The generalised diffusion equation (11.44) can also be written in a form that reproduces the continuity equation that you have seen in the context, e.g., of charge density in electromagnetism:

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}, \tag{11.45}$$

$$\text{with} \quad J(x,t) = -D\frac{\partial P(x,t)}{\partial x} + \frac{1}{\gamma}f(x)P(x,t) = -D\, e^{-\beta E(x)}\frac{\partial}{\partial x}\left[e^{\beta E(x)}P(x,t)\right] \tag{11.46}$$

where $J(x,t)$ represents the net current for the probability $P(x,t)$, or equivalently, the particle concentration $c(x,t)$. This net current arises as the sum of the *diffusion current* $-D\frac{\partial P(x,t)}{\partial x}$, which is driven by a probability (or concentration) gradient – as in Fick's law – and the *drift current* $\frac{1}{\gamma}f(x)P(x,t)$, which is driven by the applied force. The equivalent second form of writing the total current can be checked by differentiation, and implementing $D = k_BT/\gamma$. For the force-free Brownian motion, the total current is just the diffusion current, i.e. the negative gradient of concentration: $J = -D\nabla c(x,t)$.

The Kramers problem: escape over a potential barrier

As a final illustration of the application of principles of Brownian motion we shall consider the problem of the escape of particles over potential barriers. The solution to this problem has important implications on a variety of physical, chemical and astronomical problems, known as the *thermal activation.*

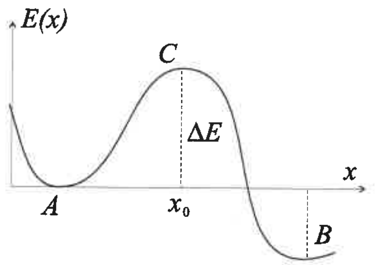

Figure 11.6: The potential energy profile of the Kramers problem. The key parameter is the height of the energy barrier, ΔE, at a position x_0.

As usual, for simplicity limiting ourselves to a 1-dimensional problem, consider a particle moving in a potential field (x) shown in Fig. 11.6. We suppose that the particles are initially caught in the *metastable* state at A, and we wish to find the rate at which the particles will escape from this state over the potential, as a result of thermal motion.

Let us concentrate on the long-time limit of this process, when the steady current of particles is established. Eq. (11.46) tells us that, at constant current J, integration between points A and B along the x-axis gives:

$$J \cdot \int_A^B e^{\beta E(s)} ds = -D\left[e^{\beta E(x)}P(x)\right]_A^B, \tag{11.47}$$

where on the right-hand side the integral of the full derivative d/dx just gives us the difference between the initial and final values of the argument. Let us now approximate the potential near the metastable equilibrium point A as $E(x) \approx E_A + \frac{1}{2}K_Ax^2$. The number of particles in the vicinity of A can be estimated from taking

$$dN_A = P(x_A)e^{-\beta E_A}dx$$

and integrating the Gaussian exponential $e^{-\beta E_A}$ to obtain:

$$N_A \approx P(x_A)\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta K_A x^2}dx = P(x_A)\sqrt{\frac{2\pi k_BT}{K_A}}. \tag{11.48}$$

Considering point B, we can safely neglect its contribution to Eq. (11.47) if we assume the potential well $E_B(x)$ is deep enough (the end-point being an "infinite sink" of particles). Then (since $E(x_A) = 0$) the steady state current takes the form

$$J \approx \frac{DP(x_A)}{\int_A^B e^{\beta E(s)} ds} \; ; \qquad \text{rate} = \frac{J}{N_A} = D\sqrt{\frac{K_A}{2\pi k_B T}} \frac{1}{\int_A^B e^{\beta E(s)} ds} \, . \tag{11.49}$$

The principal contribution to the integral in denominator arises only from the very small region near the potential barrier C. Although the exact solution of Kramers problem may depend on the particular shape of the potential $E(x)$, a very good estimate may be obtained by simply assuming the parabolic form near the maximum: $E_C \approx \Delta E - \frac{1}{2}K_C(x-x_0)^2$. On this assumption, with a sufficient degree of accuracy we have

$$\int_A^B e^{\beta E(s)} ds \approx e^{\Delta E/k_B T} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta K_C (x-x_0)^2} dx = e^{\Delta E/k_B T} \sqrt{\frac{2\pi k_B T}{K_C}} . \tag{11.50}$$

Combining Eqs. (11.49) and (11.50) we obtain the rate of particles transit over the barrier (equivalent to the rate of leaving the metastable state A):

$$\text{rate} = \frac{J}{N_A} = De^{-\Delta E/k_B T} \frac{\sqrt{K_A K_C}}{2\pi k_B T} = \frac{\sqrt{K_A K_C}}{2\pi\gamma} \cdot e^{-\Delta E/k_B T} \, . \tag{11.51}$$

This expression gives the probability, per unit time, that a particle originally in the potential hole A, will escape to B by crossing the barrier at C. The prefactor fraction is determined by various microscopic features of the system, but the most important fact to pay attention to is the exponential. This is the form representing the *thermal activation*, often known as the empirical Arrhenius law which one encounters in a variety of physical situations.