Mobility of atoms and diffusion. Einstein relation.

In MD simulation we can describe the mobility of atoms through the mean square displacement that can be calculated as

$$\text{MSD} \equiv \left\langle \Delta \vec{r}(t)^2 \right\rangle \equiv \frac{1}{N} \sum_{i=1}^{N} (\vec{r}_i(t) - \vec{r}_i(0))^2$$

The MSD contains information on the diffusion coefficient D,

$$\text{MSD} = \left\langle \Delta\vec{r}(t)^2 \right\rangle = A + 6Dt + \text{fluctuations}$$

- This expression is called Einstein relation since it was first derived by Albert Einstein in his Ph.D. thesis in 1905 (see note below)

- <u>This expression relates macroscopic transport coefficient D with microscopic information on the mean square distance of molecular migration</u>

- The 6 in this formula becomes 4 for a two-dimensional system and 2 for a one-dimensional system (see next page)

- This equation is suitable for calculation of D in MD simulation only for sufficiently high temperatures, when $D > 10^{12}$ m^2/s

- Time t cannot be too large for a finite system (D drops to 0 when MSD approaches the size of the system)

- For periodic boundaries "true" atomic displacements should be used

- Derivation of this equation is given on pages 78-79 of the textbook by D. Frenkel and B. Smit

Historic note: Before Albert Einstein turned his attention to fundamental questions of relative velocity and acceleration (the Special and General Theories of Relativity), he published a series of papers on diffusion, viscosity, and the photoelectric effect. His papers on diffusion came from his Ph. D. thesis. Einstein's contributions were 1. to propose that Brownian motion of particles was basically the same process as diffusion; 2. a formula for the average distance moved in a given time during Brownian motion; 3. a formula for the diffusion coefficient in terms of the radius of the diffusing particles and other known parameters. Thus, Einstein connected the macroscopic process of diffusion with the microscopic concept of thermal motion of individual molecules. Not bad for a Ph. D. thesis!

Derivation of Einstein relation for 1D case

Let's consider diffusion of particles that are initially concentrated at the origin of our coordination frame, $C(x,0) = \delta(x)$ - Dirac delta function

Diffusion equation: $\dfrac{\partial C(x,t)}{\partial t} = D\,\dfrac{\partial^2 C(x,t)}{\partial x^2}$

Solution: $C(x,t) = \dfrac{1}{2\sqrt{\pi Dt}}\exp\left(-\dfrac{x^2}{4Dt}\right)$

Let's multiply the diffusion equation by x^2 and integrate over space:

$$\dfrac{\partial}{\partial t}\underbrace{\int x^2 C(x,t)dx}_{\langle x^2(t)\rangle} = D\int x^2\,\dfrac{\partial^2 C(x,t)}{\partial x^2}dx$$

$$\dfrac{\partial\langle x^2(t)\rangle}{\partial t} = D\int x^2\,\dfrac{\partial^2 C(x,t)}{\partial x^2}dx = D\int \dfrac{\partial}{\partial x}\left(x^2\,\dfrac{\partial C(x,t)}{\partial x}\right)dx\;-$$

$$-D\int \dfrac{\partial x^2}{\partial x}\,\dfrac{\partial C(x,t)}{\partial x}dx = Dx^2\,\dfrac{\partial C(x,t)}{\partial x}\Big|_{-\infty}^{+\infty} - 2D\int x\,\dfrac{\partial C(x,t)}{\partial x}dx =$$

$$= 0 - 2D\int \dfrac{\partial}{\partial x}\big(xC(x,t)\big)dx + 2D\int \dfrac{\partial x}{\partial x}C(x,t)dx =$$

$$= -2DxC(x,t)\Big|_{-\infty}^{+\infty} + 2D\int C(x,t)dx = 2D$$

$$\langle x^2(t)\rangle = 2Dt + A \qquad \text{for 1D diffusion}$$

Derivation of Einstein relation

Let's consider diffusion of particles that are initially concentrated at the origin of our coordination frame, $C(\vec{r},0) = \delta(\vec{r})$ - Dirac delta function

Diffusion equation: $\dfrac{\partial C(\vec{r},t)}{\partial t} = D\nabla^2 C(\vec{r},t)$

Solution: $C(\vec{r},t) = \dfrac{1}{(2\pi Dt)^{d/2}}\exp\left(-\dfrac{r^2}{2Dt}\right)$

Let's multiply the diffusion equation by r^2 and integrate over space:

$$\frac{\partial}{\partial t}\underbrace{\int r^2 C(\vec{r},t)d\vec{r}}_{\langle r^2(t)\rangle} = D\int r^2\nabla^2 C(\vec{r},t)d\vec{r}$$

$$\frac{\partial\langle r^2(t)\rangle}{\partial t} = D\int r^2\nabla^2 C(\vec{r},t)d\vec{r} = D\int\vec{\nabla}\cdot\left(r^2\vec{\nabla}C(\vec{r},t)\right)d\vec{r} -$$

$$-D\int\vec{\nabla}r^2\cdot\vec{\nabla}C(\vec{r},t)d\vec{r} = D\int r^2\vec{\nabla}C(\vec{r},t)d\vec{S} - 2D\int\vec{r}\cdot\vec{\nabla}C(\vec{r},t)d\vec{r} =$$

$$= 0 - 2D\int\vec{\nabla}\cdot\left(\vec{r}C(\vec{r},t)\right)d\vec{r} + 2D\int\left(\vec{\nabla}\cdot\vec{r}\right)C(\vec{r},t)d\vec{r} =$$

$$= -2D\int\vec{r}C(\vec{r},t)d\vec{S} + 2dD\underbrace{\int C(\vec{r},t)d\vec{r}}_{=1} = 2dD$$

$$\langle r^2(t)\rangle = 2dDt + A \quad \text{for diffusion in d-dimensional space}$$

Review of calculus used in the previous page

Gradient:
$$\vec{\nabla} \equiv \frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z}$$

Laplacian:
$$\nabla^2 \equiv \vec{\nabla} \cdot \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Gradient of a scalar function:
$$\vec{\nabla}\Phi(\vec{r}) \equiv \frac{\partial\Phi}{\partial x}\hat{x} + \frac{\partial\Phi}{\partial y}\hat{y} + \frac{\partial\Phi}{\partial z}\hat{z}$$

Divergence of a vector function:
$$\vec{\nabla} \cdot \vec{F}(\vec{r}) \equiv \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}$$
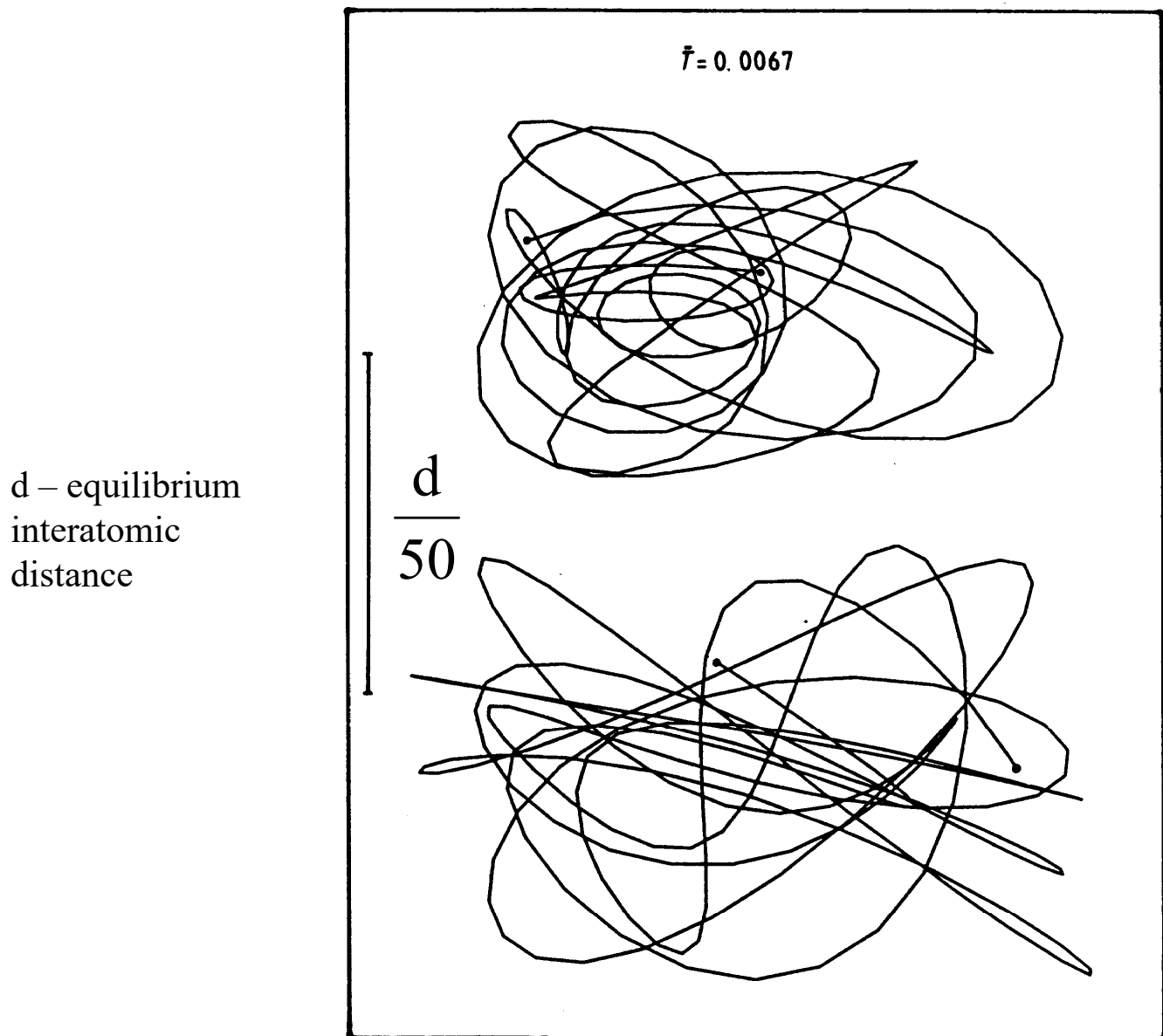
$$\vec{\nabla} \cdot \left(\Phi(\vec{r})\vec{F}(\vec{r})\right) = \Phi(\vec{r})\left(\vec{\nabla} \cdot \vec{F}(\vec{r})\right) + \left(\left(\vec{\nabla}\Phi(\vec{r})\right) \cdot \vec{F}(\vec{r})\right)$$

The divergence theorem:
$$\int_V \vec{\nabla} \cdot \vec{F}(\vec{r})\,d\vec{r} = \int_S \vec{F}(\vec{r})\,d\vec{S}$$

L'Hopital's rule: if lim g(x)/f(x) result in the indeterminate form 0/0 or inf/inf, then
$$\lim \frac{g(x)}{f(x)} = \lim \frac{dg/dx}{df/dx}$$

Mobility of atoms and diffusion (I)

$\bar{T} = 0.0067$

d – equilibrium
interatomic
distance

$\dfrac{d}{50}$

Atomic paths of two atoms in FCC lattice at temperature below the melting temperature. Figures are from MD simulations by E. H. Brandt, J. Phys: Condens. Matter **1**, 10002-10014 (1989).

Can we use the Einstein relation to calculate the Diffusion coefficient from these atomic trajectories?

Mobility of atoms and diffusion (II)

d – equilibrium interatomic distance
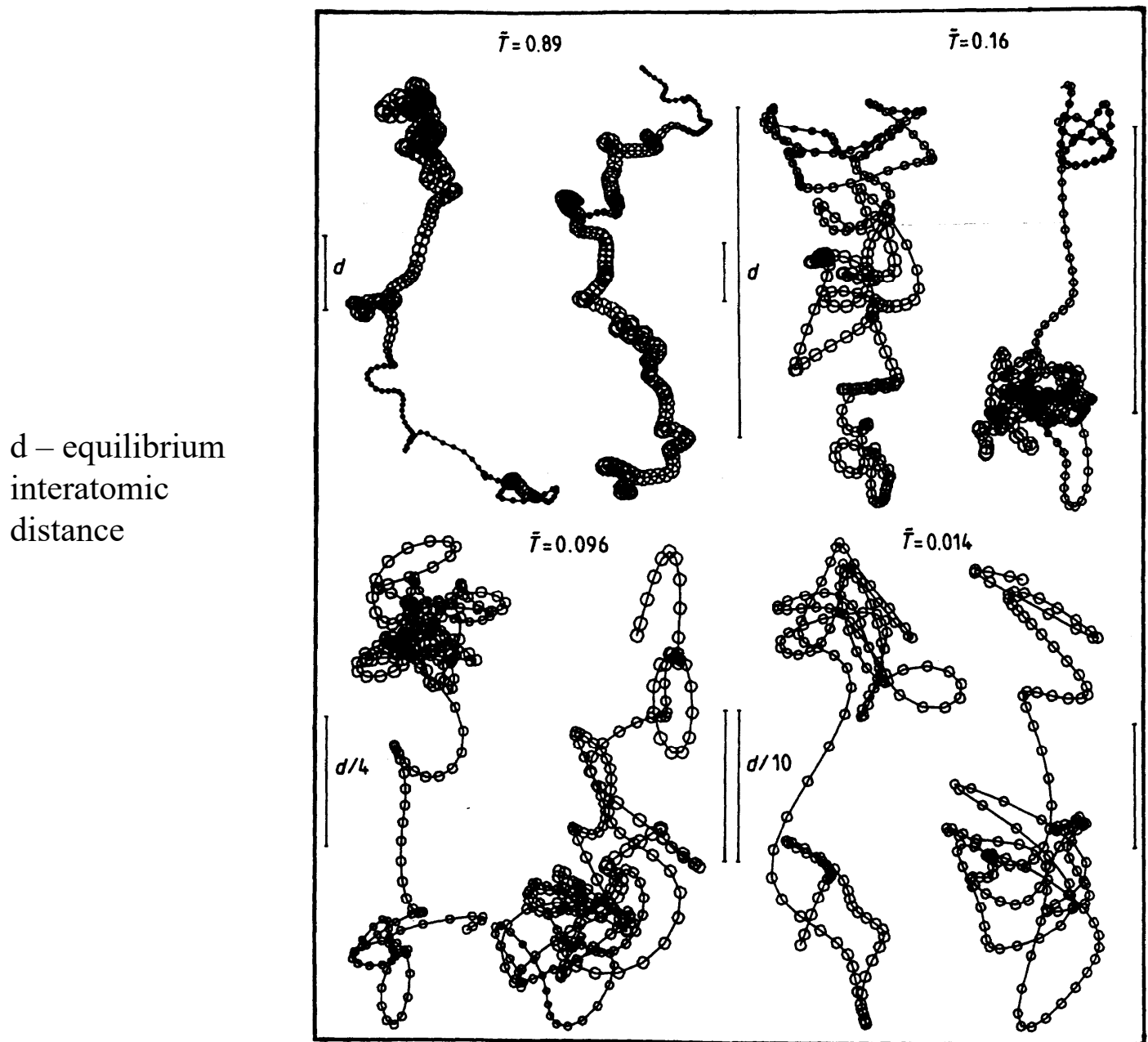
Atomic paths of two atoms in amorphous and liquid systems. Figures are from molecular dynamics simulations by E. H. Brandt, J. Phys: Condens. Matter 1, 10002-10014 (1989). Two longest atomic paths for each simulation are shown.

Can we use the Einstein relation to calculate the Diffusion coefficient from these atomic trajectories?

Using Einstein relation. Example.
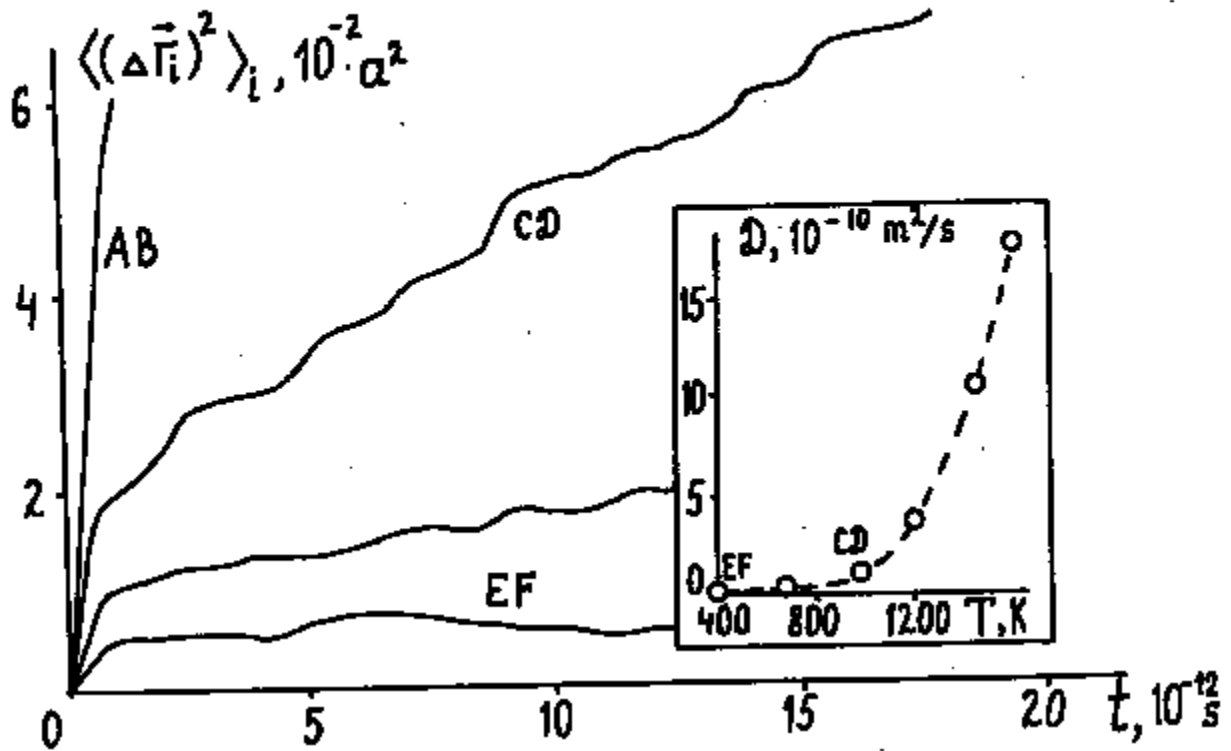
Changes in atomic mobility during solidification from the melt.
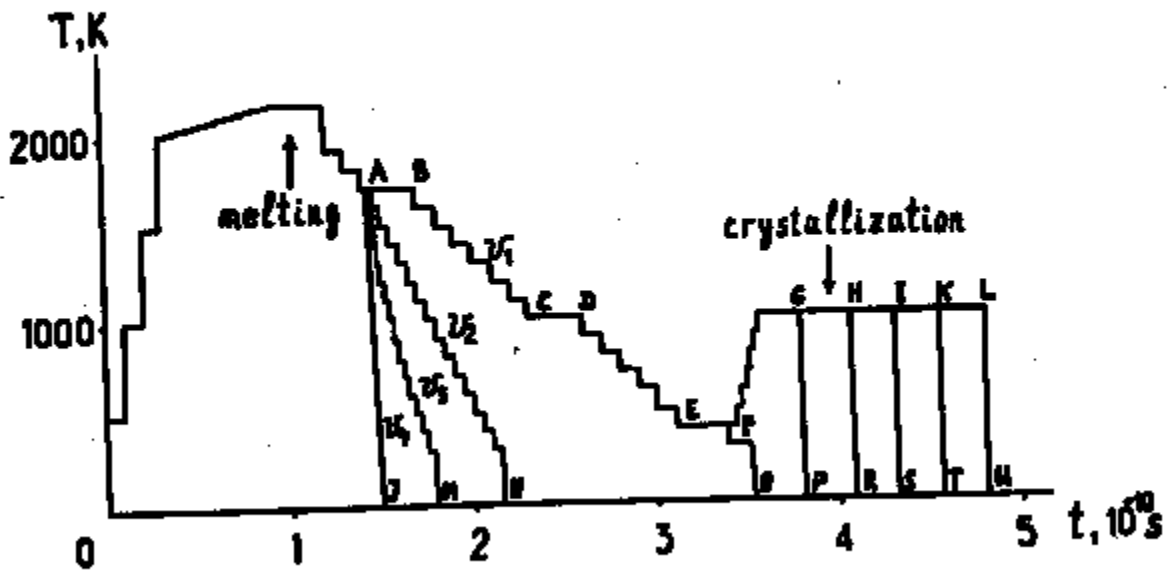
$$\left\langle \Delta \vec{r}(t)^2 \right\rangle = A + 6Dt + fluctuations$$

Green-Kubo formula for diffusion coefficient

An alternative way to define D in MD simulation is through Velocity Autocorrelation Function (Green-Kubo expression):

$$D = \frac{1}{3}\int_0^\infty \langle \vec{v}(t) \cdot \vec{v}(0) \rangle dt = \frac{1}{3N}\int_0^\infty \sum_{i=1}^N (\vec{v}_i(t) \cdot \vec{v}_i(0)) dt$$

- For reliable calculation of D trajectories should be computed for as long as the velocities remain correlated

- Green-Kubo and Einstein expressions for D are equivalent

- We will discuss the meaning of the Velocity Autocorrelation Function later

- Derivation of this equation is given on page 80 of the textbook by D. Frenkel and B. Smit

- To get most from your MD trajectories you can use averaging over starting times.

Temperature dependence of diffusion

Assuming Arrhenius behavior for the jump-frequency one can extract a vacancy migration energy or an average activation energy for atomic migration in a disordered system,

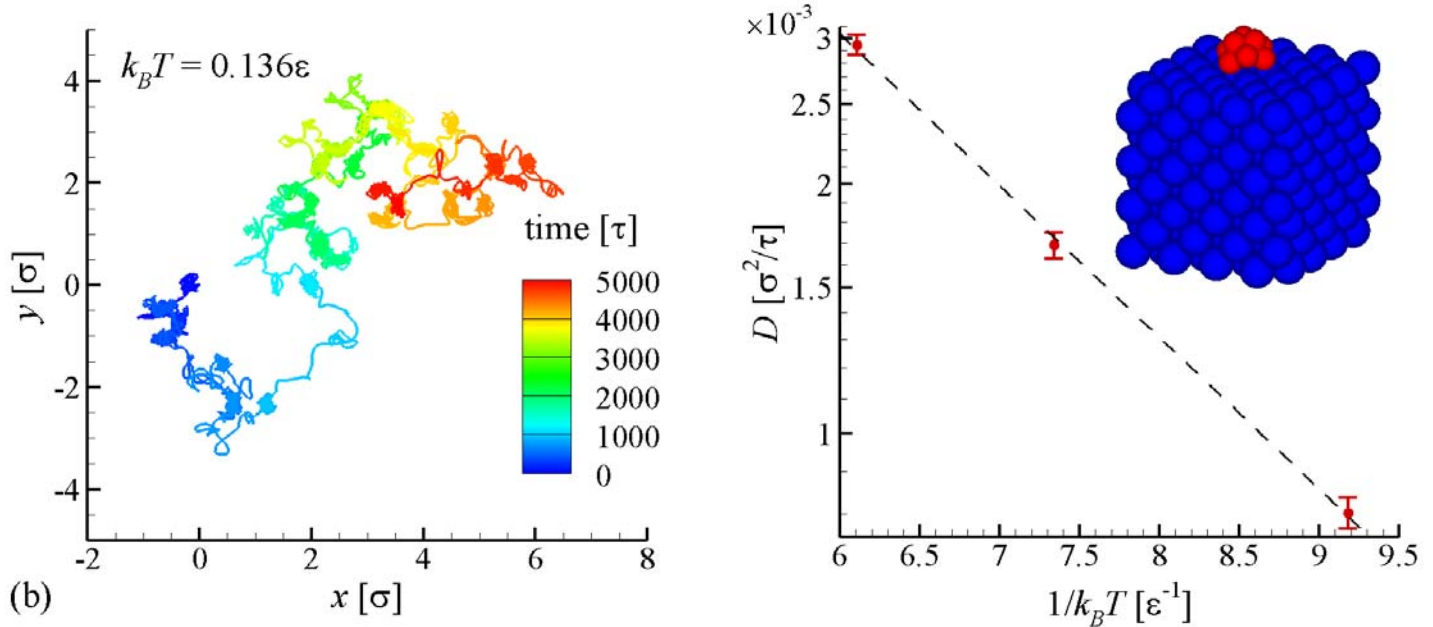$$D(T) = D_0 \exp\left(-\frac{E_a}{k_B T}\right)$$
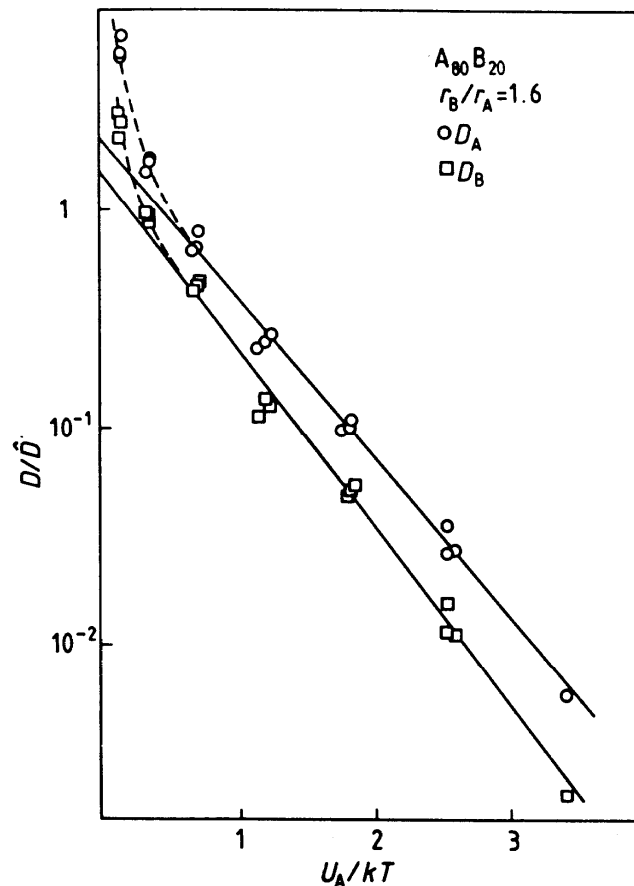
Arrhenius plot for an amorphous alloy, by E. H. Brandt,
J. Phys.:Condens. Matter **1**, 10002-10014 (1989).

Note the deviation of the diffusivities from the Arrhenius behavior at high temperatures, when $k_B T$ becomes comparable or larger than the activation energies. This indicates a change in the mechanism of atomic mobility (change in E_a, collective motions..?).

Temperature dependence of diffusion

Diffusion of a cluster of 10 atoms on a substrate.

Shugaev *et al.*, PRB **91**, 235450, 2015].

(b)

$$D(T) = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \implies E_a = 0.421\varepsilon$$

Lennard-Jones potential with parameters σ and ε used for the substrate A cutoff function defined in [Phys. Rev. A **8**, 1504, 1973] is applied at 3σ

LJ parameters for atoms in the cluster are $\sigma_{cc} = 0.60\sigma$ and $\varepsilon_{cc} = 3.72\varepsilon$

LJ parameters for cluster-substrate interactions are $\sigma_{cs} = \sigma$ and $\varepsilon_{cs} = 0.5\varepsilon$
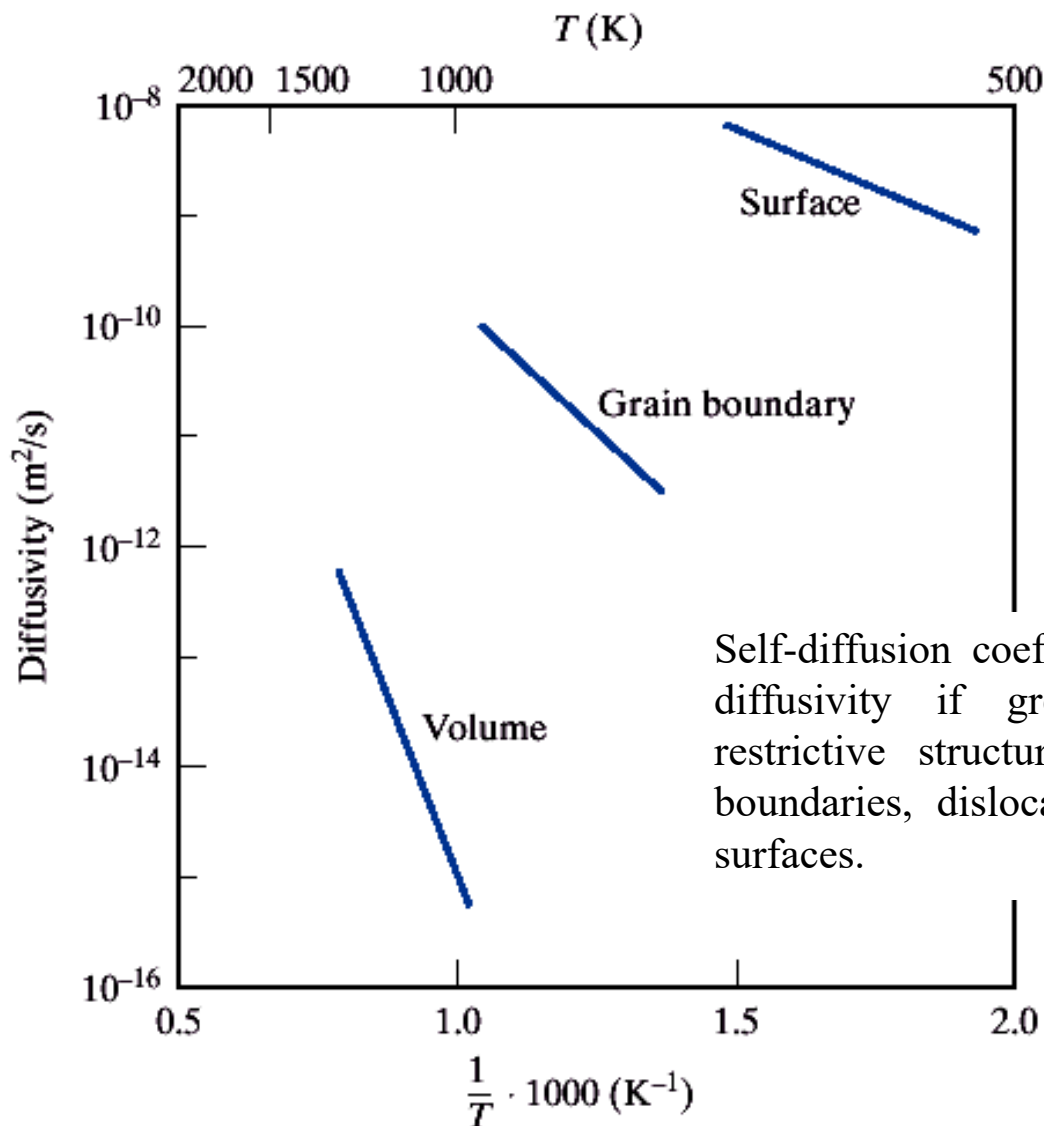
The mass of an atom in a cluster is $m_c = 1.74m$, where m is the mass of an atom in the substrate.

Temperature dependence of diffusion: Fast diffusion paths

Diffusion coefficient along a defect (e.g. grain boundary) can also be described by an Arrhenius equation,

$$D^{G.B.} = D_0^{G.B.} \exp\left(-\frac{\varepsilon_{G.B.}^m}{k_B T}\right)$$

with the activation energy for grain boundary diffusion significantly lower than the one for the bulk.   However, the effective cross-sectional area of the boundaries is only a small fraction of the total area of the bulk (an effective thickness of a grain boundary is ~0.5 nm). The grain boundary diffusion is less sensitive to the temperature change – becomes important at low T.

Self-diffusion coefficients for Ag. The diffusivity if greater through less restrictive structural regions – grain boundaries, dislocation cores, external surfaces.

Partial diffusivities. Diffusion in heterogeneous systems.

Partial diffusivities in multicomponent systems can be calculated by averaging over atoms of one type only.

Heterogeneous diffusion. In calculation of the mean square displacement one can average not over all the atoms, but over a certain subclass. For example, the plots below show the difference between atomic mobility in the bulk crystal and in the grain boundary region.
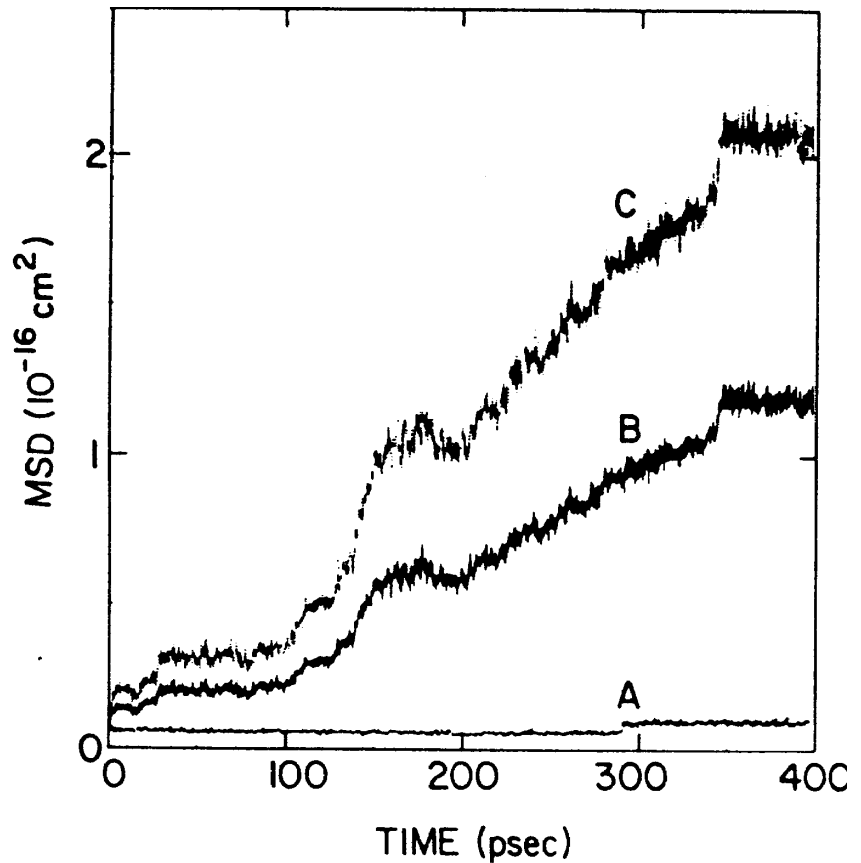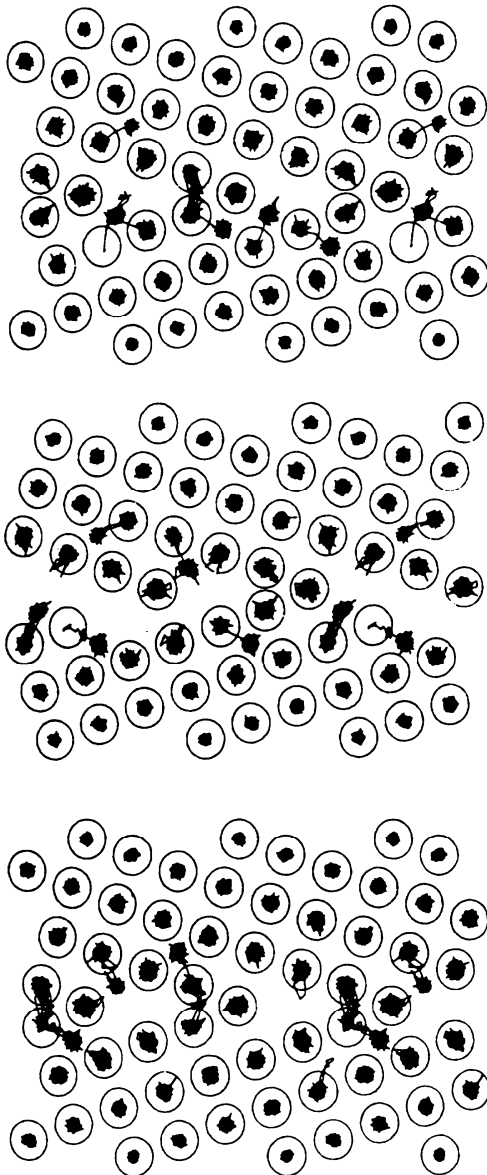

Mean-square displacement of all atoms in the system (B), atoms in the grain boundary region (C), and bulk region of the system (A).

The plots are from the computer simulation by T. Kwok, P. S. Ho, and S. Yip. Initial atomic positions are shown by the circles, trajectories of atoms are shown by lines. We can see the difference between atomic mobility in the bulk crystal and in the grain boundary region.

Estimation of the diffusion coefficient from the jump-frequency information

If diffusion proceeds through vacancy migration, then one can obtain a diffusion coefficient from the jump-frequency information. Assuming Arrhenius behavior for the jump-frequency (R) one can extract a vacancy migration energy (E^m).
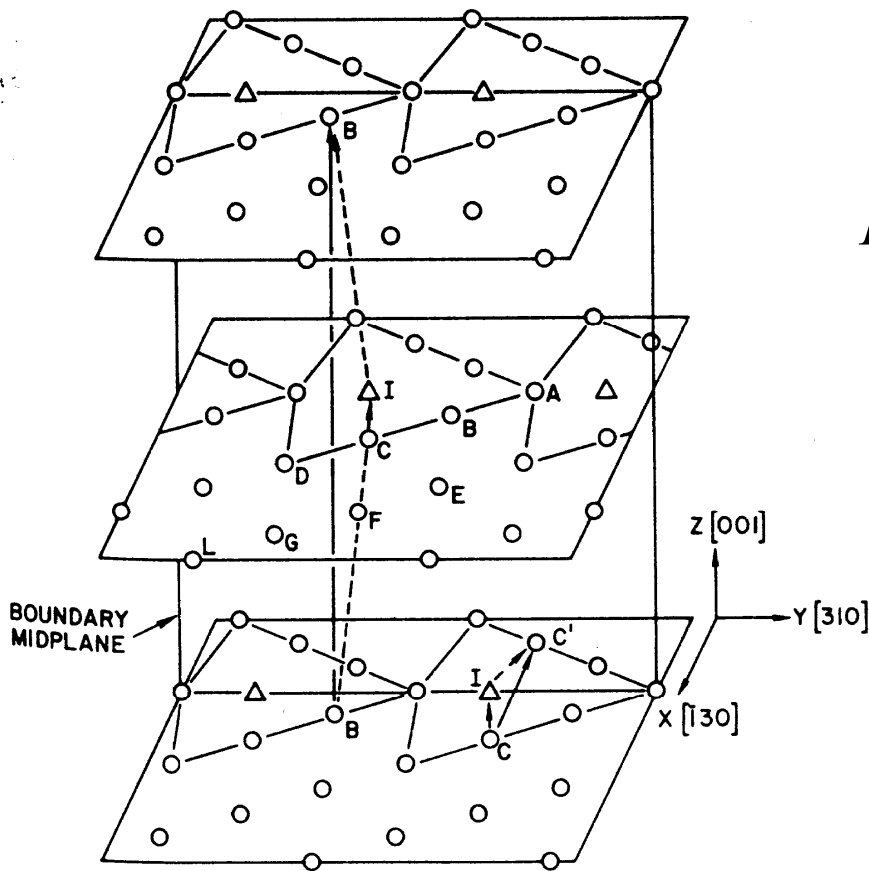
$$R_v = R_0 \exp\left(-\frac{E_v^m}{k_B T}\right)$$

$$D_v \sim a^2 N_v R_v$$

T. Kwok, P. S. Ho, and S. Yip, MD studies of grain-boundary diffusion, *Phys. Rev. B* **29**, 5354 (1984).

R_v - the effective vacancy jump frequency

R_0 - pre-exponential factor ~ effective coordination number × attempt frequency

N_v - equilibrium vacancy concentration that is ~ exp($-E_v^f$/kT) where E_v^f is the effective vacancy formation energy

a^2 - effective squared jump distance
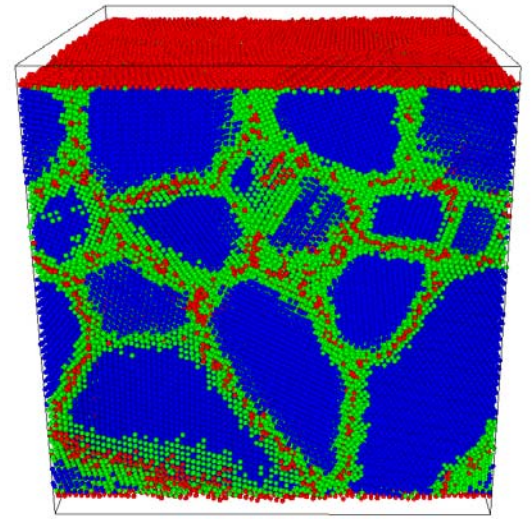
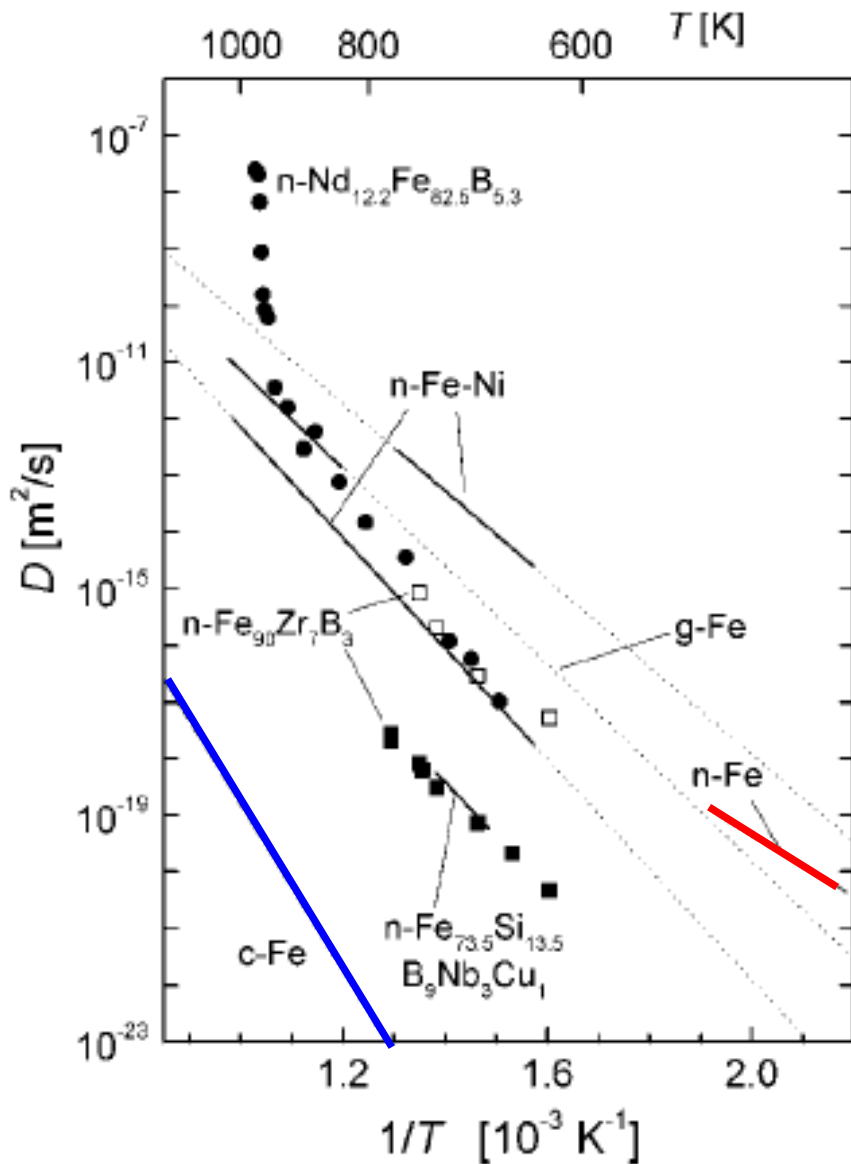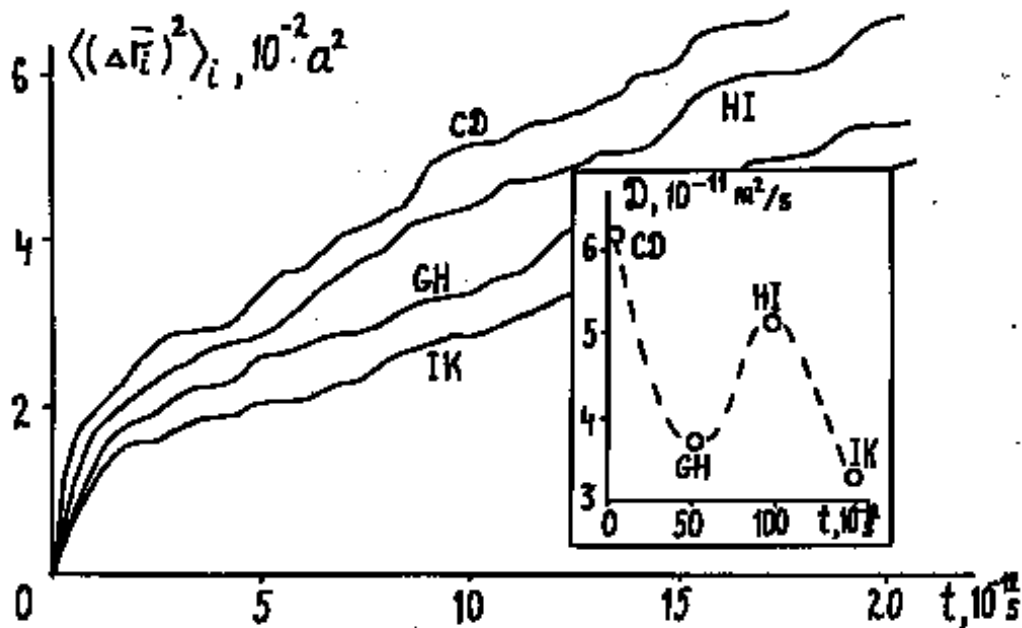# Diffusion in nanocrystalline materials: Examples

image by Zhibin Lin et al.
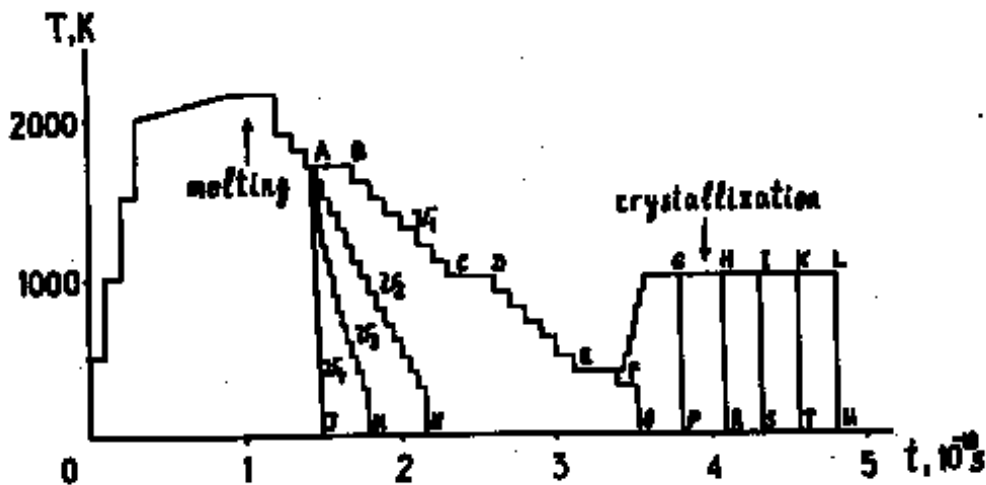
J. Phys. Chem. C 114, 5686, 2010

Arrhenius plots for ^{59}Fe diffusivities in nanocrystalline Fe and other alloys compared to the crystalline Fe (ferrite).
[Wurschum et al. Adv. Eng. Mat. **5**, 365, 2003]

Spatially heterogeneous mobility of atoms. Example.

Changes in atomic mobility during crystallization of amorphous metal.

Atomic mobility is much more active at the front of crystallization. D is not really a diffusion coefficient in statistical thermodynamics sense, but rather a quantity that reflects **an average mobility** in this material undergoing phase transformation.