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3.21 Kinetics of Materials—Spring 2006

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Lecture 10: Activated Jump Processes.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Sections 7.1–7.1.2 and 7.2

Key Concepts

- Diffusing particles in a solid move between neighboring positions of minimum energy, making what are called *jumps*. This is a cooperative process involving not only the jumping particle but also the surrounding ones—hence, the process is *many-bodied* and difficult to describe in detail.
- In *KoM* we describe three models for *thermally activated* jumps of of an interstitial species in a crystal, with gradually increasing complexity: a one-particle model in which the diffusing species sit in a square-well potential, a one-particle model in which the potential is harmonic, and a many-particle model with a harmonic potential. The resulting relations for the interstitial jump frequency Γ', Eqs. 7.9, 7.13, and 7.25 all have the form $\Gamma' = \nu \exp[-G^m/(kT)]$. The jump rate is equal to the product of an "attempt frequency" and a Boltzmann-Arrhenius exponential factor containing a migration activation free energy.
- Diffusion of a particle involves a series of discrete jumps $\vec{r}_i$ and the total displacement of a given particle is a sum over all the individual jump vectors. The "spreading" of a distribution of jumping particles is quantified by the *mean-square displacement* $\langle R^2(N_\tau)\rangle$ in *KoM* Eq. 7.31. Equation 7.31 is completely general.
- The relation between the mean square displacement and the diffusivity can be obtained from the second moment of the concentration distribution from a point source (see *KoM* Section 7.2.1). In three dimensions, isotropic diffusion for a time τ obeys the relation $\langle R^2(N_\tau)\rangle = 6D\tau$.
- 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, and jumps are confined to a specific set of directions.
- *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 a point source in one dimensional random walks. 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. The degree of nonrandom jumping is quantified by the *correlation coefficient* $\mathbf{f}$ defined in *KoM* Eq. 7.49. $\mathbf{f} = \mathbf{1}$ for a random walk. For diffusion in three dimensions, $D = \Gamma\langle r^2\rangle\mathbf{f}/\mathbf{6}$.

Related Exercises in *Kinetics of Materials*

Review Exercises 7.1; 7.3–7.6, pp. 159–161.