

3.21 Kinetics of Materials—Spring 2006

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Lecture 11: Diffusion Resulting from Discrete Jumps.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 7.2

Key Concepts

- If a particle moves by a series of displacements, each of which is independent of the one preceding it, the particle moves by a *random walk*. In crystals, random walks are confined to specific sites in the crystal, jumps are confined to a specific set of directions, and jumps have specific jump lengths. The mean square displacement in a random walk is given by  $\langle R^2 \rangle = N_\tau \langle r^2 \rangle$  and the double-sum term in *KoM* Eq. 7.31 vanishes.
- *KoM* Section 7.2.2 presents a random-walk model for diffusion on a one-dimensional lattice that provides an elegant way to connect microscopic jumping processes to macroscopic diffusion by considering the probability distribution arising from diffusion from a point source. This approach leads to the important relation in one dimension  $D = \Gamma \langle r^2 \rangle / 2$  and in three dimensions the analogous relation is  $D = \Gamma \langle r^2 \rangle / 6$ .
- In many important diffusion processes diffusion is not a random walk because successive jumps do not occur at random. Self-diffusion in a crystal by the *vacancy mechanism* is an example of a correlated jumping process; diffusion of a dilute interstitial component in a crystal is uncorrelated when the interstitial jumps are confined to the (mostly unoccupied) interstitial sites.
- The degree of nonrandom jumping is quantified by the double-sum term in *KoM* Eq. 7.31, leading of the definition of the *correlation coefficient*  $\mathbf{f}$  in Eq. 7.49:

$$\mathbf{f} = 1 + \frac{2}{N_\tau \langle r^2 \rangle} \left\langle \sum_{j=1}^{N_\tau-1} \sum_{i=1}^{N_\tau-j} |\vec{r}_i| |\vec{r}_{i+j}| \cos \theta_{i,i+j} \right\rangle \quad (1)$$

$\mathbf{f} = 1$  for a random walk. For nonrandom jumping,  $\mathbf{f}$  is often less than one but in some cases may be greater than one. For perfectly correlated jumping the diffusing species simply jumps back and forth between the same two sites and  $\mathbf{f} = 0$ .

- The mean square displacement in a correlated jumping process is given by  $\langle R^2 \rangle = N_\tau \langle r^2 \rangle \mathbf{f}$ , and the relation between the diffusivity and the jump rate for diffusion in three dimensions becomes  $D = \Gamma \langle r^2 \rangle \mathbf{f} / 6$ .

Related Exercises in *Kinetics of Materials*

Review Exercises 7.3–7.6, pp. 160–161.