Diffusion equation: oxygen vacancies moving under a tip with voltage

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We are interested in the diffusion equation of type

$$\frac{\partial c(\vec{r},t)}{\partial t} = D\vec{\nabla}\cdot\left[\vec{\nabla}c(\vec{r},t) + c(\vec{r},t)\beta\vec{\nabla}V(\vec{r})\right] = -\vec{\nabla}\cdot\vec{j}(\vec{r},t) \tag{1}$$

for current

$$\vec{j}(\vec{r},t) = -D\vec{\nabla}c(\vec{r},t) - Dc(\vec{r},t)\beta\nabla V(\vec{r},t)$$

where $c(\vec{r},t)$ is the concentration or density, D is the diffusion constant, and $\beta = 1/(k_B T)$ is the inverse temperature (inverse energy units). Here the particles diffusing around feel a total potential given by $V(\vec{r})$. This equation can be true in any number of dimensions but we're really interested in 2D so $\vec{r}$ has two Cartesian components. As a side note, this is also called a master equation or the Fokker-Planck equation. From a stochastic viewpoint, this is the equation for the probability/density distribution of independent particles giggling around when each of them moves as per the Langevin equation

$$\frac{d\vec{r}(t)}{dt} = -D\beta\vec{\nabla}V(\vec{r}(t)) + \vec{g}(t)$$

where $\vec{g}(t)$ is a Gaussian random variable (random kicks in time)

$$\langle\vec{g}(t)\vec{g}(t')\rangle = 2D\delta(t-t')I\,.$$

This is a bit hard to digest or define, so in practice people would do discrete time simulations with time step Δt and then the positions one step forward is

$$\vec{r}_{n+1} = \vec{r}_n + \Delta t\left(-D\beta\vec{\nabla}V(\vec{r}_n) + \vec{g}_n\right)$$

where $\vec{g}_n$ is a random Gaussian variable with variance $2D/\Delta t$ along each component and the $\vec{g}$ at different time steps are uncorrelated.

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At any rate, the diffusion equation is very hard to solve in general for an arbitrary potential V. All one can really say is that the distribution $c(\vec{r}, t)$ will approach equilibrium which is given by the Boltzmann distribution

$$c(\vec{r}, t \to \infty) = c_{equil}(\vec{r}) = \frac{\exp(-\beta V(\vec{r}))}{Z}.$$

This follows immediately from setting $\vec{j} = 0$ and integrating the equation. A formal approach is to define a propagator $K(\vec{r}, \vec{r}', t)$ that says what the probability is for a particle starting at $\vec{r}'$ at $t = 0$ to end up at $\vec{r}$ after time t. If one knows this, then the solution is straightforward given the initial distribution:

$$c(\vec{r}, t) = \int d\vec{r}' \, K(\vec{r}, \vec{r}', t) c(\vec{r}', 0). \tag{2}$$

If no time elapses, the particle can't go anywhere. So for short times

$$K(\vec{r}, \vec{r}', t \to 0) = \delta(\vec{r} - \vec{r}').$$

Clearly, the propagator itself must reduce to the equilibrium distribution for long times: i.e. it must forget the initial distribution

$$K(\vec{r}, \vec{r}', t \to \infty) = \frac{\exp(-\beta V(\vec{r}))}{Z}.$$

At present, I know of two simple cases where analytical solutions are available. The first is really simple and represents pure diffusion with constant potential so $\vec{\nabla} V = 0$. The propagator is the Gaussian one

$$K_{diff}(\vec{r}, \vec{r}', t) = \left[\frac{1}{4\pi D t}\right]^{d/2} \exp\left(-\frac{(\vec{r} - \vec{r}')^2}{4Dt}\right)$$

Here, d is the number of dimensions being considered, so $d = 2$ for us. This just says that the particle does a random walk away from $\vec{r}'$ and each axial component has a standard deviation of $\sqrt{2Dt}$ about the starting point. Then to find the final distribution, one must do the integral of Eq. (2) with this K.

The second case with analytical answer is that of a harmonic potential: $V = \vec{r} \cdot K \cdot \vec{r}/2$. Here K is a $d \times d$ matrix of spring constants (the Hessian matrix) that must be positive definite so the minimum is at $\vec{r} = 0$. The diffusion case above is actually then a subclass of this problem with $K = 0$. If we decompose this matrix into its eigenbasis with eigenvalues k_α and we represent $\vec{r}$ in the eigenbasis with components x_α, then the propagator is given by

$$K_{harm}(\vec{r}, \vec{r}', t) = \prod_{\alpha=1}^{d} \left[\frac{\beta k_\alpha}{2\pi(1 - e^{-2D\beta k_\alpha t})}\right]^{1/2} \exp\left(-\frac{\beta k_\alpha (x_\alpha - x'_\alpha e^{-D\beta k_\alpha t})^2}{2(1 - e^{-2D\beta k_\alpha t})}\right).$$

This is a long and complicated looking result but one can digest is step by step. First, for $t \to \infty$, all the exponential factors go to zero and we recover the equilibrium distribution

$$K_{harm}(\vec{r}, \vec{r}', t \to \infty) = \prod_{\alpha=1}^{d} \left[\frac{\beta k_\alpha}{2\pi}\right]^{1/2} \exp\left(-\frac{\beta k_\alpha x_\alpha^2}{2}\right) = \left[\frac{\beta}{2\pi}\right]^{d/2} \sqrt{\det(K)} \exp\left(-\frac{\beta \vec{r} \cdot K \cdot \vec{r}}{2}\right).$$

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Although somewhat tedious, one can show that the $t \to 0$ limit is correct (it is the same as the diffusion result in the same limit since for very short times the particles only diffuse and have not time to feel the force on them). Finally, the time dependence comes in only through the factor $\exp(-D\beta k_\alpha t)$. Namely, short times are when $t \ll (D\beta k_\alpha)^{-1}$ and the distribution has not had time to evolve much at all towards the equilibrium (although its shape may change from the initial one: e.g. the diffusion cases changes from a delta function to a Gaussian shown above); in this short time limit, there is only really diffusion happening so one can ignore the harmonic potential along axes α where this relation is obeyed. Long times are when $t \gg (D\beta k_\alpha)^{-1}$ and the distribution approaches equilibrium. If you make plots of this over time, you see it starts as a Gaussian centered around $\vec{r}'$ at short times, and then the Gaussian changes width and its center moves to $\vec{r} = 0$.

For the case we are interested in, which is oxygen vacancies on an oxide surface like $SrTiO_3$ and a tip with voltage that attracts them, our present best guess at reasonable parameters are

$$D \sim 10^{-12} \text{ cm}^2\text{s}^{-1} \quad , \quad \beta \approx 39 \text{ eV}^{-1} \text{ (about 300 K)}$$

and for the potential we have something like

$$V(\vec{r}) = \frac{zeV_{tip}R}{\sqrt{(R+\delta)^2 + \vec{r}^2}}$$

where

$$zeV_{tip} \approx -4 \text{ eV} \quad , \quad R \approx 50 \text{ nm} \quad , \quad \delta \approx 1 \text{ nm}.$$

Since zeV_{tip} is so huge compared to k_BT, it turns out that the equilibrium distribution is very narrow. I made a crude plot and found that for $|\vec{r}| > 4$ nm, the equilibrium distribution is drops by a factor like $1/2$. Anyways, this is much smaller than R which is the scale over which the function V starts departing from quadratic behavior. So it seems reasonable to use a harmonic approximation for V to make some estimates. (Basically, the tip potential is big compared to k_BT.)

Taylor expanding, I get

$$V(\vec{r}) = zeV_{tip}\left(1 - \frac{\vec{r}^2 R}{2(R+\delta)^3} + \cdots\right)$$

so here the K matrix is nice and diagonal and the two axes are equivalent by symmetry, so

$$k_x = k_y = k = -\frac{zeV_{tip}R}{(R+\delta)^3} \approx 1.5 \times 10^{11} \text{ eV cm}^{-2}.$$

So the time scale for the evolution is

$$\tau = (D\beta k)^{-1} \approx 0.17 \text{ s}.$$

For an example of what this means, consider an initially flat distribution over a square of very large sides L: $c(\vec{r}, t=0) = 1/L^2$. Let's ask what the density is right under the tip as

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a function of time $c(\vec{0}, t)$ (this makes the integrals easy to do for me — an alternative is to start with a really wide Gaussian like $c(\vec{r}, t = 0) = \exp(-\vec{r}^2/(2\sigma^2))/(2\pi\sigma^2)$ for very large σ and have Maple to the Gaussian double integral of Eq. (2) since it can be done in closed form for any $\vec{r}$ and not just $\vec{r} = 0$). Large here means compared to the final equilibrium distribution. In this case, we have

$$c(0, t) = \frac{1}{L^2} \int_{-L/2}^{L/2} dx' \int_{-L/2}^{L/2} dy' \frac{\beta k}{2\pi(1 - e^{-2D\beta kt})} \exp\left(-\frac{\beta k(x'^2 + y'^2)e^{-2D\beta kt}}{2(1 - e^{-2D\beta kt})}\right).$$

For times short enough so that the exponential factor $e^{-D\beta kt}$ is not too small so that $\beta k L^2 e^{-D\beta kt} \gg 1$, the integration can be extended to infinity and then it is just some Gaussian integrals that give

$$c(0, t) \approx \frac{e^{2D\beta kt}}{L^2}.$$

This says that the central density for short times is growing exponentially compared to its initial value. (In fact this result should be true for a range of $|\vec{r}| < Le^{-D\beta kt}$ for such short times.) At longer times, the distribution starts looking more like the equilibrium one.