**Diffusion in Multicomponent Solids**
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**Lecture 33**
**Theory of Random Walk: Mean Squared Displacement**

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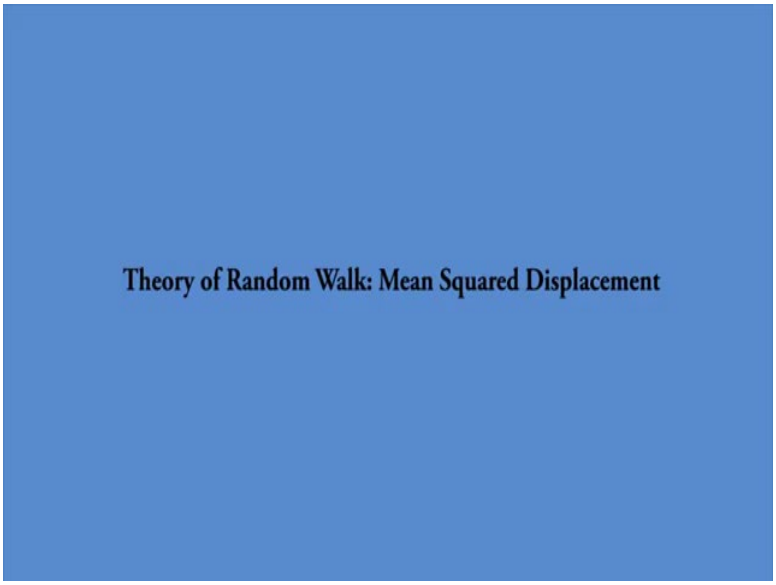


Welcome into the 8th week of the open course on Diffusion in Multicomponent Solids. This is the 33rd lecture in the series. In this lecture, we will discuss the theory of random walk of particles. We will show that root mean squared displacement of a large ensemble of particles, making random walk is proportional to the square root of the number of jumps an average particle has made. So far we have seen the significance and applicability of diffusivity term which is defined as a phenomenological coefficient. In next two classes, we will try to understand the theoretical significance of this term diffusivity. The unit of diffusion coefficient is meter square per second. So, it indicates some kind of rate, specifically, the rate at which the compositional front travels. But why the unit is meter square per second and not meter per second? We will get answer for this question in next two classes.

Fick's Law came into existence in 1855. But it was not until 1905 that the theoretical significance of this term diffusivity was established. It happened when Einstein developed the theory of random walk around 1905. What is random walk to do with diffusion? Let us first try to understand what is random walk. We know at any temperature above 0 Kelvin, atoms or molecules of a substance continuously undergo thermal motions.

In solids, this thermal motion is in the form of vibrations. The atoms vibrate about their mean position continuously and the energy of vibration keeps changing. The way the available energy is distributed among all the atoms keeps changing continuously with time. In liquids and gases, the particles undergo translational motion. So, if you track any one particle it is undergoing a translational motion. It is moving from one position to another until it collides with another particle. After the collision, the particle will change its direction and now would move in new direction. Now this motion will occur again until the particle hits with another particle. Again, upon the collision, it will change its direction and this will continue. So, we say each particle is undergoing a random walk.

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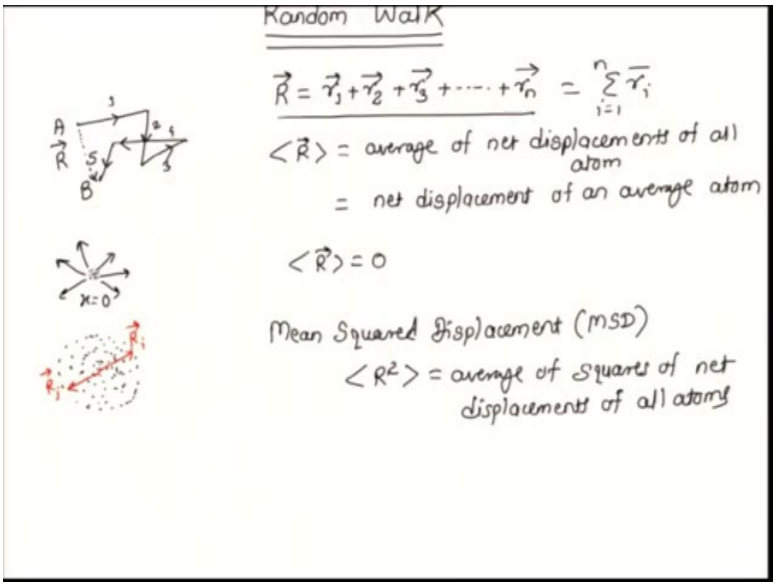


If we track a particle in a liquid or gas, let us say it starts from a position A, it moves in a particular direction until it hits another particle. After the collision, it changes its direction of travel, moves in another direction, until it again hits with another particle. Then it changes its direction and this continues. And in some time $t$, the particle has made some net displacement. After let us say 5 such jumps, the particle has made a net displacement from A to B. Let us call this $\vec{R}$. Now obviously, the net displacement $\overrightarrow{AB}$ is the summation of all the displacement vectors corresponding to these individual jumps from 1 to 5. If a particle makes $n$ jumps and each jump vector is denoted as $\vec{r}_i$, then we can write:

$$\vec{R} = \vec{r}_1 + \vec{r}_2 + \vec{r}_3 \ldots\ldots + \vec{r}_n = \sum_{i=1}^{n} \bar{r}_i$$

Now, if we consider an ensemble of particles, which is located at $x = 0$ initially, each particle will undergo random walk and will make some net displacement in certain amount of time. The particles will randomly move in all directions and each jump of the particle or each jump vector is random, which means each jump is independent of its previous jump in both direction and magnitude. Because of the random walk, this particle distribution will slowly spread in space with time. Now if we want to track, how much this distribution has spread in certain amount of time, what is the right parameter that we should use? One of the option is obviously the average displacement of all the atoms. It is denoted as $\vec{R}$ in triangular bracket:

$$\langle \vec{R} \rangle = average\ of\ net\ displacements\ of\ all\ atoms$$

This is also referred to as net displacement of an average atom. Now if the particles are undergoing truly random walk, then the average net displacement would be 0. If we look at this particle ensemble and if we track the front after certain time, we would see this front is growing. We will see that this distribution is spreading isotropically. That means if you have a particle which has made a net displacement $\overrightarrow{R_i}$, there is almost certain chance that there would be another particle, which has made an equal and opposite net displacement, $\overrightarrow{R_j}$. And they will cancel each other. Since we are dealing with a large number of particles, it would happen that the average net displacement will be 0:

$$\langle \vec{R} \rangle = 0$$

So, obviously the average net displacement of all atoms is not a good parameter to work with. Then, what is the right parameter that we should use? As we will see later, Einstein realized that it is the Mean Squared Displacement or MSD in short. And it will be denoted as:

$$\langle R^2 \rangle = average\ of\ squares\ of\ net\ displacements\ of\ all\ atoms$$

Let us try to find out the expression for Mean Squared Displacement. If we consider any one particle which has undergone $n$ jumps, we have the expression:

$$\vec{R} = \sum_{i=1}^{n} \bar{r}_i$$

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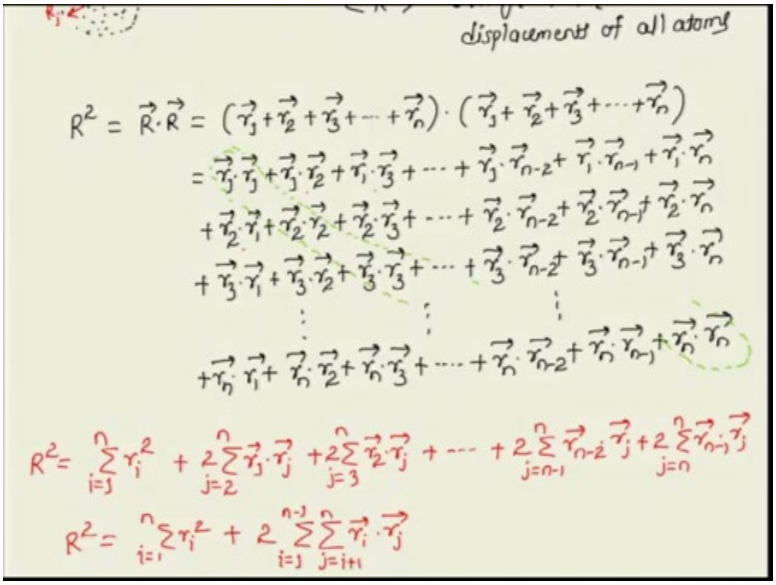


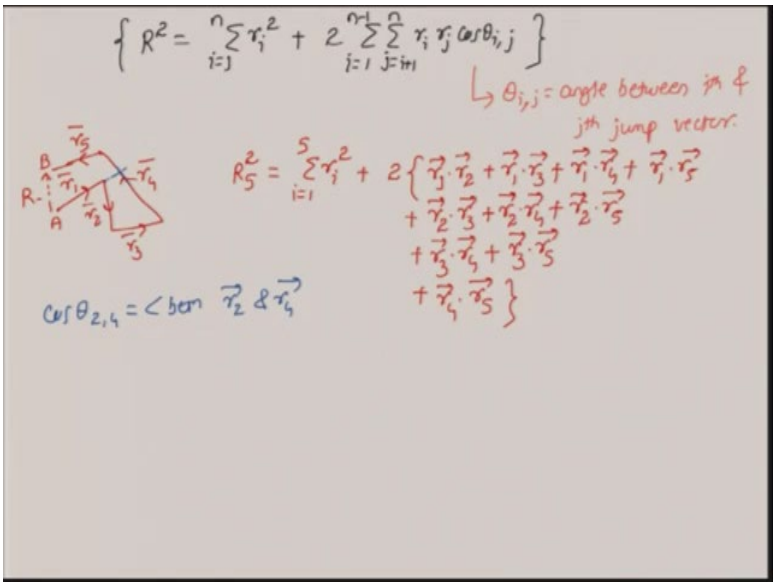


For a particular particle $R^2$ would be:

$$R^2 = \vec{R}.\vec{R}$$

which I can write as:

$$R^2 = \vec{R}.\vec{R} = (\vec{r}_1 + \vec{r}_2 + \vec{r}_3 \ldots\ldots + \vec{r}_n).(\vec{r}_1 + \vec{r}_2 + \vec{r}_3 \ldots\ldots + \vec{r}_n)$$

If we expand this, we get:

$$\begin{aligned} R^2 = {} & (\vec{r}_1.\vec{r}_1 + \vec{r}_1.\vec{r}_2 + \vec{r}_1.\vec{r}_3 + \cdots\ldots\ldots + \vec{r}_1.\vec{r}_{n-2} + \vec{r}_1.\vec{r}_{n-1} + \vec{r}_1.\vec{r}_n) \\ & + (\vec{r}_2.\vec{r}_1 + \vec{r}_2.\vec{r}_2 + \vec{r}_2.\vec{r}_3 + \cdots\ldots\ldots + \vec{r}_2.\vec{r}_{n-2} + \vec{r}_2.\vec{r}_{n-1} + \vec{r}_2.\vec{r}_n) \\ & + (\vec{r}_3.\vec{r}_1 + \vec{r}_3.\vec{r}_2 + \vec{r}_3.\vec{r}_3 + \cdots\ldots\ldots + \vec{r}_3.\vec{r}_{n-2} + \vec{r}_3.\vec{r}_{n-1} + \vec{r}_3.\vec{r}_n) \\ & + \cdots\ldots\ldots + (\vec{r}_n.\vec{r}_1 + \vec{r}_n.\vec{r}_2 + \vec{r}_n.\vec{r}_3 + \cdots\ldots\ldots + \vec{r}_n.\vec{r}_{n-2} + \vec{r}_n.\vec{r}_{n-1} + \vec{r}_n.\vec{r}_n) \end{aligned}$$

Now we can simplify this expression by writing it in terms of summations. we can start with the diagonal terms. If we take all the diagonal terms, we see they are of the form $\vec{r}_i.\vec{r}_i$. Now let us consider the non-diagonal terms. We see this is a symmetric matrix about the diagonal. So the off-diagonal terms are similar. So, we can consider one side of the diagonal and just double it.

So, we can write:

$$R^2 = \sum_{i=1}^{n} r_i^2 + 2\sum_{j=2}^{n} r_1 . r_j + 2\sum_{j=3}^{n} r_2 . r_j + \cdots \ldots . + 2\sum_{j=n-1}^{n} r_{n-2} . r_j + 2\sum_{j=n}^{n} r_{n-1} . r_j$$

Now for further simplification, if you write in terms of double summation:

$$R^2 = \sum_{i=1}^{n} r_i^2 + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \vec{r}_i . \vec{r}_j$$

We can write expression for $R^2$ as:

$$R^2 = \sum_{i=1}^{n} r_i^2 + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} r_i\, r_j \cos\theta_{i,j}$$

$r_i, r_j$ are the magnitudes of the $i^{th}$ and $j^{th}$ jump vectors and:

$$\theta_{i,j} = angle\ between\ i^{th}\ and\ j^{th}\ jump\ vector$$

If you look at the above summation, we are considering each jump vector and taking its dot product with every jump vector that occurred after it. If for example, a particle making let us say 5 number of jumps, so:

$$R_5^2 = \sum_{i=1}^{5} r_i^2 + 2\{\vec{r}_1.\vec{r}_2 + \vec{r}_1.\vec{r}_3 + \vec{r}_1.\vec{r}_4 + \vec{r}_1.\vec{r}_5 + \vec{r}_2.\vec{r}_3 + \vec{r}_2.\vec{r}_4 + \vec{r}_2.\vec{r}_5 + \vec{r}_3.\vec{r}_4 + \vec{r}_3.\vec{r}_5 + \vec{r}_4.\vec{r}_5\}$$

as we have to take dot product of every jump vector with the jump vector that occurred after it. Now we need to know angle between each jump vector and every other jump vector that occurred after it. For example:

$$\theta_{2,4} = angle\ between\ \vec{r}_2\ and\ \vec{r}_4$$

Now, we have to evaluate the cosine of the angle $\theta_{2,4}$. We have to do this for all the pairs of the jump vectors. If we consider the case of solid, this expression becomes a little bit simpler. And the reason being, in solids all the jump lengths are equal.

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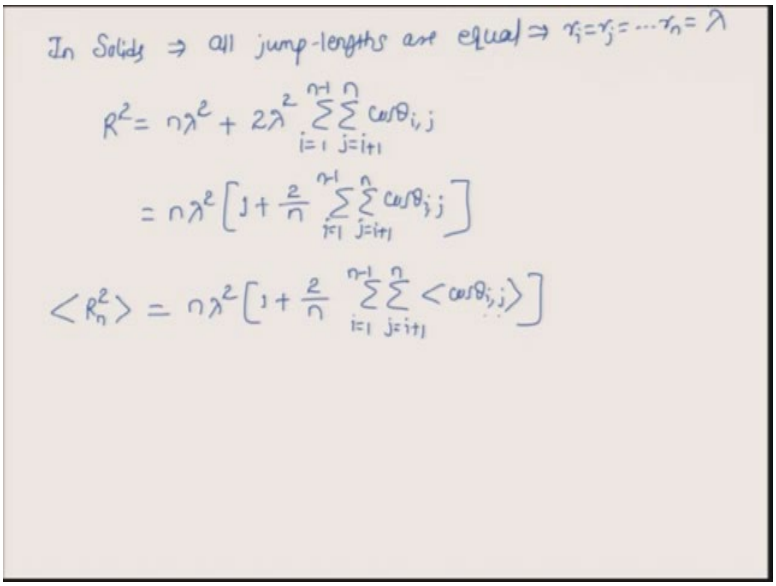


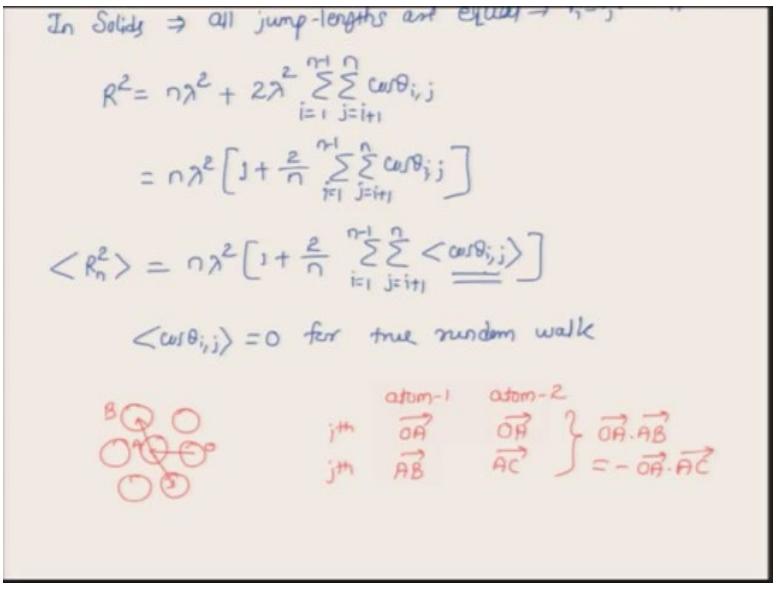


That is:

$$r_i = r_j = \cdots r_n = \lambda$$

If we write the expression for solids $R^2$ will be:

$$R^2 = n\lambda^2 + 2\lambda^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \cos\theta_{i,j}$$

Since all jump vectors are same, we have $\lambda^2$ term. And that simplifies this as:

$$R^2 = n\lambda^2 + 2\lambda^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \cos\theta_{i,j} = n\lambda^2 \left[1 + \frac{2}{n} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \cos\theta_{i,j}\right]$$

Now this is for one particle. We need the average of square of net displacements of all the particles. So, we need to evaluate $\langle R_n^2 \rangle$. Here subscript $n$ denotes that each particle has undergone $n$ jumps. If we try to evaluate this, we will get the expression as:

$$\langle R_n^2 \rangle = n\lambda^2 \left[1 + \frac{2}{n} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \cos\theta_{i,j} \rangle\right]$$

Now, let us try to understand what is this average $\langle \cos\theta_{i,j} \rangle$? So, we consider each pair of jump $i$ and $j$, we consider this pair for each atom. Evaluate $\cos\theta_{i,j}$ for each atom and take the average of it. That is this average $\langle \cos\theta_{i,j} \rangle$ and then we sum it over all $i$ and $j$. If I consider $\vec{r}_1$ and $\vec{r}_5$, I need to know $\theta_{1,5}$ for one atom. Then I evaluate $\cos\theta_{1,5}$ for all the atoms and then take the average. That gives me $\langle \cos\theta_{1,5} \rangle$ and we do this for every pair of the atom.

Now, this can further be simplified. If we are considering a true random walk, that is the atom is free to jump randomly in the solid then:

$$\langle \cos\theta_{i,j} \rangle = 0 \quad for\ true\ random\ walk$$

Why? Because here we are considering a large number of atoms. If we consider a pair of particular jumps $i$ and $j$, for every $\vec{r}_i$ and $\vec{r}_j$ that 1 atom undergoes, there is almost a certain chance that you will find another atom, which has made $i^{th}$ and $j^{th}$ jump such that its $\vec{r}_i.\vec{r}_j$ is exactly equal and opposite to the first atom. And they will cancel out each other since we are considering large number of atoms and a truly random walk problem.

For example, let us consider the jumps on (1 1 1) plane of an FCC crystal. Let us consider 2 atoms, atom-1 and atom-2. Then:

| | $atom-1$ | $atom-2$ |
|---|---|---|
| $\{i^{th}$ | $\overrightarrow{OA}$ | $\overrightarrow{OA}\}$ |
| $\{j^{th}$ | $\overrightarrow{AB}$ | $\overrightarrow{AC}\}$ |

Atom-1 makes a jump from site O to A as $i^{th}$ jump, which is $\overrightarrow{OA}$ and $j^{th}$ jump is to B, let us call this $\overrightarrow{AB}$. For another atom, $i^{th}$ jump vector is $\overrightarrow{OA}$ and another jump vector is $\overrightarrow{AC}$. And we see that:

$$\overrightarrow{OA}.\overrightarrow{AB} = -\overrightarrow{OA}.\overrightarrow{AC}$$

In solids, angles between the jumps are restricted because the coordination shell is fixed in a solid. The atoms can jump only on the particular sites and in FCC case, for any pair of $i^{th}$ and $j^{th}$ jump, the average for true random walk will be:

$$\langle \cos \theta_{i,j} \rangle = 0$$

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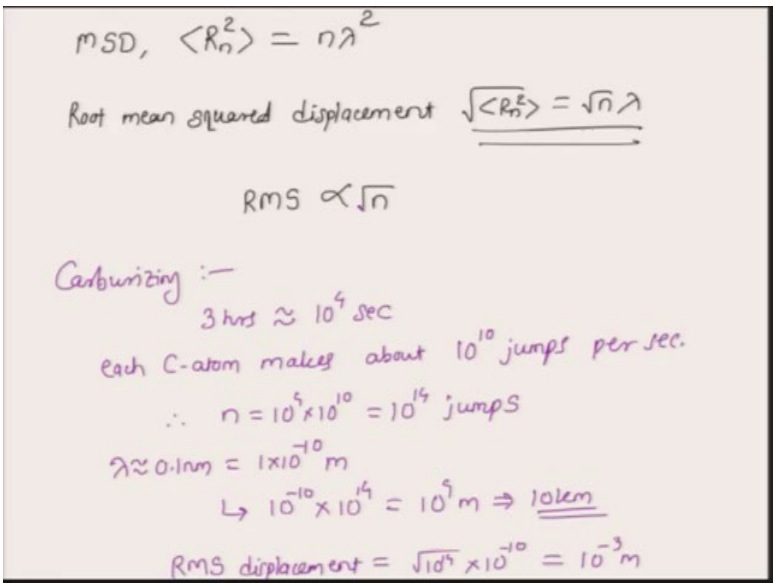


We can very simply write this expression:

$$MSD, \quad \langle R_n^2 \rangle = n\lambda^2$$

Or if we write root mean square:

$$Root\ mean\ squared\ displacement, \quad \sqrt{\langle R_n^2 \rangle} = \sqrt{n}\lambda$$

What it tells me is that root mean square displacement is proportional to square root of the number of jumps and not to the number of jumps:

$$RMS \propto \sqrt{n}$$

And this is important because if we consider an individual particle making $n$ jumps, it might have travelled a large total distance but the net displacement will be much lower, because the net displacement will be proportional to $\sqrt{n}$.

Here, we can consider a good example, which is given by Paul Shewmon in his book. If we consider the problem of carburizing, typically the carburizing times employed are of few hours to obtain a case depth of few 100s of microns. Let us consider 3 hours of carburizing time which is roughly:

$$3\ hrs \approx 10^4\ sec$$

and each carbon atom makes about $10^{10}$ jumps per second. In 3 hours, total number of jumps an average carbon atom will make:

$$\therefore\ n = 10^4 \times 10^{10} = 10^{14}\ jumps$$

Now, the jump distance in case of carbon is around 0.1 nanometre, which is:

$$\lambda \approx 0.1\ nm = 1 \times 10^{-10}\ m$$

If we just wrongly consider that root mean squared displacement would be proportional to $n$, then the distance travelled in 3 hours by an average atom would be:

$$10^{-10} \times 10^{14} = 10^4\ m = 10\ Km$$

But typically, we see the case depth that we get in 3 hours is about 600-700 $\mu m$. Although the case depth is not the total distance or the total penetration of carbon atoms in the steel. The total penetration would be larger than that, about 1 mm or so which can easily be obtained because the root mean squared displacement is proportional to $\sqrt{n}$.

We can write the RMS displacement of an average carbon atom as:

$$RMS\ displacement = \sqrt{10^{14}} \times 10^{-10} = 10^{-3} m$$

It is around 1 millimetre which is consistent with what we observe in practice.

So, we got an important result that the root mean squared displacement is proportional to square root of the number of jumps that an average atom has made. Okay, we will stop here, thank you.