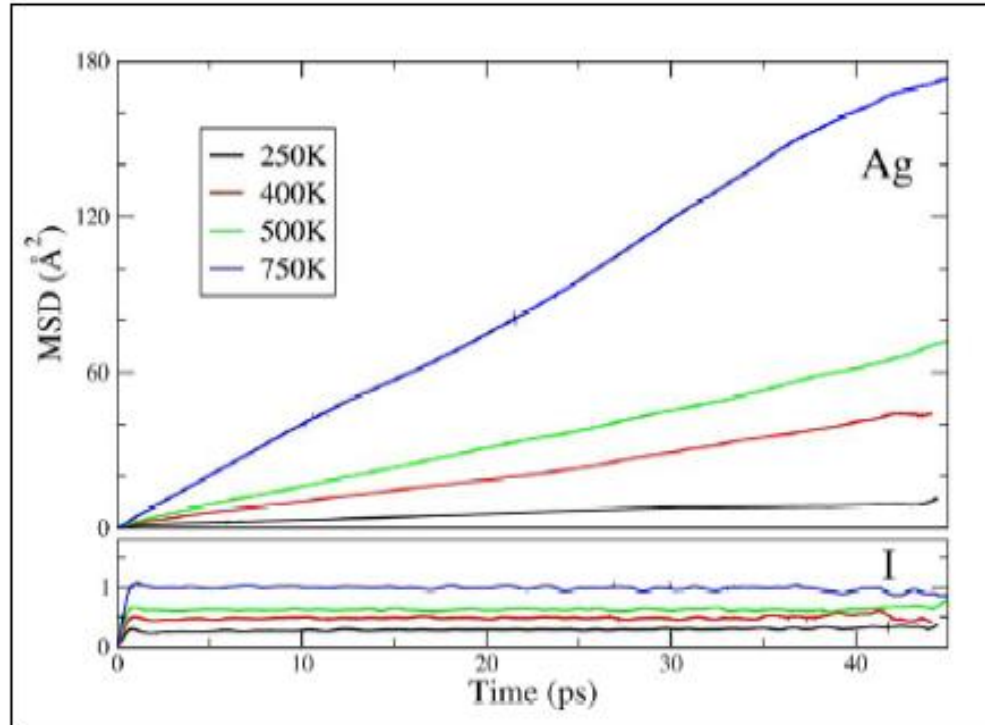


Silver atoms

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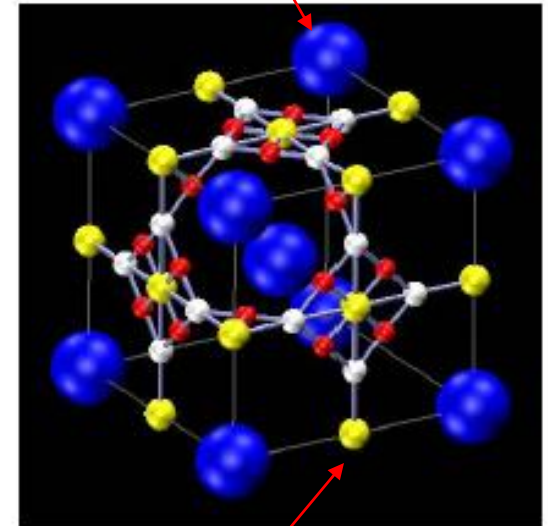
# *An example of the mean square displacement*

➢ Let us calculate for the iodine atoms what is the average mean square displacement (you average on all the iodine atoms their $\Delta r^2$, i.e. how much they move around).
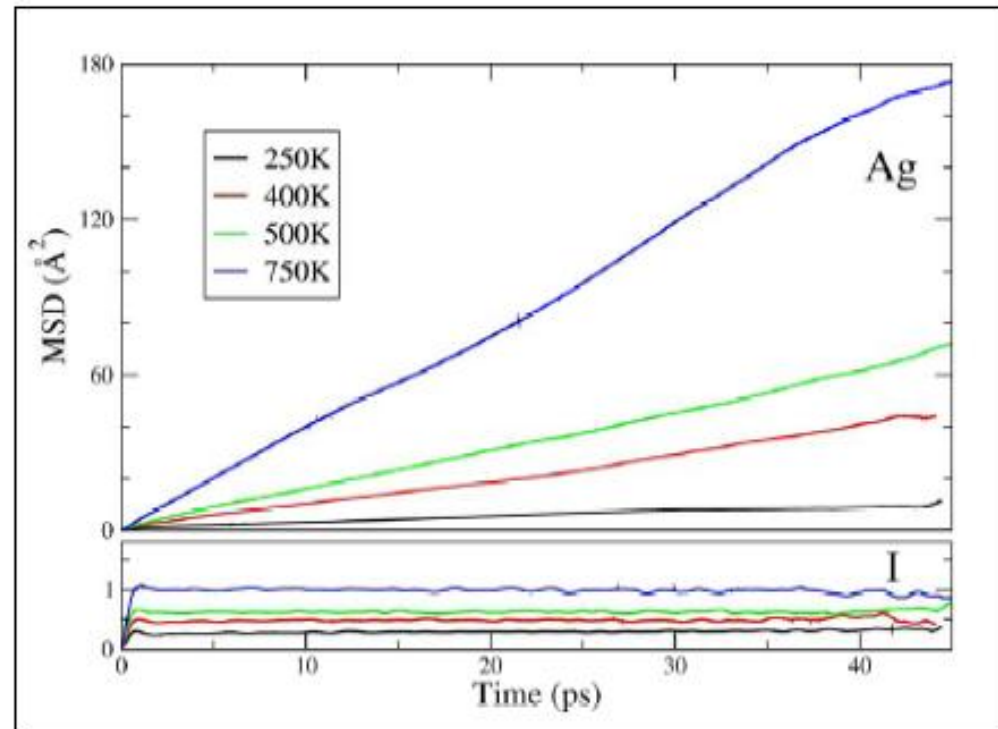


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➢ Since iodine atoms are as crystalline solid, they oscillate around their equilibrium position. You calculate that average during a MD simulation. Note that after a very short period of thermalization, **the atoms start moving but oscillate around their equilibrium positions.** Their instantaneous mean square displacement has a constant value. This is typical of a crystalline solid.

# *An example of the mean square displacement*

➢ You now do the same thing for Silver as a function of temperature. At 250 K below the superionic transition, also the Ag atoms mean square displacement looks more or less flat.  But when you increase the temperature, their mean square displacement starts becoming a linear function of time --  the Ag atoms are diffusing as a  liquid.

➢ In the mean square displacement, you can see the signature of a liquid when it increases linearly with time. If the atoms vibrate around their equilibrium position, that's a signature of a solid.



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# *Velocity autocorrelation function*

➢ So <r²> is the quantity that we could calculate in our MD simulation.  The average of the mean square displacement is going to be equal to 2 times the diffusion coefficient time the dimensionality of your system.

$$\frac{\partial}{\partial t}\left\langle r^2(t)\right\rangle = 2dD$$

➢ Now we introduce this alternative definition of the displacement of an atom.

$$\Delta x(t) = \int_0^t dt' \, v_x(t')$$

# *Displacement of an atom in periodic boundary conditions*

➤ Be careful when you work in periodic boundary conditions. MD codes for simplicity show you the coordinates of the ions as they were sitting in your first unit cell. So, if an atom is diffusing as a liquid and it moves from one unit cell to another unit cell, your code will actually bring it back by a lattice translation to the first unit cell.

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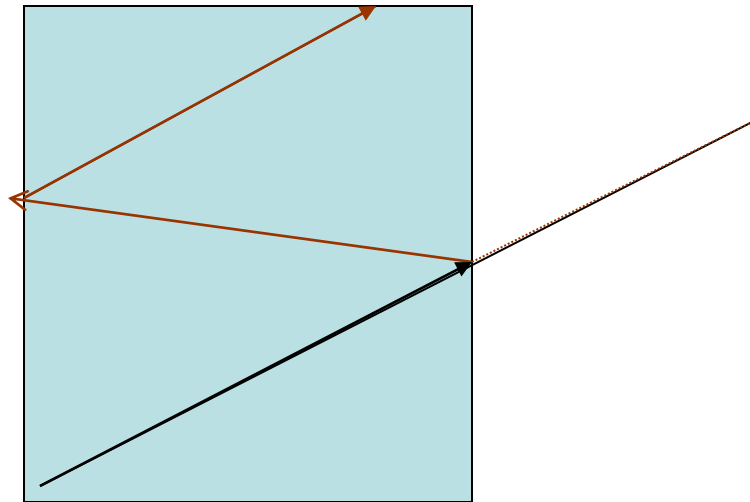
# *Velocity autocorrelation function*

➤ We need to write the position as a vector that satisfies the periodic boundary condition. We do this by writing the position as an integral of the velocity.

$$\Delta x(t) = \int_0^t dt' \, v_x(t')$$

➤ We now take correctly into account all the distance that each particle has been traversed. You integrate correctly your trajectory by doing the integral of the velocity while your algorithm would actually bring back the particle once it crosses a barrier.

➤ We can now return to the expression for the average of the mean square displacement.

$$\left\langle \Delta x(t)^2 \right\rangle = \frac{1}{N} \sum_{i=1}^N \Delta x_i(t)^2$$

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# *Velocity autocorrelation function*

$$\left\langle \Delta x(t)^2 \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \Delta x_i(t)^2$$

➤ We write it as the square of the integral of the velocity at the instant *t*. The bracket <> denotes the ensemble average on all your particles (note that it commutes with the integral).

$$\left\langle \Delta x(t)^2 \right\rangle = \left\langle \left( \int_0^t dt' v_x(t') \right)^2 \right\rangle = \int_0^t dt' \int_0^t dt'' \left\langle v_x(t') v_x(t'') \right\rangle$$

$$= 2 \int_0^t dt' \int_0^{t'} dt'' \left\langle v_x(t') v_x(t'') \right\rangle$$

➤ We have written this average mean square displacement as an integral of the average product between the velocity at a certain instant and the velocity at a different instant.  This is where our connection with the equilibrium properties is starting to emerge.  This is called **velocity autocorrelation function**.

# *Velocity autocorrelation function*

$$\langle \Delta x(t)^2 \rangle = 2 \int_0^t dt' \int_0^{t'} dt'' \langle v_x(t')v_x(t'') \rangle$$

➤ Let us return to the Einstein relation in 1D (d=1):

$$\frac{\partial}{\partial t} < r^2(t) > = 2D$$

➤ When you take the derivative with respect to *t*, one of the integrals cancels out.

$$2D = \lim_{t \to \infty} \frac{\partial \langle x^2(t) \rangle}{\partial t} = \lim_{t' \to \infty} 2 \int_0^{t'} dt'' \langle v_x(t')v_x(t'') \rangle$$

# *Green-Kubo relation*

$$2D = \lim_{t \to \infty} \frac{\partial \langle x^2(t) \rangle}{\partial t} = \lim_{t' \to \infty} 2 \int_0^{t'} dt'' \langle v_x(t') v_x(t'') \rangle$$

➤ We can exploit translational invariance in time. If we are looking at what is the average value of the product of the velocity at a certain instant t' times the velocity of another instant t", the average product is not going to be different if we translate it in time so we can refer it to an arbitrary origin. So we shift t" to 0:

$$\langle v_x(t') v_x(t'') \rangle = \langle v_x(t' - t'') v_x(0) \rangle$$

➤ This is our final expression and this is what is called a **velocity-velocity autocorrelation function.**

$$D = \lim_{t' \to \infty} \int_0^{t'} dt'' \langle v_x(t' - t'') v_x(0) \rangle = \int_0^{\infty} d\tau \langle v_x(\tau) v_x(0) \rangle$$

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# *Velocity-velocity autocorrelation function*

$$D = \lim_{t' \to \infty} \int_0^{t'} dt'' \left\langle v_x(t' - t'') v_x(0) \right\rangle = \int_0^{\infty} d\tau \left\langle v_x(\tau) v_x(0) \right\rangle$$

Velocity-velocity autocorrelation

➤ On the left hand side we have the macroscopic property, the diffusion coefficient (that is really telling you how a system respond to a perturbation). On the right side we see that D is related to an equilibrium property of the system (the mean square displacements, how atoms microscopically move around).

➤ In the velocity-velocity autocorrelation function you look at the product of 2 velocities at two instances that are apart by time $\tau$. If $\tau$ is very small, the velocity is not going to have changed very much. So, in the limit of small $\tau$, **your velocity at 0 and your velocity at $\tau$ are going to be very similar – we say that there is a lot of correlation.** When you take the product of the velocities, it's going to look a lot like v(0) squared and when things are normalized it could look like 1.

# *Velocity-velocity autocorrelation function*

$$D = \lim_{t' \to \infty} \int_0^{t'} dt'' \left\langle v_x(t' - t'') v_x(0) \right\rangle = \int_0^{\infty} d\tau \left\langle v_x(\tau) v_x(0) \right\rangle$$

Velocity-velocity autocorrelation

➤ As you move away in time, there is going to be no correlation. Your velocity at 0 and your velocity at an instant that is very far away in time it's not going to be correlated and, so, the product of the two velocities can be any number. When you take the ensemble average (the bracket, averaging on all your particles in the system) this is just going to be 0. This is the case since the product of the velocities can have any positive or negative value because there is no correlation between the velocity at 0 and the velocity at a large $\tau$.

➤ So the limit of this velocity-velocity autocorrelation for very large $\tau$ is going to be equal to 0. The limit for very small $\tau$ is going to be equal to 1 (your normalization factor). Of course, there could be some interesting structure at a certain times.

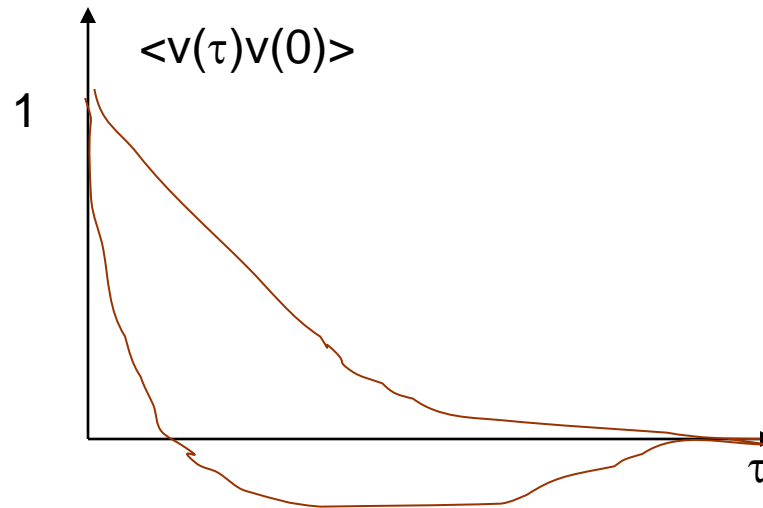# *Velocity-velocity autocorrelation function*

$$D = \lim_{t' \to \infty} \int_0^{t'} dt'' \left\langle v_x(t' - t'') v_x(0) \right\rangle = \int_0^{\infty} d\tau \left\langle v_x(\tau) v_x(0) \right\rangle$$

Velocity-velocity autocorrelation

➢ Lets suppose that our system is actually oscillating (e.g. looking at the crystalline iodines oscillating around from our earlier example).

➢ Suppose that your iodine atom has a certain period of oscillation.  Then there will be a lot of correlation. If you look at your velocity at a time 0 and your velocity at an instant that is roughly equal to a period of oscillation, every period you would have that the velocity has become the same.  In this case, you will see a very definite structure in this correlation function.

➢ If your system is diffusing away as a liquid, as time increases, the correlation becomes 0.  And even if it's a crystal but it's not oscillating perfectly like a harmonic oscillator around the period, when you go to very long time away, you start losing this correlation.  And the velocity-velocity autocorrelation function starts in itself to be 0.

# *Velocity-velocity autocorrelation function*

$\langle v(\tau)v(0) \rangle$



➤ We are plotting here the ensemble average of $v(\tau)$ times $v(0)$. For large $\tau$, it's going to be 0 since there is no correlation between these two velocities. At very small $\tau$, there is maximum correlation. What happens in between depends on the dynamics of the particular system.

# *Green-Kubo relation*

$$D = \lim_{t' \to \infty} \int_0^{t'} dt'' \langle v_x(t' - t'') v_x(0) \rangle = \int_0^{\infty} d\tau \langle v_x(\tau) v_x(0) \rangle$$

➤ The Einstein relation and the Green-Kubo formula relate the integral from 0 to infinity of the velocity-velocity autocorrelation function to the diffusion coefficient.

➤ The velocity-velocity autocorrelation function represents the microscopic fluctuations at equilibrium, how the velocities are correlated, so how the atoms vibrate around.

➤ The equation above provides you with one way of calculating the diffusion coefficient. The other way would be just calculating the derivative with respect to time of the mean square displacements.

$$\frac{\partial}{\partial t} \langle r^2(t) \rangle = 2dD$$

In a liquid we've seen that mean square displacements become linear if you wait enough time with respect to time. **So the diffusion coefficient is also equivalently given by the slope of the mean-squared displacement curve**.

# *Power spectrum*

➢ From the velocity-velocity autocorrelation function you can also obtain what is called the power spectrum.
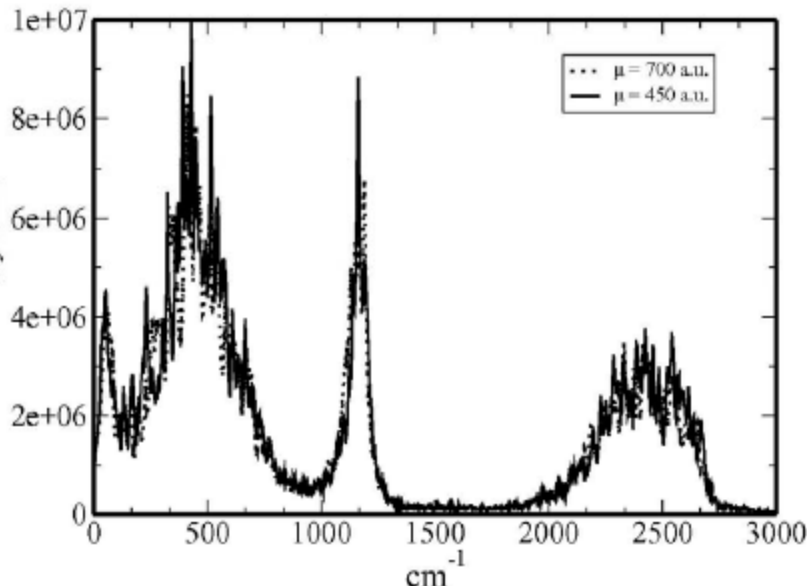


The velocity-velocity autocorrelation function shows periodic features that are related to the typical dynamics of the particles. If you do the Fourier transform of that, the Fourier transform picks up **the typical frequencies of your system.**

On the left you see an example from the MD simulation of water.

➢ You can **figure out what are the typical vibrations in your system**. If an atom is oscillating around an equilibrium position, there is going to be a lot of correlation. If we look at time 0 and if you look after times T, 2T, 3T,.. the velocities are going to be very similar. So in the velocity-velocity autocorrelation function, you will see not only a peak at 0, but also peaks at T, 2T, 3T and so on and they will slowly decay.

# *Power spectrum of Water*
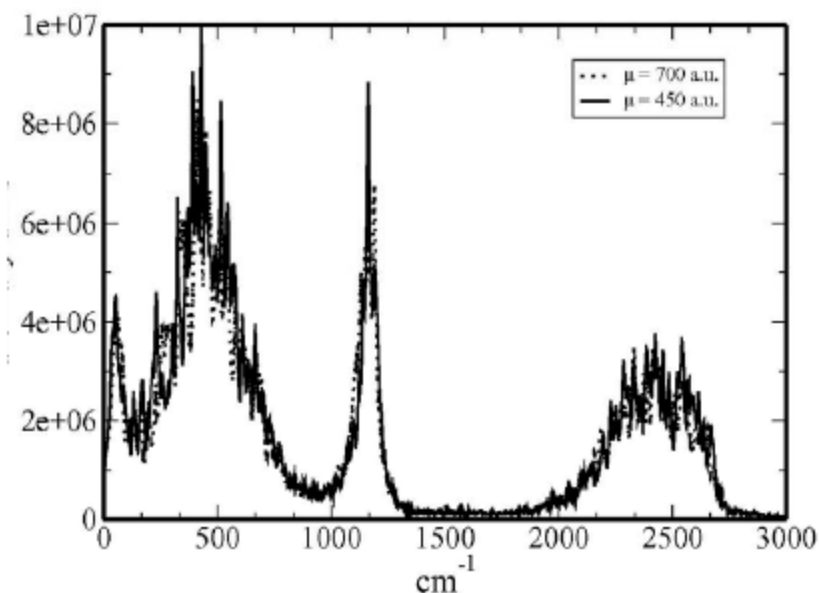


> In liquid water away from freezing, you need 30 to 50 molecules in a unit cell to simulate the infinite system.

> We let the system here evolve and then we calculate at every instant in time t, the product of the velocities. You average that on all the molecules and you have the velocity-velocity autocorrelation function. That as a function of time will show typical peaks that have to do with the frequencies in your system.

> You do the Fourier transform of the velocity-velocity autocorrelation function and you find a vibrational spectrum of your liquid.

> You can identify a very large peak (~2500 cm$^{-1}$) (this is heavy water, Deuterium). This is a very typical set of vibrations that have to do with the stretching mode of the Deuterium-Oxygen distance in the water molecule, so, the modes in which the 2 atoms vibrate one against the other. The other picks would be the optical intramolecular modes.

# *Power spectrum*
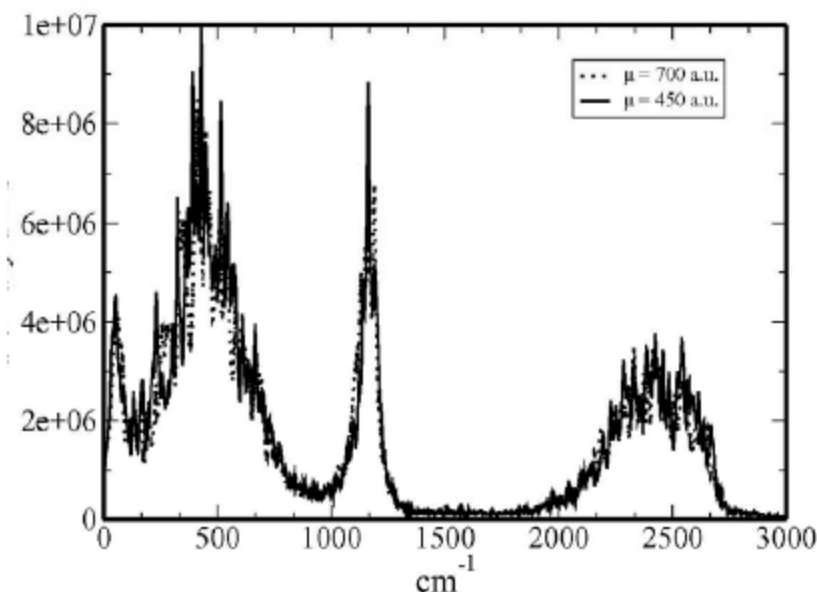


> A lot of spectroscopic properties are correlated with this vibrational density of states. Suppose e.g. that some of these states are infrared active. That is when the atoms move around, they create polarization and a local electric field.

> Then these infrared modes would interact and couple very strongly with electromagnetic radiation. Depending on your frequency of electromagnetic radiation, you would couple very strongly with the appropriate frequencies of your liquid system. This is one of the very important quantities that you might want to extract from a MD simulation.

> Then you see another peak that has to do with the fact that the water molecule acts like scissors and then you find a lots of lower energy modes.

> Just the Fourier transform of the velocity-velocity autocorrelation function gives you the vibrational density of states and the important vibrational systems.

> For a solid this is the vibrational density of states of your phonon modes.

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# *Green-Kubo relations: viscosity, thermal conductivity, etc.*

> **The Green-Kubo general relations make a connection between a macroscopic property (in particular, a response property of the system), to equilibrium fluctuations, something like the velocity-velocity autocorrelation function.**

> ❑ The diffusion coefficient is a response property of the system to a concentration inhomogeneity

> Using Green-Kubo relations you can **find out the shear viscosity of your liquid system** from the instantaneous fluctuations due to the thermal motion in the stress tensor.

> To study infrared adsorption, you can look at the instantaneous fluctuations in the total polarization in your system (microscopic local electric field).

> Electrical or thermal conductivity can be found out from fluctuations in the autocorrelation functions for the electrical charge or thermal carriers in your system, respectively.