

FIG. 1. AUC cell scheme. Scheme of AUC experiment with a typical sector-shaped cell, showing the position of the meniscus r_m, botton r_k and the instantaneous position of a solute particle r.

during δt . Then, the running algorithm for the particle's position would be:

$$r(t + \delta t) = r(t) + \delta r_{sed} + \delta r_{Brow}$$

where $\delta r_{soil} = \omega^2 s r \delta t$ is the deterministic sedimentation drift of the particle with instantaneous, positiondependent velocity $\omega^2 s r$, while the random Brownian displacement has zero mean and variance $-2D\delta t$.

Although - as it will be verified later on - the end effects, at the solution meniscus and the bottom of the cell are of minor importance we take them into account. As the description sedimentation and Brownian motion near boundaries or walls seems problematic, we adopt ad As criteria. As for the meniscus, if after the step r r m . we set $r = r_m$. Regarding the bottom, if $r > r_k$, the particle had hit the bottom of the cell during the step; then we assume it should become and correct the position, taking $r = 2(r - r_b) = 2r_b - r$. After testing that this algorithm, in which the trajectory is divided in a very large number of small time steps, predicts correctly the concentration profiles (see below) we intended to devise a procedure with larger times steps, which would be computationally faster. The displacement over a large time step Δt is the result of the integration of the small increments in eq. 10, so we can write

$$r(t + \Delta t) = r(t) + \Delta r_{red} + \Delta r_{Brown}$$

During the large step the sedimentation velocity changes as r changes, but this change is deterministic, and as mentioned above the sedimentation drift is easily integrated as indicated in eq. 12

$$\triangle r_{sed} = r(t) \left[1 - exp(s\omega^2 \triangle t)\right]$$

while, thanks to the fractal nature of the Brownian motion, the Brownian step follows the same law over the long time, Δr _{Brow} being a random number of zero mean and variance

$$<\Delta r^2 p_{corr}>=2D\Delta t$$

Thus the algorithm based on eqs. 11, 12 and 13 could be applicable to arbitrarily large time steps (even as large as the time interval r between registers). This is essentially true if there were no end effects, i.e., in infinite, unbound AUC cell. For the sake of simplicity, we still adopt the simple criteria that particles stop at the meniscus and bosince at the bottom. Thus the only defect introduced by this procedure would be an inaccurate prediction of the concentration near the meniscus and bottom. In this regard, we note that the end-effects also affect other prediction procedures, like those based in Lamm-equation solvers, and influence the experiment itself, so that it is a common practice to discard the two terminal regions in the analysis of AUC experiments.

C. Procedure

Summarizing from the previous description, Brownian dynamics trajectories are simulated for a large number of particles, N_{part} . The trajectory of one particle is monitored, determining at successive times t, the interval of radial position r,. Then the counter for those interval and position is increased $n(i, j) \rightarrow n(i, j) + 1$.

The initial position of the particle is assigned according to the uniform concentration in the sector-shaped cell. As the number of particles in a slice of thickness χ is proportional to r, the probability of having (in the uniform solution) a particle at a distance r is $p(r) \propto r$.

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