

Correlated Brownian Motions and the Depletion Effect in Colloids

P. Kotelenez*
M. J. Leitman†
and
J. A. Mann‡

Abstract

We briefly review the derivation of a system of N correlated Brownian motions as a kinematic mesoscopic limit for a system of nonlinear deterministic oscillators consisting of N large (solute) particles and infinitely many small (solvent) particles by Kotelenez. We then sketch the qualitative analysis of correlated Brownian motions and the depletion effect in colloids by Kotelenez, Leitman and Mann. For space dimension $d \geq 2$ they showed that two correlated Brownian particles, when sufficiently close, have an initial tendency to attract each other further. For large times (and for large separations) they perform independent Brownian motions. The key to their short time result is a generalization to $d \geq 2$ dimensions of the one-dimensional probability flux, as defined by van Kampen. We conclude with a discussion of three unresolved problems.

1 Introduction

This paper is based on our recent work involving a stochastic process that provides a fundamental understanding of the depletion effect in colloids. (For a review of the experiments relevant for observing the depletion effect and correlations, see Kotelenez, Leitman and Mann [1].) Our theory evolved from certain results of Kotelenez [2] for stochastic limits of systems of interacting particles and explicated in his recent book. (See Kotelenez [3].) Complete details and proofs of the results and assertions we present here can be found in the works just cited. In this paper we describe the depletion effect, present our model, and explore some of its consequences. Our work leads naturally to the three unresolved questions set out in Section 4

*Mathematics, Case Western Reserve University, Cleveland, OH 44106, USA, peter.kotelenez@case.edu, 216 368 4838 (analog), 216 368 5163 (fax).

†Mathematics, Case Western Reserve University, Cleveland, OH 44106, USA, marshall.leitman@case.edu, 216 368 2890 (analog), 216 368 5163 (fax).

‡Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA, j.mann@case.edu, 216 368 4122 (analog), 216 368 3016 (fax).

2 Interacting Particles — Depletion Effect

Consider a mixture of small, spherical particles of diameter a_s and large, spherical particles of diameter a_l so that $a_s \ll a_l$. Assume that the number densities (number of particles/volume) obey, $x_l \ll x_s$; the reference state is the very dilute solution with respect to the large particles. In this state, the probable separation between any two large particles is at least $10a_s$, as estimated from the average volume per large particle ($1/x_l$). This separation is sufficient to ensure that the distribution of small particles around the each large particle is uniform with spherical symmetry. This configuration is shown in Figure (1, A).

Under the assumption of sufficient separation, Einstein [4] and von Smoluchowski [5] derived a model of independent Brownian motions for the displacement of the large particles.

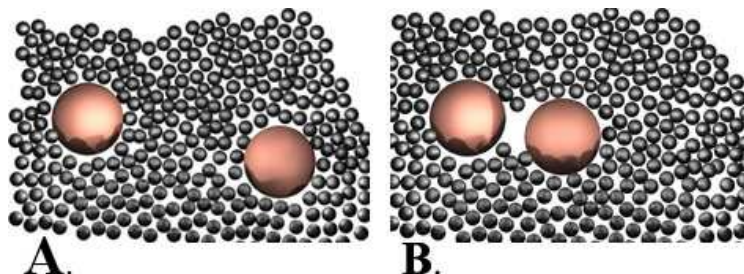


Figure 1:

A. Two large particles are separated sufficiently so that the packing around each particle is isotropic on average. *The motions of the two particles are described by two, independent Brownian motions.*

B. If the two large particles are closer than about $2a_s$ the distribution of small particles is depleted in the region between them. *The motions of the two particles can no longer be described by two, independent Brownian motions.*

Let us first comment on the classical Einstein-Smoluchowski theory, restricting ourselves for simplicity to two independent identically distributed Brownian motions whose positions in d -dimensional space at time t are the vectors $\mathbf{r}^1(t)$ and $\mathbf{r}^2(t)$. Let the $2d$ -dimensional vector

$$\hat{\mathbf{r}}(t) := \begin{bmatrix} \mathbf{r}^1(t) \\ \mathbf{r}^2(t) \end{bmatrix} \quad (2.1)$$

denote the position of the pair at time t . Under the assumption of independence, the transition probability density of this pair process, denoted by $\hat{p}(t, \hat{\mathbf{q}}, \hat{\mathbf{r}})$ is the (weak) solution of the Fokker-Planck (or Kolmogorov forward) equation¹

$$\frac{\partial}{\partial t} \hat{p}(t, \hat{\mathbf{q}}, \hat{\mathbf{r}}) = \frac{1}{2} \sum_{\alpha, \beta=1}^2 \sum_{k, l=1}^d \frac{\partial^2}{\partial r_k^\alpha \partial r_l^\beta} \left(D_{k, l}^{\alpha, \beta}(\hat{\mathbf{r}}) \hat{p}(t, \hat{\mathbf{q}}, \hat{\mathbf{r}}) \right), \quad (2.2)$$

together with the initial condition

$$\hat{p}(0, \hat{\mathbf{q}}, \hat{\mathbf{r}}) = \delta_{\hat{\mathbf{q}}}(\hat{\mathbf{r}}). \quad (2.3)$$

¹For a $2d$ -dimensional Borel set B , the transition probability, \hat{P} , is given through its density, \hat{p} , by $\hat{P}(t, \hat{\mathbf{q}}, B) = \int_B \hat{p}(t, \hat{\mathbf{q}}, \hat{\mathbf{r}}) d\hat{\mathbf{r}}$.

The $(2d \times 2d)$ pair diffusion matrix, $\hat{D}(\hat{\mathbf{r}})$, is associated with the pair of Brownian motions through the Fokker-Planck equation (2.2); it has the $(2d \times 2d)$ block structure:²

$$\hat{D}(\hat{\mathbf{r}}) := \begin{bmatrix} \mathbf{D}^{11}(\hat{\mathbf{r}}) & \mathbf{D}^{12}(\hat{\mathbf{r}}) \\ \mathbf{D}^{21}(\hat{\mathbf{r}}) & \mathbf{D}^{22}(\hat{\mathbf{r}}) \end{bmatrix} = \begin{bmatrix} D\mathbf{1} & \mathbf{0} \\ \mathbf{0} & D\mathbf{1} \end{bmatrix}, \quad (2.4)$$

where $D > 0$ is the (scalar) diffusion coefficient. For this case, the explicit solution to Equations (2.2, 2.3) is just the normal density in \mathbb{R}^{2d} :

$$\hat{p}(t, \hat{\mathbf{q}}, \hat{\mathbf{r}}) = \frac{1}{(2\pi Dt)^d} e^{-\frac{1}{2Dt}|\hat{\mathbf{r}}-\hat{\mathbf{q}}|^2}. \quad (2.5)$$

The independence of the Brownian motions is consistent with Figure (1, A). However, if the two particles move closer together, the configuration space of the small particles changes if the separation becomes less than about $2a_s$, as represented in Figure (1, B). The reduction of small particle density in the space between large particles that are sufficiently close is referred to as *depletion*. Thus, if the large particles are sufficiently close together, the anisotropic collisions of the many small particles with them cause their motions to become statistically correlated. The Einstein-Smoluchowski model fails to account for the resulting depletion effect and must be replaced by a model incorporating appropriately spatially correlated Brownian motions. The length scale at which the correlations become effective is called the *correlation length* and denoted by $\sqrt{\varepsilon}$.

Experiments early in the last century showed that colloidal systems composed of dispersions of particles and macromolecules show interesting flocculation or agglomeration phenomena, which were not understood until the paper of Asakura and Oosawa [6]. They describe the case of parallel plates immersed in a solution of hard, macromolecular particles. They then assert that, as the two plates are brought close together, an attractive osmotic force develops as a result of depletion of the macromolecules from the volume between the two plates.

Vrij and de Hek [7, 8] independently rediscovered the depletion effect and carried out experimental and theoretical studies that involved coated silica spheres, the large particles, of about 50 nm radius in dispersions containing polystyrene, the small particles, mixed in cyclohexane. The marker for the depletion effect is the phase separation, which was observed with the variation of polystyrene concentration.

The effect of correlations can be measured using techniques reviewed in Kotelenetz, Leitman and Mann [1]. For example, laser tweezers techniques can be arranged to allow two particles to move in one dimension randomly driven by small particles. It is possible to design particle systems to behave as hard spheres, see Ackerson, *et. al.* [9], and these can be synthesized close to monodispersed and to various radii. These systems do not require the inclusion of long range, colloid forces in our theory. It is also possible to develop a molecular dynamic computer simulation that will allow tracking of two large particles driven by collisions with a set of small particles. An analysis of the trajectories of a pair of hard, large particles will provide a measure of the correlations we expect.

²Of course, in this case, $\hat{D}(\hat{\mathbf{r}}) = D\mathbf{1}$ is just a constant positive multiple of the $(2d \times 2d)$ identity matrix. The symbol $\mathbf{1}$ always denotes an identity matrix.

3 Underlying Model and Stochastic Limit

Based on the preceding arguments we seek a model for correlated Brownian motions of the large particles that satisfies the following four

Desiderata:

1. The *marginal* motion of any single particle is Brownian (Wiener process).³
2. If the particles are widely separated (dilute system), they perform approximately independent Brownian motions.
3. If the separation between particles is small, their motions are correlated. Moreover, the correlation is such that if the separation is sufficiently small, as measured by the correlation length, they tend statistically to approach one another further.
4. As the correlation length tends to zero, the particles become δ -correlated in space and time.⁴

Our model must also be consistent with the Principal of Material Frame Indifference, which requires that the underlying constitutive relations be independent of the frame of the observer.⁵

Kotelenez [2, 3] obtained a class of correlated Brownian motions as a scaling limit for the positions of several large particles immersed in a medium of infinitely many smaller particles.⁶ A brief sketch of this work follows.

We consider two levels of description of the particle system. On the *microscopic* level, we suppose Newtonian mechanics governs the equations of motion of the individual atoms or molecules. Our model is essentially an elastic sphere model. No internal degrees of freedom are assumed.⁷ These equations are cast in the form of a system of deterministic coupled nonlinear equations. The next level is called *mesoscopic*. On this level the motion of the large particles is stochastic; the randomness of their motions is determined by the surrounding medium. Here, spatially extended particles are replaced by point particles; large and small particles are distinguished by their large and small masses.⁸ Further-

³We are dealing here with the joint motion of several large particles and each motion is, in a sense, an infinite dimensional random variable. Therefore, the terms *marginal* and *joint* are straightforward generalizations of the corresponding terms for finite dimensional random variables.

⁴That is, in the limit the particles become uncorrelated unless they collide.

⁵As formulated by Noll [10], it asserts:

The constitutive laws governing the internal interactions between the parts of a system should not depend on whatever external frame of reference is used to describe them.

There is an extensive literature on this subject See, for example, the comprehensive article in the *Encyclopedia of Physics - The Non-Linear Field Theories of Mechanics* by Truesdell and Noll [11].

⁶Kotelenez [12, 13] introduced correlated Brownian motions as a driving term in stochastic ordinary differential equations (SODEs) and stochastic partial differential equations (SPDEs). (See, for example, Equation (3.2).)

⁷With some effort, it should be possible to include internal degrees of freedom.

⁸For a rare gas a mean-field force can be a result of coarse graining in space and time, where on a finer scale the interaction is governed by collisions.

more, the interaction between small particles is assumed to be negligible and interactions between large particles can (temporarily) be neglected.⁹

We suppose that the interaction between large and small particles is elastic. Specifically, the forces are determined by a scalar-valued potential of the form $\varphi(|\mathbf{r} - \mathbf{q}|^2)$, where \mathbf{r} denotes the position of a large particle and \mathbf{q} denotes the position of a small particle. Thus we assume that the potential does not depend on the absolute locations of the two particles but only on their relative, vector difference, $\mathbf{r} - \mathbf{q}$; it is a *shift invariant* function of \mathbf{r} and \mathbf{q} . In fact, we assume that the potential depends only on the magnitude of the difference or the *separation*, $|\mathbf{r} - \mathbf{q}|$; it is an *isotropic* function of the difference.¹⁰ Recall that classical Brownian motion is interpreted to be the result of collisions between many, rapidly moving, small particles and a few, slowly moving, large particles. These collisions are often assumed to be elastic.

We therefore suppose that the force $\hat{\mathbf{g}}_{\varepsilon,\mu}(\mathbf{r} - \mathbf{q})$ acting on a large particle at position \mathbf{r} exerted by a small particle at position \mathbf{q} is derivable from the potential $\hat{\varphi}_{\varepsilon,\mu}$:

$$\hat{\mathbf{g}}_{\varepsilon,\mu}(\mathbf{r} - \mathbf{q}) := -\nabla_{\mathbf{r}}\hat{\varphi}_{\varepsilon,\mu}(|\mathbf{r} - \mathbf{q}|^2) = -2(\mathbf{r} - \mathbf{q})\hat{\varphi}'_{\varepsilon,\mu}(|\mathbf{r} - \mathbf{q}|^2). \quad (3.1)$$

The potential function $\hat{\varphi}_{\varepsilon,\mu}$ and, hence, the force $\hat{\mathbf{g}}_{\varepsilon,\mu}$ are assumed to depend on two parameters: the correlation length $\sqrt{\varepsilon}$ and a time-scale parameter μ . As the time-scale decreases, the parameter μ increases.¹¹ The stochastic limit results in a mesoscopic model of correlated Brownian motions.¹²

At time t there are N large particles located at $\mathbf{r}^\alpha(t)$, $\alpha = 1, \dots, N$. In the stochastic limit, the positions of the large particles are shown to be the solutions, $\mathbf{r}^\alpha(t, \mathbf{r}_0^\alpha)$, of the N kinematic stochastic integral equations¹³

$$\mathbf{r}^\alpha(t) = \mathbf{r}_0^\alpha + \int_0^t \int_{\mathbb{R}^d} \mathbf{g}_\varepsilon(\mathbf{r}^\alpha(s) - \mathbf{q})w(d\mathbf{q}, ds), \quad \alpha = 1, \dots, N, \quad (3.2)$$

where $\mathbf{r}_0^\alpha, \alpha = 1, \dots, N$ are their random initial locations. In Equation (3.2) $w(d\mathbf{q}, ds)$ denotes standard Gaussian white noise on $\mathbb{R}^d \times \mathbb{R}_+$, which is the space-time generalization of the time increments of a standard scalar-valued Brownian motion. The white noise and the random initial data are defined on the same probability space and are assumed independent.

The kernel, \mathbf{g}_ε , in Equations (3.2) is induced by the force density field $\hat{\mathbf{g}}_{\varepsilon,\mu}$ of Equations (3.1) through the transition from a second order system in time

⁹As the interaction between large particles occurs on a much slower time scale than the interaction between large and small particles, it can be included after the scaling limit employing fractional steps (See Goncharuk and Kotelenetz [14]).

¹⁰This assumption is entirely consistent with the Principle of Material Frame Indifference. Indeed, for a shift-invariant scalar function of two vector arguments, **isotropy** is equivalent to isotropy in their difference. Here $|\mathbf{r} - \mathbf{q}|$ denotes the Euclidean distance in the state space \mathbb{R}^d between the two particles.

¹¹The parameter μ has the units of reciprocal time $[\frac{1}{T}]$. The symbol $\nabla_{\mathbf{r}}$ denotes the spatial gradient in \mathbb{R}^d and the prime ($'$) denotes differentiation with respect to the scalar argument.

¹²See Kotelenetz [2]

¹³Kotelenetz [3], Ch. 2, shows that in our context the space-time white noise integrator $w(d\mathbf{q}, ds)$ should be interpreted as a centered "number density" times a space-time volume element. (This "number density" times the mass of a small particle is related to the van Hove density of the small particles.) Hence $w(d\mathbf{q}, ds)$ should have the units of time: $[\frac{1}{L^d}L^dT] = [T]$. Since $\hat{\mathbf{g}}_{\varepsilon,\mu}(\mathbf{r})$ has the units of acceleration, namely $[\frac{L}{T^2}]$, it follows, in view of Equation (3.3) and Footnote 11, that $\mathbf{g}(\mathbf{r})$ must have the units of velocity, namely $[\frac{L}{T}]$. This is consistent with the kinematic Equation (3.2), since $\mathbf{g}(\mathbf{q})w(d\mathbf{q}, ds)$ has the units of length, namely $[L]$.

(dynamic description) to a first order system in time (kinematic description). This transition requires that the force density field $\hat{\mathbf{g}}_{\varepsilon,\mu}$ increases as the time scale decreases:

$$\hat{\mathbf{g}}_{\varepsilon,\mu}(\mathbf{r}) \sim \mu \mathbf{g}_\varepsilon(\mathbf{r}) \quad \text{as } \mu \rightarrow \infty. \quad (3.3)$$

In the sequel, we refer to the function \mathbf{g}_ε as the **forcing kernel**. It is important to emphasize that our model excludes interactions among large particle as well as interactions among small particles. The former assumption can be relaxed, but it is essential that the motions of the infinitely many small particles be independent. Thus, our model retains only the effects of the small particles upon the large, the result of which is the mean-field action on a large particle governed by Equation (3.2).

The solutions to Equations (3.2), $\mathbf{r}^\alpha(t) = \mathbf{r}^\alpha(t, \mathbf{r}_0^\alpha)$, $\alpha = 1, \dots, N$, together with suitable initial conditions, constitute an Nd -dimensional Markov diffusion process. For two particles, say $\mathbf{r}^1(t)$ and $\mathbf{r}^2(t)$, $\hat{\mathbf{r}}(t)$ denotes the $2d$ -dimensional Markov pair diffusion process, as shown in Equation (2.1).

As before, the transition probability density of this pair process $\hat{p}(t, \hat{\mathbf{q}}, \hat{\mathbf{r}})$ is the (weak) solution of the Fokker-Planck (or Kolmogorov forward) problem consisting of Equations (2.2, 2.3). Again, the $(2d \times 2d)$ pair diffusion matrix, $\hat{\mathbf{D}}(\hat{\mathbf{r}})$, is associated with the pair diffusion through the Fokker-Planck equation (2.2). However, assuming that the underlying physics has the invariance properties prescribed by the Principal of Material Frame Indifference, the pair diffusion matrix is no longer just the scalar multiple of the identity given in Equation (2.4); it must now have the special block structure described below.

$\hat{\mathbf{D}}(\hat{\mathbf{r}})$ has the (2×2) block structure:

$$\hat{\mathbf{D}}(\hat{\mathbf{r}}) := \begin{bmatrix} \mathbf{D}^{11}(\hat{\mathbf{r}}) & \mathbf{D}^{12}(\hat{\mathbf{r}}) \\ \mathbf{D}^{21}(\hat{\mathbf{r}}) & \mathbf{D}^{22}(\hat{\mathbf{r}}) \end{bmatrix} = \begin{bmatrix} D\mathbf{1} & \mathbf{D}^{12}(\hat{\mathbf{r}}) \\ \mathbf{D}^{12}(\hat{\mathbf{r}}) & D\mathbf{1} \end{bmatrix}, \quad (3.4)$$

where D can still be construed as a (scalar) diffusion constant. The off-diagonal $(d \times d)$ matrix blocks $\mathbf{D}^{12}(\hat{\mathbf{r}})$ and $\mathbf{D}^{21}(\hat{\mathbf{r}})$ no longer vanish and will determine the nature of the correlation between the two motions.

The $(d \times d)$ matrix blocks $\mathbf{D}^{\alpha\beta}(\hat{\mathbf{r}})$ are computed through the forcing kernel by the formula¹⁴

$$\mathbf{D}^{\alpha\beta} \left(\begin{bmatrix} \mathbf{r}^\alpha \\ \mathbf{r}^\beta \end{bmatrix} \right) = \int_{\mathbb{R}^d} \mathbf{g}(\mathbf{r}^\alpha - \mathbf{q}) \mathbf{g}^T(\mathbf{r}^\beta - \mathbf{q}) d\mathbf{q}, \quad \alpha, \beta = 1, 2. \quad (3.5)$$

(Unless it plays a direct role, we suppress the dependence of the forcing kernel upon the correlation length.) From Equation (3.5) it follows that each of these matrices is a function of the difference $(\mathbf{r}^2 - \mathbf{r}^1)$. For instance,

$$\mathbf{D}^{12} \left(\begin{bmatrix} \mathbf{r}^1 \\ \mathbf{r}^2 \end{bmatrix} \right) = \mathbf{D}^{12} \left(\begin{bmatrix} 0 \\ \mathbf{r}^2 - \mathbf{r}^1 \end{bmatrix} \right). \quad (3.6)$$

¹⁴From the Fokker-Planck Equation (2.2), the physical units of $\hat{\mathbf{D}}(\hat{\mathbf{r}})$ must be $[\frac{L^2}{T}]$. The blocks $\mathbf{D}^{\alpha\beta}(\hat{\mathbf{r}})$ must carry the same units. Now the right-hand side of Equation (3.5) does not have these units, since $\mathbf{g}(\mathbf{r})$ has units $[\frac{L}{T}]$. (See Footnote 13.) There is no inconsistency. The block $\mathbf{D}^{\alpha\beta}(\hat{\mathbf{r}})$ is the time-derivative of the cross quadratic variation associated with the Markov processes $\mathbf{r}^\alpha(t, \mathbf{r}_0^\alpha)$ and $\mathbf{r}^\beta(t, \mathbf{r}_0^\beta)$. Since the cross quadratic variation has units $[L^2]$, $\mathbf{D}^{\alpha\beta}(\hat{\mathbf{r}})$ has units $[\frac{L^2}{T}]$. The expression on the right-hand-side of Equation (3.5) is the value of $\mathbf{D}^{\alpha\beta}(\hat{\mathbf{r}})$. (See Kotelenetz, Leitman, and Mann [1], Appendix B.3, for more details.)

As a consequence of the invariance required by the Principal of Material Frame Indifference, they are *even* functions of the difference $(\mathbf{r}^2 - \mathbf{r}^1)$. Summarizing the symmetries:

$$(\mathbf{D}^{12})^T = \mathbf{D}^{21} = \mathbf{D}^{12}. \quad (3.7)$$

As a further consequence of our assumptions, $\hat{\mathbf{D}}(\hat{\mathbf{r}})$ is positive definite (non-degenerate). In particular, $D > 0$, so the (marginal) time evolution of each particle is governed by a Fokker-Planck equation in \mathbb{R}^d with the constant diffusion matrix $D\mathbf{1}$ and, hence, each particle performs a d -dimensional Brownian motion.¹⁵ The correlation between the motions of two distinct large particles is determined through the matrix block $\mathbf{D}^{12}(\hat{\mathbf{r}})$. This correlation depends upon the difference $(\mathbf{r}^2 - \mathbf{r}^1)$ and does not vanish. Therefore, the *joint* motion of the pair is not Gaussian and, hence, not Brownian.

The (*normalized*) *difference process* in \mathbb{R}^d and its magnitude, the *separation process*, defined by

$$\mathbf{x}(t) := \frac{1}{\sqrt{2}}(\mathbf{r}^2(t) - \mathbf{r}^1(t)) \quad \xi(t) := |\mathbf{x}(t)| = \frac{1}{\sqrt{2}}|\mathbf{r}^2(t) - \mathbf{r}^1(t)| \quad (3.8)$$

are also Markov diffusions in \mathbb{R}^d and \mathbb{R} . It can be shown that the difference process (and, hence, its magnitude) is never zero (almost surely) in finite time, provided it is not zero initially. The diffusion matrix for the difference process $\mathbf{x}(t)$, the *difference diffusion matrix*, is given by

$$\tilde{\mathbf{D}}(\mathbf{x}) := D\mathbf{1} - \mathbf{D}^{12} \left(\begin{bmatrix} 0 \\ \sqrt{2}\mathbf{x} \end{bmatrix} \right). \quad (3.9)$$

It is convenient at this point to record some of the structure of $\tilde{\mathbf{D}}(\mathbf{x})$ induced by the Principal of Material Frame Indifference and the smoothness and integrability hypotheses on \mathbf{g} . For $\mathbf{x} \neq \mathbf{0}$, $\mathbf{P}(\mathbf{x})$ denotes the *radial projection* onto the sub-space spanned by $\{\mathbf{x}\}$ and $\mathbf{P}^\perp(\mathbf{x})$ denotes its orthogonal complement, the *lateral projection*.¹⁶

For $\mathbf{x} \neq \mathbf{0}$, the *difference diffusion matrix* $\tilde{\mathbf{D}}(\mathbf{x})$ has the form

$$\tilde{\mathbf{D}}(\mathbf{x}) = \sigma_\perp(|\mathbf{x}|^2)\mathbf{P}^\perp(\mathbf{x}) + \sigma(|\mathbf{x}|^2)\mathbf{P}(\mathbf{x}), \quad (3.10)$$

where $\sigma, \sigma_\perp : \mathbb{R}_+ \rightarrow \mathbb{R}$ satisfy

$$0 < \sigma_\perp(\xi^2) < D, \text{ for } \xi > 0, \quad \sigma_\perp(0) = 0, \quad \lim_{\xi \rightarrow \infty} \sigma_\perp(\xi^2) = D, \quad (3.11)$$

and

$$0 < \sigma(\xi^2), \text{ for } \xi > 0, \quad \sigma(0) = 0, \quad \lim_{\xi \rightarrow \infty} \sigma(\xi^2) = D. \quad (3.12)$$

Note that $\sigma(|\mathbf{x}|^2)$ and $\sigma_\perp(|\mathbf{x}|^2)$ are the eigenvalues of $\tilde{\mathbf{D}}(\mathbf{x})$. Unless they are equal, $\sigma(|\mathbf{x}|^2)$ is a simple eigenvalue and $\sigma_\perp(|\mathbf{x}|^2)$ has geometric multiplicity $d - 1$. We refer to σ as the *radial eigenvalue* and σ_\perp as the *lateral eigenvalue*. Observe that $\tilde{\mathbf{D}}(\mathbf{0}) = \mathbf{0}$, $\lim_{|\mathbf{x}| \rightarrow \infty} \tilde{\mathbf{D}}(\mathbf{x}) = D\mathbf{1}$ and, for $\mathbf{x} \neq \mathbf{0}$, $\tilde{\mathbf{D}}(\mathbf{x})$ is positive definite, symmetric, and $\tilde{\mathbf{D}}(\mathbf{x}) = \tilde{\mathbf{D}}(-\mathbf{x})$. We say the *diffusion matrix* $\tilde{\mathbf{D}}$ is *radially dominant* whenever its eigenvalues satisfy:

$$\sigma_\perp(\xi^2) < \sigma(\xi^2), \quad \forall \xi > 0. \quad (3.13)$$

¹⁵To satisfy Desideratum 4, take $c = 1$. In this case they are standard Brownian motions.

¹⁶Had we considered the case where $d = 1$, the lateral projection would vanish.

The separation process, $\xi(t)$, can be shown to satisfy the following stochastic Itô ordinary differential equation:

$$d\xi = \frac{1}{2} \frac{(d-1)}{\xi} \sigma_{\perp}(\xi^2) dt + \sqrt{\sigma(\xi^2)} \beta(dt), \quad (3.14)$$

where $\beta(\cdot)$ is a standard real-valued Brownian motion. (See Kotelenez, Leitman and Mann [1] for details.) Observe that the (deterministic) drift term in Equation (3.14) is proportional to $(d-1)$ and depends only on the lateral eigenvalue while the diffusive (stochastic) term depends only on the radial eigenvalue. Thus the presence of a drift term is entirely a consequence of the fact that the underlying physical space has dimension $d \geq 2$.

We can apply the criteria from stochastic analysis of one-dimensional diffusions to assess the behavior of the **separation process** for $d \geq 2$ for large times.

1. For $d = 2$, the solution of Equation (3.14) is recurrent whenever the **diffusion matrix \tilde{D}** is **radially dominant**.
2. For $d \geq 3$, the solution of Equation (3.14) is transient.

As a consequence, if $d = 2$, the two large particles will attract and repel each other infinitely often almost surely as $t \rightarrow \infty$ and, if $d \geq 3$, the distance between the two large particles will tend to ∞ almost surely as $t \rightarrow \infty$.¹⁷ These conclusions are, of course, consistent with well-known results about random walks. However, the process under consideration here is *not* Brownian, but is expected to be Brownian in the large separation limit. Asymptotically, for $d \geq 3$, Equation (3.14) determines a Bessel process, so these conclusions are certainly plausible.

In contrast with the long-time behavior of the separation process, we will see that there is an initial statistical tendency for large particles to move together when starting from a uniform state, provided they are sufficiently close to begin with.

To quantify this initial tendency we generalize van Kampen's notion of *probability flux rate* to vector processes $\mathbf{x}(\cdot)$ in \mathbb{R}^d in order to characterize regions with a bias in favor of attraction or repulsion between particle pairs.¹⁸ The *regions* in \mathbb{R}^d to which we refer in the sequel are regions in the space of the variable \mathbf{x} , the normalized vector difference of the positions of the large particles. Thus, if one particle is located at the origin, the other is located at $\sqrt{2}\mathbf{x}$. Since we consider distinct large particles we exclude $\mathbf{x} = \mathbf{0}$.¹⁹

A point \mathbf{x} and a unit vector \mathbf{v} determine an oriented hyperplane in \mathbb{R}^d through \mathbf{x} with orienting normal \mathbf{v} . Let $X(\mathbf{x}, t)$ denote the probability density for the process $\mathbf{x}(\cdot)$ at the point \mathbf{x} and time t . We define the *probability flux rate vector (at (\mathbf{x}, t) with the orientation \mathbf{v})* by

$$\mathbf{j}(\mathbf{x}, t, \mathbf{v}) := -\frac{1}{2} X(\mathbf{x}, t) \tilde{D}(\mathbf{x}) \mathbf{v}. \quad (3.15)$$

The vector $\mathbf{j}(\mathbf{x}, t, \mathbf{v})$ may be interpreted as the area density of the instantaneous probability flow rate at time t through a surface element at \mathbf{x} oriented

¹⁷These two assertions depend upon the presence of the drift term.

¹⁸See van Kampen [15].

¹⁹It can be shown that two particles which are distinct at some time will, almost surely, remain distinct for all future times. (See Kotelenez, Leitman and Mann [1] for details.)

by \mathbf{v} .²⁰ The *flux rate* (at (\mathbf{x}, t) with orientation \mathbf{v}), denoted by $J(\mathbf{x}, \mathbf{v}, t)$, is defined as the divergence of the probability flux rate vector, namely²¹

$$\begin{aligned} J(\mathbf{x}, t, \mathbf{v}) &:= \nabla_{\mathbf{x}} \bullet \mathbf{j}(\mathbf{x}, t, \mathbf{v}) = \nabla_{\mathbf{x}} \bullet \left(-\frac{1}{2} X(\mathbf{x}, t) \tilde{\mathbf{D}}(\mathbf{x}) \mathbf{v} \right) \\ &= -\frac{1}{2} X(\mathbf{x}, t) \mathbf{div} \tilde{\mathbf{D}}(\mathbf{x}) \bullet \mathbf{v} - \frac{1}{2} \tilde{\mathbf{D}}(\mathbf{x}) \nabla_{\mathbf{x}} X(\mathbf{x}, t) \bullet \mathbf{v}. \end{aligned} \quad (3.16)$$

Note that $J(\mathbf{x}, t, \mathbf{v})$ is associated with an *oriented* surface element at \mathbf{x} ; in fact, the functional $\mathbf{v} \mapsto J(\mathbf{x}, t, \mathbf{v})$ is linear.

For simplicity, we henceforth assume that, at time t , the probability density, $\mathbf{y} \mapsto X(\mathbf{y}, t)$, is uniform (constant) in a neighborhood of \mathbf{x} . In this case, the flux rate reduces to²²

$$J(\mathbf{x}, t, \mathbf{v}) = -\frac{1}{2} X(\mathbf{x}, t) \mathbf{div} \tilde{\mathbf{D}}(\mathbf{x}) \bullet \mathbf{v}, \quad (3.17)$$

the \mathbf{v} component of the vector $-\frac{1}{2} X(\mathbf{x}, t) \mathbf{div} \tilde{\mathbf{D}}(\mathbf{x})$. Roughly speaking, the local spatial uniformity assumption means that, at time t , the probability of finding a second large particle near $\sqrt{2}\mathbf{x}$, given that the first is at the origin, is locally constant in \mathbf{x} . Since our computations will be essentially local with respect to a given point \mathbf{x} , the assumption is reasonable, provided $\mathbf{y} \mapsto X(\mathbf{y}, t)$ at time t is reasonably regular.

In view of the special form of $\tilde{\mathbf{D}}(\mathbf{x})$, given in Equation (3.10), $\mathbf{div} \tilde{\mathbf{D}}(\mathbf{x})$ is radial (parallel to \mathbf{x}). Let $\mathbf{u}(\mathbf{x}) := \frac{\mathbf{x}}{|\mathbf{x}|}$, the outward radial unit vector at \mathbf{x} .²³ Then,

$$\begin{aligned} \mathbf{div} \tilde{\mathbf{D}}(\mathbf{x}) &= \nabla_{\mathbf{x}} \sigma_{\perp}(|\mathbf{x}|^2) + \mathbf{P}(\mathbf{x}) (\nabla_{\mathbf{x}} \sigma(|\mathbf{x}|^2) - \nabla_{\mathbf{x}} \sigma_{\perp}(|\mathbf{x}|^2)) \\ &\quad + (\sigma(|\mathbf{x}|^2) - \sigma_{\perp}(|\mathbf{x}|^2)) \mathbf{div} \mathbf{P}(\mathbf{x}) \\ &= \nabla_{\mathbf{x}} \sigma(|\mathbf{x}|^2) + (\sigma(|\mathbf{x}|^2) - \sigma_{\perp}(|\mathbf{x}|^2)) \mathbf{div} \mathbf{P}(\mathbf{x}) \\ &= \left(2\sigma'(|\mathbf{x}|^2) |\mathbf{x}| + \frac{d-1}{|\mathbf{x}|} (\sigma(|\mathbf{x}|^2) - \sigma_{\perp}(|\mathbf{x}|^2)) \right) \mathbf{u}(\mathbf{x}). \end{aligned} \quad (3.18)$$

For convenience, define $\xi \mapsto \psi(\xi)$ on $(0, \infty)$ by

$$\psi(\xi) := \frac{d}{d\xi} \sigma(\xi^2) + \frac{d-1}{\xi} (\sigma(\xi^2) - \sigma_{\perp}(\xi^2)), \quad (3.19)$$

so $\mathbf{div} \tilde{\mathbf{D}}(\mathbf{x}) = \psi(|\mathbf{x}|) \mathbf{u}(\mathbf{x})$.²⁴

We will be concerned with the *radially oriented* flux rate,

$$J(\mathbf{x}, t) := J(\mathbf{x}, t, \mathbf{u}(\mathbf{x})), \quad (3.20)$$

²⁰Since the physical units of $X(\mathbf{x}, t)$ are $[\frac{1}{L^d}]$, the physical units of \mathbf{j} are $[\frac{L}{T} \frac{1}{L^{d-1}}]$, a flux rate area density.

²¹ $\nabla_{\mathbf{x}}$ denotes the spatial gradient in \mathbb{R}^d . The symmetry of $\tilde{\mathbf{D}}$ is used in the second line of Equation (3.16).

²²For a square matrix valued function $\mathbf{M}(\mathbf{y})$, $\mathbf{div} \mathbf{M}(\mathbf{y})$ is defined through the identity $\mathbf{div} \mathbf{M}(\mathbf{y}) \bullet \mathbf{a} = \nabla_{\mathbf{y}} \bullet \mathbf{M}^T(\mathbf{y}) \mathbf{a}$. Recall that $\tilde{\mathbf{D}}$ is symmetric.

²³ $\mathbf{div} \mathbf{P}(\mathbf{x}) = \frac{d-1}{|\mathbf{x}|} \mathbf{u}(\mathbf{x})$.

²⁴For $d \geq 2$ all spatial integrals involving ψ will converge at the origin.

which we call the d -dimensional van Kampen flux rate.²⁵ It is a generalization to d -dimensions of the 1-dimensional flux rate introduced by van Kampen [15]. Our van Kampen flux rate then has the form²⁶

$$J(\mathbf{x}, t) = -\frac{1}{2}X(\mathbf{x}, t)\psi(|\mathbf{x}|) = -\frac{1}{2}X(\mathbf{x}, t)\left(\frac{d}{d\xi}\sigma(\xi^2) + \frac{d-1}{\xi}(\sigma(\xi^2) - \sigma_{\perp}(\xi^2))\right). \quad (3.21)$$

Note that, except for the probability density multiplier $X(\mathbf{x}, t)$, here assumed locally constant, $J(\mathbf{x}, t)$ depends only on the magnitude ξ of \mathbf{x} ; that is, on the separation.

Fix $\mathbf{x} \neq \mathbf{0}$ and consider a sufficiently regular, sufficiently small region $B(\mathbf{x}) \subset \mathbb{R}^d$ whose interior is a neighborhood of \mathbf{x} .²⁷ The net probability flux rate vector out of $B(\mathbf{x})$ (at (\mathbf{x}, t)) is the surface integral

$$\int_{\partial B(\mathbf{x})} \mathbf{j}(\mathbf{y}, t, \mathbf{n}(\mathbf{y})) dA(\mathbf{y}) = \int_{\partial B(\mathbf{x})} -\frac{1}{2}X(\mathbf{x}, t)\tilde{\mathbf{D}}(\mathbf{y})\mathbf{n}(\mathbf{y}) dA(\mathbf{y}), \quad (3.22)$$

where $\mathbf{n}(\mathbf{y})$ always denotes the unit outward normal vector to $\partial B(\mathbf{x})$ at \mathbf{y} . Using the Divergence Theorem and the form of $\tilde{\mathbf{D}}(\mathbf{y})$ in Equation (3.10), we can compute this flux:

$$\begin{aligned} \int_{\partial B(\mathbf{x})} -\frac{1}{2}X(\mathbf{x}, t)\tilde{\mathbf{D}}(\mathbf{y})\mathbf{n}(\mathbf{y}) dA(\mathbf{y}) &= -\frac{1}{2}X(\mathbf{x}, t) \int_{B(\mathbf{x})} \mathbf{div} \tilde{\mathbf{D}}(\mathbf{y}) dV(\mathbf{y}) \\ &= -\frac{1}{2}X(\mathbf{x}, t) \int_{B(\mathbf{x})} \psi(|\mathbf{y}|)\mathbf{u}(\mathbf{y}) dV(\mathbf{y}). \end{aligned} \quad (3.23)$$

Since $V(B(\mathbf{x}))$ is small we have²⁸

$$\begin{aligned} \int_{\partial B(\mathbf{x})} \mathbf{j}(\mathbf{y}, t, \mathbf{n}(\mathbf{y})) dA(\mathbf{y}) &\approx -\frac{1}{2}X(\mathbf{x}, t)\psi(|\mathbf{x}|)V(B(\mathbf{x}))\mathbf{u}(\mathbf{x}) \\ &\approx J(\mathbf{x}, t)V(B(\mathbf{x}))\mathbf{u}(\mathbf{x}). \end{aligned} \quad (3.24)$$

Thus, the vector $J(\mathbf{x}, t)\mathbf{u}(\mathbf{x})$ is (approximately) the volume average of the net probability flux out of $B(\mathbf{x})$.²⁹ The latter is (approximately) radial and its magnitude and sense — inward or outward — are completely determined by the d -dimensional van Kampen flux $J(\mathbf{x}, t)$.

If $\psi(|\mathbf{x}|) > 0$, the flux is inward, in which case there is an initial statistical tendency for particles to move together or an *attraction bias*. If $\psi(|\mathbf{x}|) < 0$, the flux is outward, in which case there is an initial statistical tendency for particles to move apart or a *repulsion bias*. If $\psi(|\mathbf{x}|) = 0$, we have a *neutral bias*.

To make our computations more explicit, we use a forcing kernel of the following specific form:

$$\mathbf{g}_{\varepsilon}(\mathbf{r}) = \phi_{\varepsilon}(|\mathbf{r}|^2)\mathbf{r} = \kappa_{\varepsilon}e^{-\frac{|\mathbf{r}|^2}{2\varepsilon}}\mathbf{r}, \quad (3.25)$$

²⁵Under our assumptions, it is the (outward) radial component of the vector $-\frac{1}{2}X(\mathbf{x}, t)\mathbf{div} \tilde{\mathbf{D}}(\mathbf{x})$.

²⁶Provided the initial probability density $X(\mathbf{x}, t)$ is locally spatially constant.

²⁷Sufficiently regular means the Divergence Theorem holds on $B(\mathbf{x})$. Sufficiently small means that the volume $V(B(\mathbf{x}))$ is small, $\mathbf{0} \notin B(\mathbf{x})$, and $\mathbf{y} \mapsto X(\mathbf{y}, t)$ is constant on $B(\mathbf{x})$.

²⁸The oriented flux rate $J(\mathbf{x}, t, \mathbf{v})$ and the van Kampen flux rate, $J(\mathbf{x}, t)$ are, in fact, flux rate densities, with physical units $[\frac{L}{T} \frac{1}{L^d}]$.

²⁹The probability flux out of $B(\mathbf{x})$ is exactly radial whenever $\partial B(\mathbf{x})$ consists of coordinate surfaces in spherical coordinates.

where $\sqrt{\varepsilon}$ is a correlation length and κ_ε is a constant that depends on the correlation parameter ε and the physical dimension d . The forcing kernel has this form if the velocities of the small particles are assumed to have a Maxwell distribution, which is physically plausible. We call \mathbf{g}_ε the *Maxwell kernel*.

In this case, the **difference diffusion matrix** $\tilde{\mathbf{D}}_\varepsilon(\mathbf{x})$, defined in Equation (3.9), has the explicit form:³⁰

$$\begin{aligned}\tilde{\mathbf{D}}_\varepsilon(\mathbf{x}) &= D_\varepsilon \mathbf{1} - \mathbf{D}_\varepsilon(\mathbf{x}) \\ &= \sigma_{\varepsilon\perp}(|\mathbf{x}|^2) \mathbf{P}^\perp(\mathbf{x}) + \sigma_\varepsilon(|\mathbf{x}|^2) \mathbf{P}(\mathbf{x}) \\ &= D_\varepsilon \left(1 - e^{-\frac{|\mathbf{x}|^2}{2\varepsilon}}\right) \mathbf{P}^\perp(\mathbf{x}) + D_\varepsilon \left(1 - e^{-\frac{|\mathbf{x}|^2}{2\varepsilon}} + \frac{|\mathbf{x}|^2}{\varepsilon} e^{-\frac{|\mathbf{x}|^2}{2\varepsilon}}\right) \mathbf{P}(\mathbf{x}),\end{aligned}\tag{3.26}$$

where

$$D_\varepsilon = \frac{\varepsilon}{2} \kappa_\varepsilon^2 (\pi\varepsilon)^{\frac{d}{2}}.\tag{3.27}$$

In Equation (3.26)

$$\sigma_{\varepsilon\perp}(|\mathbf{x}|^2) = D_\varepsilon \left(1 - e^{-\frac{|\mathbf{x}|^2}{2\varepsilon}}\right) \quad \text{and} \quad \sigma_\varepsilon(|\mathbf{x}|^2) = D_\varepsilon \left(1 - e^{-\frac{|\mathbf{x}|^2}{2\varepsilon}} + \frac{|\mathbf{x}|^2}{\varepsilon} e^{-\frac{|\mathbf{x}|^2}{2\varepsilon}}\right).\tag{3.28}$$

The **Maxwell kernel** clearly induces a positive-definite, symmetric, radially dominant **difference diffusion matrix**, provided $\mathbf{x} \neq \mathbf{0}$. To satisfy Desideratum 4, take $D_\varepsilon = \kappa_\varepsilon^2 \frac{\varepsilon}{2} (\pi\varepsilon)^{d/2} = 1$.

For the Maxwell kernel, the d -dimensional van Kampen flux is:

$$J(\mathbf{x}, t) = -\frac{1}{2} X(\mathbf{x}, t) \frac{D_\varepsilon}{\varepsilon^2} e^{-\frac{|\mathbf{x}|^2}{2\varepsilon}} |\mathbf{x}| ((2+d)\varepsilon - |\mathbf{x}|^2).\tag{3.29}$$

Therefore, the region $\{\mathbf{x} \in \mathbb{R}^d : |\mathbf{x}| < \sqrt{(2+d)\varepsilon}\}$ has an attraction bias, and the region $\{\mathbf{x} \in \mathbb{R}^d : |\mathbf{x}| > \sqrt{(2+d)\varepsilon}\}$ has a repulsion bias. The points of neutral bias have measure zero in \mathbb{R}^d . Figure (2) is a graph of the normalized van Kampen flux, $\frac{J(\mathbf{x}, t)}{X(\mathbf{x}, t)}$, as a function of the separation, $\xi = |\mathbf{x}|$, for the Maxwell kernel.

³⁰The formula given in Equation (3.5) is used in this computation. So, in view of the comment in Footnote 14, the units of κ_ε must be adjusted to be consistent with those of c_ε , namely $[\frac{L^2}{T}]$.

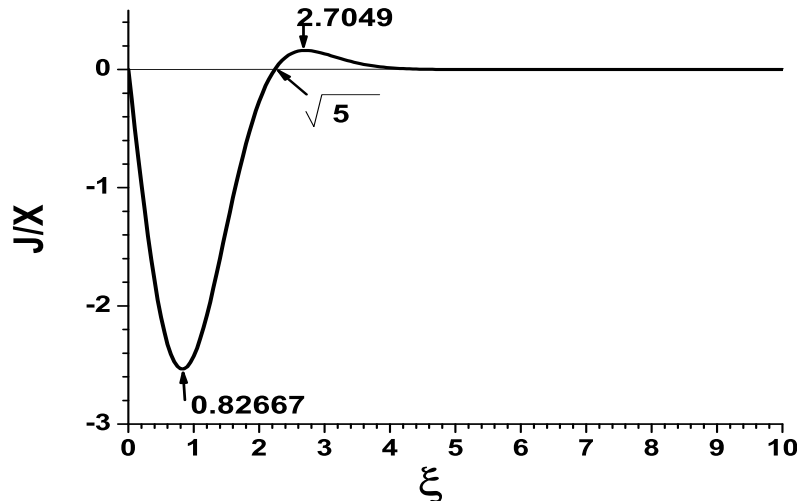


Figure 2: The normalized van Kampen flux , $\frac{J(\mathbf{x},t)}{X(\mathbf{x},t)}$, as a function of the separation, $\xi = |\mathbf{x}|$. Computation shown for the Maxwell kernel (Equation (3.29)) with $\varepsilon = 1$, $d = 3$, and $D_\varepsilon = 1$.

Note that the radius of the attraction-biased region is proportional to the correlation length $\sqrt{\varepsilon}$ and increases with dimension. The ratio of the minimum value to the maximum value is independent of the correlation length $\sqrt{\varepsilon}$ and increases with dimension. For $d = 3$, the magnitude of this ratio is about 16, so we can say that the tendency to move apart is much weaker than the tendency to move together. For a given dimension, the magnitudes of the minimum and maximum increase as the correlation length decreases. We expect the same results for any unimodular distribution.

4 Conclusions, Comments, and Open Questions

We begin with a model for a solute of finitely many large particles in a solvent of infinitely many small particles. Our model is a stochastic limit from Newtonian particle interactions. It retains only the effects of interactions between the small and the large particles; interactions among the large particles and interactions among the small particles are systematically neglected. We then analyze the resulting correlated Brownian motions for a pair of large particles. Our specific computations assume that the velocities of the small particles have a Maxwellian distribution. By use of a generalized van Kampen flux rate, we show that there is an initial statistical tendency for the pair to move together from a uniform state, provided they are sufficiently close to begin with. On the other hand, we also show that the particles always tend to move apart in the long term, provided the dimension of the physical space is three or higher. (In two dimensions the long term behavior is recurrent.) The transition between our short term and long term results is not yet understood and needs further study. It is possible

that our analysis no longer holds in its simple form once there is a significant deviation from a uniform state.

Furthermore, our computations also show that there is a much weaker initial tendency for the particles to move apart from a uniform state if they are not close to start with. This is unexpected and also requires further thought. Is there a physical basis for this? Or, might it be an artifact of the model? Since our model isolates a pure second-order effect, it may be that there are higher-order effects to consider which would alter the conclusion.

These comments beg another question: Can correlated Brownian motions be defined in spatial dimension $d \geq 2$ for which a pair of Brownian particles are trapped for all time at a sufficiently close distance from one another?

Finally, it would be useful to be able to estimate or compute from our model the time it would take for the transition from the initial depletion effect to the long-term transient behavior. Even for the Maxwell case, we do not have a way to do this.³¹

5 Acknowledgements

The final presentation of the paper has profited from careful refereeing. In particular, the authors thank an anonymous referee who suggested the third open question. One of the authors, JAM, gratefully acknowledges partial support from the following: grant number CBET 0730626 from the National Science Foundation and grant number MURI DAAD 19-03-1-0169 from the Army Research Office.

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³¹The authors thank an anonymous referee who suggested this question.

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