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NOTE

The Master-Equation Formulation of Chromatography Theory

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Summary

De Clerk et al. have recently proposed that if chromatography theory were based on a master equation rather than a Fokker-Planck equation, asymmetries could readily arise [*Separation Sci.*, 1, 443 (1966)]. It is shown here that the master-equation description of an infinitely long homogeneous column also leads to a Gaussian limiting distribution.

In a recent paper de Clerk et al. have proposed a stochastic approach to chromatography theory based on the master equation (*1*). In it they suggest that their theory generalizes previous theories in that the limiting distribution is not Gaussian. It is the purpose of this note to point out that even if the master equation is regarded as a valid starting point for chromatography theory, a Gaussian distribution is characteristic at sufficiently long times provided physical properties are homogeneous along the column.

Let us consider a random walk on a discrete infinite line as the starting point of our investigation, and let $p(n\ \Delta L,t) = p_n(t)$ denote the probability of being at point $n\ \Delta L$ at time t, where $n = \ldots,$ $-2, -1, 0, 1, 2, \ldots.$ We shall assume that $p_n(t)$ satisfies a master equation of the form

$$\dot{p}_n(t) = \sum_{j=-\infty}^{\infty} A_j p_{n-j}(t) \tag{1}$$

where

$$A_0 = -\sum_{j=-\infty}^{\infty}{}' A_j \tag{2}$$

in which the prime denotes omission of the zero term and $A_j \geqslant 0$ for $j \neq 0$. The assumption of homogeneous physical properties along the line is equivalent to the requirement that the set of rate constants appearing in the equation for $p_n(t)$ are independent of n. To solve Eq. (1), let us introduce the generating functions

$$\begin{aligned} g(\theta,t) &= \sum_{n=-\infty}^{\infty} p_n(t) \exp(in\,\Delta L\theta) \\ A(\theta) &= \sum_{n=-\infty}^{\infty} A_n(1 - e^{in\Delta L\theta}) \end{aligned} \tag{3}$$

The inversion formula relating $p_n(t)$ to $g(\theta,t)$ is

$$p_m(t) = \frac{\Delta L}{2\pi} \int_{-\pi/\Delta L}^{\pi/\Delta L} g(\theta,t) \exp(-im\,\Delta L\theta)\, d\theta \tag{4}$$

If Eq. (1) is multiplied by $\exp(in\,\Delta L\theta)$ and summed over all n, the following equation results:

$$\frac{\partial g}{\partial t} = -A(\theta) g \tag{5}$$

Without loss of generality we can take the initial conditions to be $p_0(0) = 1$, $p_n(0) = 0$, $n \neq 0$, or $g(\theta,0) = 1$. The solution to Eq. (5) is $g(\theta,t) = \exp[-A(\theta)t]$ and moments of $p_n(t)$ are easily calculated as

$$\mu_r(t) = \sum_{n=-\infty}^{\infty} n^r (\Delta L)^r p_n(t) = \frac{1}{i^r} \frac{\partial^r g}{\partial \theta^r}\bigg|_{\theta=0} \tag{6}$$

In particular, the first three moments are

$$\mu_1 = \nu_1 t \qquad \mu_2(t) = \nu_2 t + \nu_1^2 t^2 \qquad \mu_3(t) = \nu_3 t + 3\nu_1\nu_2 t^2 + \nu_1^3 t^3 \tag{7}$$

where

$$\nu_r = (\Delta L)^r \sum_{n=-\infty}^{\infty} n^r A_n \tag{8}$$

The fact that $\mu_3(t)$ approaches infinity does not imply that $p_n(t)$ cannot tend to a Gaussian limit, nor does the fact that the third central moment

$$\mu_3'(t) = \mu_3(t) - 3\mu_2(t)\mu_1(t) + 2\mu_1^3(t) = \nu_3 t \tag{9}$$

goes to infinity with t imply it.*

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* One could conclude that $\{p_n(t)\}$ does not tend to a Gaussian limit if $\mu_3(t)/[\mu_2'(t)]^{3/2}$ had a limit different from zero. This is clearly not the case for the present models.

In fact, the Gaussian limit can be demonstrated in a heuristic way from the representation

$$p_m(t) = \frac{\Delta L}{2\pi} \int_{-\pi/\Delta L}^{\pi/\Delta L} \exp[-A(\theta)t - im\ \Delta L\theta]\ d\theta \tag{10}$$

We note, first of all, that Re $A(\theta) \geqslant 0$, so that for sufficiently large t the only contributions to the integral come from neighborhoods of the zeros of $A(\theta) = 0$. One of these zeros is $\theta = 0$. For $A(\theta_0) = 0$ for $\theta_0 \neq 0$ to hold, it is necessary that the A_n be periodic in n (2), which would lead to an unreasonable physical model. (In general A_n is a monotone-nonincreasing function of $|n|$.) Hence $\theta = 0$ is the only zero of interest. The function $A(\theta)$ can be expanded around $\theta = 0$ as

$$A(\theta) = -i\nu_1\theta + \frac{\nu_2\theta^2}{2} + \frac{i\nu_3\theta^3}{6} + \cdots \tag{11}$$

Let us now rewrite $\exp[-A(\theta)t]$ as

$$\exp[-A(\theta)t] = \exp\left(i\nu_1 t\theta - \frac{\nu_2 t\theta^2}{2}\right)\left(1 - \frac{i\nu_3 t}{6}\theta^3 + \cdots\right) \tag{12}$$

so that

$$p_m(t) \sim \frac{\Delta L}{2\pi} \int_{-\pi/\Delta L}^{\pi/\Delta L} \left(1 - \frac{i\nu_3 t\theta^3}{6} + \frac{\nu_4 t\theta^4}{24} + \cdots\right) \exp\left[i\theta(\nu_1 t - m\ \Delta L) - \frac{\nu_2 t\theta^2}{2}\right] d\theta \tag{13}$$

The indicated integrals can be evaluated by noting that only the limit $\Delta L \rightarrow 0$ is of interest, so that the limits of integration in Eq. (13) go to $(-\infty,\infty)$. We therefore find the asymptotic representation

$$\begin{aligned} p_m(t) &\sim \frac{\Delta L}{2\pi} \int_{-\infty}^{\infty} \exp\left[-\frac{\nu_2 t\theta^2}{2} + i\theta(\nu_1 t - m\ \Delta L)\right] \left(1 - \frac{i\nu_3 t\theta^3}{6} + \frac{\nu_4 t\theta^4}{24} - \cdots\right) d\theta \\ &= \frac{\Delta L}{(2\pi\nu_2 t)^{1/2}} \exp - [(m\ \Delta L - \nu_1 t)^2/(2\nu_2 t)] \left[1 + \frac{\nu_3(\nu_1 t - m\ \Delta L)}{\nu_2^2 t}\left(3 - \frac{(\nu_1 t - m\ \Delta L)^2}{\nu_2^3 t^2}\right) + \cdots\right] \end{aligned} \tag{14}$$

In the region of space for which

$$\lim_{t\to\infty} \frac{(m\,\Delta L - \nu_1 t)^2}{t^2} = 0 \tag{15}$$

i.e., in the region centered at the moving mean, $\nu_1 t$, we have the Gaussian limit:

$$p_m(t) \sim \frac{\Delta L}{(2\pi\nu_2 t)^{1/2}} \exp\left[-\frac{(m\,\Delta L - \nu_1 t)^2}{2\nu_2 t}\right] \tag{16}$$

for sufficiently large t. Higher terms in the expansion of Eq. (14) likewise go to zero as $t \to \infty$. Hence the use of a master equation in a homogeneous medium still leads to a Gaussian limit. The preceding argument can be made rigorous and the conclusions can be checked on the particular example $A_1 \neq 0, A_{-1} \neq 0, A_r = 0, r \neq 0, 1$. In this case an exact solution to the master equation is

$$p_n(t) = \left(\frac{A_{-1}}{A_1}\right)^{n/2} e^{-(A_1+A_{-1})t} I_n[2t(A_1A_{-1})^{1/2}] \tag{17}$$

and the Gaussian approximation can be verified in detail as in (*3*).

The use of the moment equations (25)–(28) of de Clerk et al. leads to correct results for the central moments, but the underlying partial differential equations [Eqs. (23) or (30) of that paper] can lead to incorrect conclusions. In particular, the solution to Eq. (23) can become negative (*4*). The difficulty of finding an improvement over the Fokker-Planck approximation has been discussed in the literature of statistical mechanics (*5*). The analysis just presented does not lead to an explanation or to an adequate description of asymmetric profiles without introducing spatial inhomogeneities into either a master equation or a Fokker-Planck description of the chromatographic process.

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