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On the Diffusion Coefficient: The Einstein Relation and Beyond*

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We present a detailed derivation of the closed-form expression for the diffusion coefficient that was initially obtained by Einstein [4]. The present derivation does not make use of a fictitious force as did the original Einstein derivation, but instead concentrates directly on establishing a dynamic equilibrium between the forces of pressure and friction acting on a Brownian particle. This approach makes it easier to understand the true essence of the argument, and thus makes it simpler to apply the argument in a more general case or setting. We demonstrate this by deriving the equation of motion of a Brownian particle that is under the influence of an external force in the fluid with a non-constant temperature. This equation extends the well-known Smoluchowski approximation [24] to the case of non-constant temperature, and offers new insights into the Ludwig-Soret and Enskog-Chapman effects (providing also a scholar example explaining the need for a stochastic integral). The key point in the derivation is reached by applying the Einstein dynamic equilibrium argument together with the conservation of the number of particles law. We show that this approach leads directly to the Kolmogorov forward equation whenever the setting is Markovian. The same method can also be applied in the case of interacting Brownian particles satisfying the van der Waals equation. In this setting we first demonstrate that the presence of short-range repulsive forces between Brownian particles tends to increase the diffusion coefficient, and the presence of long-range attractive forces between Brownian particles tends to decrease it. The method of derivation then leads to a nonlinear partial differential equation which in the case of weak interaction reduces to the Fokker-Planck equation. One of the main aims of the present article is to demonstrate that the Einstein argument leads to a truly dynamical theory of diffusion.

1. Introduction

Stochastic differential equations are presently used in a diversity of scientific areas to model various phenomena. It appears to be common practice in many of these models to derive a stochastic differential equation by incomplete and ad hoc arguments rather than from the first principles that describe the laws governing the phenomenon under consideration. (As an illustration take the field of financial mathematics.) In order to examine possibilities of improving upon such a practice, it is our aim in this paper to revisit the origins of stochastic differential equations and display some key points of modelling which lead to a dynamical theory of diffusion.

As a point of departure we take Fick's law [7] which is a definition of the diffusion coefficient D . Next we show that a dynamic equilibrium of Einstein [4] between the forces of pressure and

* This is an expanded version of the Research Report No. 416 (2000) (17 pp) in which refinements of the Ludwig-Soret and Chapman-Enskog effects predicted by the equation (5.13) are displayed (Subsections 5-10 of Section 5 are a new addition). The present version also includes 16 new references that are found related to assumptions and results of the theory exposed.

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friction, applied together with the conservation of the number of particles law, lead directly to the Kolmogorov forward equation [16] i.e. the Fokker-Planck equation ([8], [22]). Itô's theory ([11], [12]) of a stochastic integral can then be used to transform the forward equation into a stochastic differential equation of motion.

The train of thought followed in this derivation reflects the historical development of these ideas and concepts throughout the first half of the twentieth century, and we fully take advantage of subsequent developments and powerful mathematical techniques. Nonetheless, for the sake of simplicity we do not state many of the mathematical conditions explicitly. Likewise, we do not review historical facts in full detail but instead refer to the relevant literature.

The above derivation is carried out under different physical conditions (presence of external forces, non-constant temperature, interacting Brownian particles) and a physical interpretation of the diffusion coefficient in each case is given. It is important to understand, however, that the role of this interpretation is largely hypothetical. Indeed, by introducing $\widetilde{D}$ in the analysis below we in essence address the question of determining a diffusion coefficient which would produce the same particle flow without any external influence.

Section 2 introduces the notation and recalls some basic facts and definitions. Section 3 presents a detailed derivation of the Einstein relation [4]. This derivation does not make use of a fictitious force but instead concentrates directly on establishing a dynamic equilibrium between the forces of pressure and friction (*Figure 3*). Section 4 shows how the Einstein argument can be extended to yield the equation of motion of a Brownian particle that is under the influence of an external force. This re-establishes the classic Smoluchowski result [24]. Section 5 examines consequences of the Einstein argument in the case when the fluid temperature is not constant. A physical interpretation of the correction term appearing in the diffusion coefficient is given, and the equation of motion derived offers new insights into the Ludwig-Soret and Enskog-Chapman effects (providing also a scholar example explaining the need for a stochastic integral). Section 6 unifies the two derivations of Sections 4 and 5 into a single derivation. In this way a complete physical interpretation of the stochastic differential equation (6.5) is obtained. This extends the classic Smoluchowski argument [24] to the case of non-constant temperature. The main novelty in this context is the fact that functions $\mu(t,x)$ and $\sigma(t,x)$ from (6.5) solve partial differential equations (with initial-boundary conditions). A more explicit analysis shows that this provides a unification of the diffusion equation and the heat equation. Section 7 examines changes in the diffusion coefficient when the equation of state of Brownian particles in the Einstein argument deviates from the general-gas law to the van der Waals equation. This leads to a nonlinear partial differential equation which in the case of weak interaction reduces to the Fokker-Planck equation.

2. Preliminaries

In this section we will fix the notation and collect basic facts and definitions that will be used in the rest of the paper.

A spherical particle with a diameter of the order of several μm $(= 10^{-6}m)$ will be called a *Brownian particle*. Its mass will be denoted by m . Below we will consider a collection of N Brownian particles suspended in a fluid. It presumes that each of these particles is identical to the others, and that N is a large number (of the order of 10^{13} for instance). The fluid is at rest and

at a sufficiently high temperature such that quantum effects do not matter. Temperatures around room temperature ($20^{\circ}C$) are good examples.

By *fluid* we mean a *gas* or a *liquid*. A fluid consists of identical molecules of a diameter of the order of several Å ($= 10^{-10}m$) . Thus a Brownian particle has a diameter about ten thousand times larger than a fluid molecule. The molecules are separated by "great distances" in a gas, while they are "touching" in a liquid. Their number is of the order of *Avogadro's number* $N_0 = 6.023 \cdot 10^{23}$.

Due to the impacts by molecules of the fluid, each Brownian particle executes a Brownian motion. The collective motion of all Brownian particles in the fluid is termed a *diffusion*. It is established experimentally that this motion tends to distribute the Brownian particles uniformly within the fluid. A possible mutual interaction between Brownian particles is assumed negligible and completely ignored until Section 7.

In the case of a gas the impacts by molecules are perfectly elastic collisions. It is known that the number of collisions may be of the order of 10^{21} per second. The impacts by molecules are more complicated in the case of a liquid. They are produced by vibrations of liquid molecules and their translations. In this case Brownian particles may be thought of as "sliding" through the "touching" liquid molecules.

Letting $N(t, B)$ denote the number of Brownian particles in a set B at time t , we interpret the *average number* of Brownian particles at position x at time t as

$$\nu(t,x) \approx \frac{N(t,B)}{vol(B)} \quad (\text{for } B \ni x \text{ small}). \tag{2.1}$$

Then $\int_B \nu(t,x)\,dx$ represents the *total number* of Brownian particles in a measurable set B at time t , and this leads (using the law of large numbers) to a probabilistic interpretation of

$$p(t,x) \approx \frac{\nu(t,x)}{N} \quad (\text{for } N \text{ large}) \tag{2.2}$$

as the *transition density* of the position process, i.e.

$$P(X_t \in C) = \int_C p(t,x)\,dx \tag{2.3}$$

for each measurable set C , where X_t is the position of a Brownian particle at time t .

The simultaneous coexistence of N Brownian particles in the fluid may be thought of as N independent realisations of the position process $X = (X_t)_{t \geq 0}$, and the probabilistic interpretation (2.3) is therefore in terms of *relative frequencies*. (On this point we refer to Fürth's note (10) in [6] pp. 99-101. See also his note (17) in [6] pp. 108-111.) It should be kept in mind however that this interpretation may be fully valid only as long as the Brownian particles do not interact with each other.

Fick's law [7] states that the number of Brownian particles passing through a small area ΔA during a small time interval Δt is given by

$$\Delta N = -D\,\frac{\partial \nu}{\partial n}\,\Delta A\,\Delta t \tag{2.4}$$

where n is the unit vector normal to the area ΔA pointing in the direction of the particle flow, and D is the *diffusion coefficient* of the fluid. This relation is a *definition* of the diffusion

coefficient, it has been established experimentally, and the diffusion equation $\nu_t = D\,\nu_{xx}$ is an easy consequence of (2.4). We shall return to this issue later (cf. (4.5)-(4.7)).

The general-gas law is the equation of state of an ideal gas given by

$$pV = n\,R\,T \tag{2.5}$$

where p is the *pressure* of the gas on the walls of the container (attributed to the molecular bombardment), V is the *volume* of the container, n is the *number of moles* of the gas, R is the *universal gas constant*, and T is the *temperature* of the gas. We recall that one mole of the gas contains N_0 molecules, and that the temperature T is a measure of the average *translational* kinetic energy per gas molecule:

$$\tfrac{1}{2}m\,v_{rms}^2 = \tfrac{3}{2}k\,T \tag{2.6}$$

where m is the mass of a gas molecule, v_{rms} is the root-mean-square velocity of a gas molecule, and $k = R/N_0$ is the *Boltzmann constant*. The identity (2.6) is a fundamental result of the kinetic theory of gases. We display it here although we will not use it explicitly in the sequel.

The general-gas law (2.5) is an experimental fact established in stages (for more details see e.g. [28] pp. 493-495). It can also be derived from statistical mechanics (see e.g. [23] pp. 124-126). Any gas behaves as an ideal gas if its density its very low. This is true for most gases at room temperature and atmospheric pressure. Deviations from the general-gas law (2.5) correspond to the change in state from a gas to a liquid (cf. Section 7).

A key point in the Einstein argument (cf. Section 3) is found on pages 86-87 of [4]: "But a different interpretation arises from the standpoint of the molecular-kinetic theory of heat. According to this theory, a dissolved molecule differs from a suspended body *only* in size, and it is difficult to see why suspended bodies should not produce the same osmotic pressure as an equal number of dissolved molecules." In a likewise manner it will be assumed in the derivation below that *the system of N Brownian particles suspended in a fluid with temperature T satisfies the equation of state (2.5)* with $n = N/N_0$. In Section 2 of [4] Einstein demonstrates that the same statistical-mechanics arguments which lead to the equation of state (2.5) can also be applied to the system of N Brownian particles. He concludes the section with the following words (cf. [4] pp. 90-91): "This analysis shows that the existence of osmotic pressure can be deduced from the molecular-kinetic theory of heat, and that, according to this theory, equal numbers of solute molecules and suspended particles behave identically as regards osmotic pressure."

It is beyond our reach in the present text to enter into the arguments of statistical mechanics that lead to (2.5) or any of its variants. Instead we take the fact that the system of N Brownian particles suspended in a fluid satisfies the equation of state (2.5) as a point of departure to what follows. A physical explanation can be given that makes this premise quite intuitive, if one makes a simple comparison with the basic hypotheses of the kinetic theory of ideal gases (see e.g. [28] pp. 507-508). When the average number per unit volume is not uniform, this premise becomes even more inherent to Brownian particles than gas molecules, because the Brownian particles move very slowly. It follows that a large irrelevant portion of the container not close to the wall where p is exerted or measured can be disregarded so that V in (2.5) can be taken small. This local argument is used implicitly in (3.1) below and is related to the final remark in Section 3. In Section 7 we shall briefly analyse what happens when (2.5) is superseded by *the van der Waals equation*.

We shall conclude this section by recalling two basic facts for the sake of completeness. First, the *pressure at a point* within the fluid is defined by $p = \lim_{\Delta A \to 0} \Delta F / \Delta A$ where ΔF is the average force upon the surface area ΔA containing the point. Second, if a particle of mass m moves with velocity v throughout the medium with a *friction coefficient* β , then the *frictional force* exerted upon the particle equals $F_f = -m\beta v$. It follows that if a force F is exerted upon such a particle, the particle will move with velocity $v = F/m\beta$.

Following Einstein [4] we shall apply the preceding argument to a Brownian particle moving in a fluid. If the fluid is an ideal gas, then the friction may be called a *Doppler friction* (cf. [27] p. 824). It is based on the fact that the Brownian particle will be hit by more gas molecules from the direction in which it moves. If the fluid is a liquid, then the friction may be called a *Stokes friction*. In this case classic hydrodynamic arguments (see e.g. [21] p. 291) lead to *the Stokes formula*:

$$\beta = \frac{6\pi r}{m}\,\eta \tag{2.7}$$

where r is the radius of the Brownian particle, m is its mass, and η is the *viscosity coefficient* of the liquid. A detailed discussion of a valid application of the Stokes formula (2.7) is given in the Fürth's note (6) of [6] (pp. 92–96).

3. Derivation of the Einstein relation

1. Our main aim in this section is to present a detailed derivation of the closed-form expression for the diffusion coefficient D of (2.4) that was initially obtained by Einstein [4]. The derivation below does not make use of a fictitious force as did the original Einstein derivation [4] (or its review in [19] pp. 18-20) but instead concentrates *directly* on establishing a dynamic equilibrium between the forces of pressure and friction acting upon a Brownian particle. This approach makes it easier to understand the true essence of the argument, and thus makes it easier to apply the argument in a more general case or setting (cf. Sections 4-6).

Fürth states in his note (7) of [6] (pp. 96-97): "It is notable that the result for D no longer contains the applied force K . This must, however, be the case, if the method introduced here" (this refers to [4]) "is successful in its aim, since K is a completely fictitious force which has nothing to do with the process of diffusion itself. This circumstance indicates that it must also be possible to obtain the result without the introduction of the fictitious force". He then continues by saying that "such deductions have actually been carried out" and quotes two papers by Ph. Frank from 1915 and 1917. Fürth fails to note, however, that the Einstein subsequent paper [5] (reproduced in [6] as the fifth paper on pages 68-85), presents such an argument (see pp. 69-76). The argument which follows, apart from minor details, is essentially identical.

2. *Derivation*. Take a cylindrical vessel filled with a fluid, and suspend N Brownian particles into the fluid at time $t = 0$ as shown on *Figure 1*. Due to the impacts by fluid molecules, Brownian particles will begin the process of diffusion (cf. Section 2).

Consider the state in the vessel at a time $t > 0$ later on. As there will be a higher concentration of Brownian particles on the left-hand side than on the right-hand side, as shown on *Figure 2*, the forces of pressure $p(x)$ and $p(x+\Delta x)$ will be exerted on the (imaginary) cross-sectional surfaces

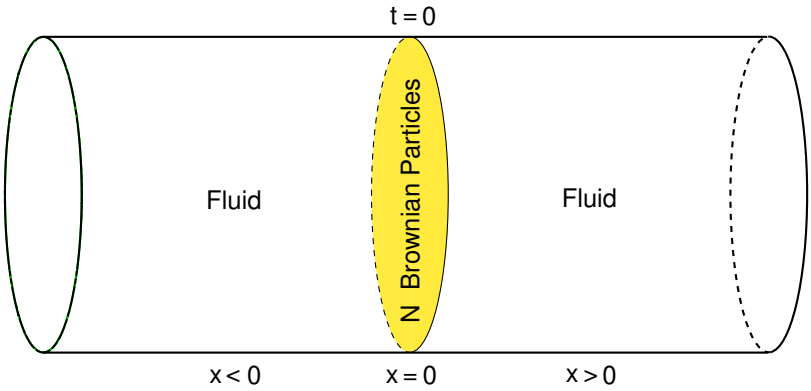

Figure 1. Brownian particles suspended in a fluid at time $t = 0$ so that all N of them are lying uniformly distributed in the cross-section at $x = 0$. In terms of the position process $(X_t)_{t\geq 0}$ it means that $X_0 = 0$ with probability one. Due to the impacts by fluid molecules, Brownian particles will begin the process of diffusion.

S_1 and S_2 so that $p(x) > p(x+\Delta x)$. As a result we have:

$$\frac{p(x) - p(x+\Delta x)}{\Delta x} = \frac{F(x) - F(x+\Delta x)}{A\,\Delta x} = \frac{N_1 F_p}{A\,\Delta x} \tag{3.1}$$

where A is the area of S_1 and S_2 respectively, N_1 is the number of Brownian particles contained in the volume ΔV surrounded by S_1 and S_2 , and F_p is the force exerted upon each Brownian particle from ΔV . Passing to the limit in (3.1) for $\Delta x \to 0$, we find:

$$\frac{\partial p}{\partial x} = -\nu F_p \tag{3.2}$$

where $\nu = \nu(t, x)$ is the average number of Brownian particles given by (2.1).

Thus, due to the concentration difference, each Brownian particle in the volume ΔV is being acted upon by a force F_p satisfying (3.2). The force F_p will impose on each Brownian particle from ΔV a velocity v satisfying:

$$F_p = m\beta v \tag{3.3}$$

where β is the friction coefficient of the fluid. The identity (3.3) embodies a *dynamic equilibrium between the forces of pressure and friction*, i.e. $F_p = -F_f$ (cf. Section 2) as shown on *Figure 3*.

The system of N_1 Brownian particles in the volume ΔV satisfies (cf. Section 2) the equation of state (2.5) with $N_1 = nN_0$. It follows:

$$p = \frac{nN_0}{\Delta V}\,\frac{R}{N_0}\,T = \nu kT \ . \tag{3.4}$$

Differentiating in (3.4), and using (3.2) and (3.3), we find:

$$\frac{\partial p}{\partial x} = kT\,\frac{\partial \nu}{\partial x} = -\nu F_p = -m\beta\nu v \ . \tag{3.5}$$

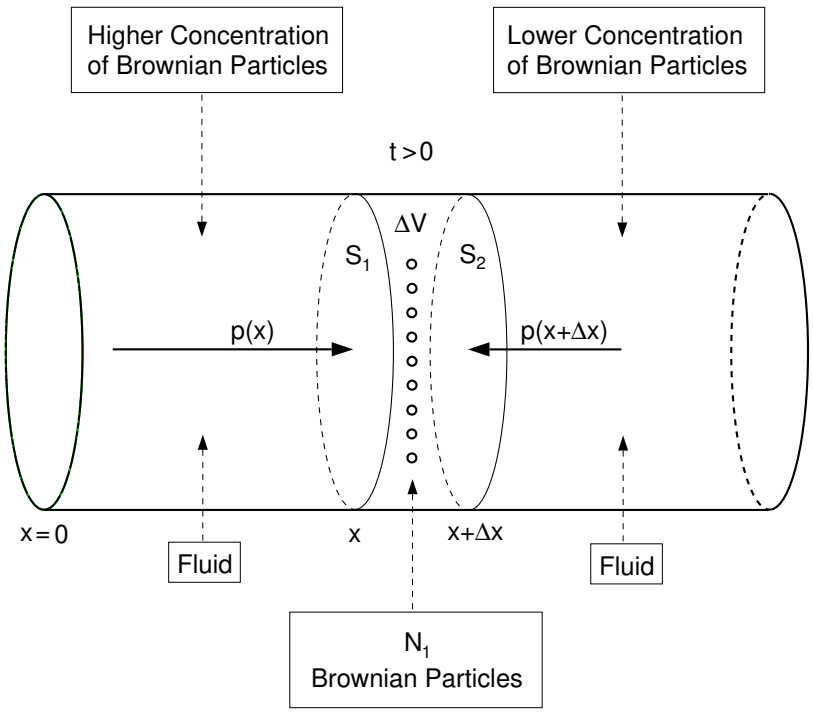

Figure 2. A sequel to Figure 1 showing the state in the vessel at a time $t > 0$ later on. Due to the difference in concentration, the forces of pressures $p(x)$ and $p(x+\Delta x)$ are exerted upon the cross-sectional surfaces S_1 and S_2 so that $p(x) > p(x+\Delta x)$. As a result each Brownian particle in the volume ΔV is being acted upon by a force F_p imposing a velocity v in accordance with (3.3).

On the other hand, it follows from (2.4) that

$$\nu v = \frac{N_1}{A\,\Delta x}\,\frac{\Delta x}{\Delta t} = \frac{N_1}{A\,\Delta t} = -D\,\frac{\partial \nu}{\partial x}\ . \tag{3.6}$$

Inserting this into (3.5) we obtain:

$$kT\,\frac{\partial \nu}{\partial x} = m\beta D\,\frac{\partial \nu}{\partial x}\ . \tag{3.7}$$

Cancelling the term $\partial\nu/\partial x$ on both sides, and dividing through by $m\beta$, we conclude:

$$D = \frac{kT}{m\beta}\ . \tag{3.8}$$

This completes the derivation. The formula (3.8) is called *the Einstein relation*. The quantity $1/m\beta$ is said to be a *mobility* (by definition it represents a frictional velocity per unit force).

3. When the fluid is a liquid and Brownian particles are spheres of radius r , we may insert (2.7) into (3.8), and this leads to the following identity:

$$D = \frac{kT}{6\pi r\eta} \tag{3.9}$$

where η is the viscosity coefficient of the liquid. The formula (3.9) is sometimes referred to as *the*

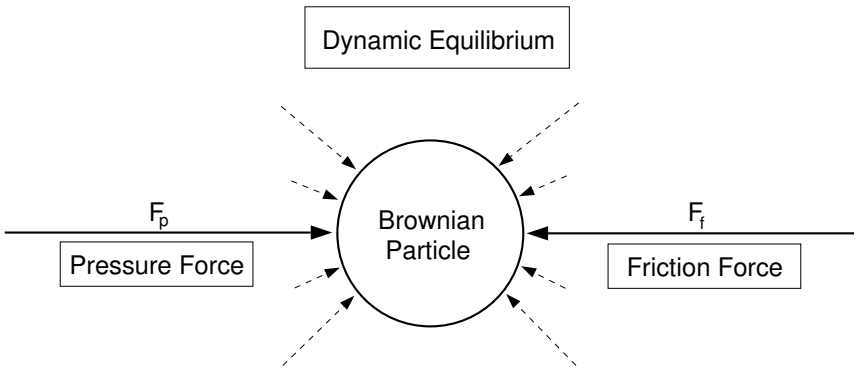

Figure 3. A sequel to Figure 2 showing one Brownian particle from the volume ΔV . The impacts by fluid molecules from the left constitute the pressure force or the pushing part of the impacts. The impacts by fluid molecules from the right constitute the friction force or the damping part of the impacts. A dynamic equilibrium states that these two forces are opposite in direction but equal in magnitude.

Stokes-Einstein formula. It is the key result of [4] where it is used in conjunction with a fundamental solution of the diffusion equation $\nu_t = D\,\nu_{xx}$. (The latter is an easy consequence of (2.4) although Einstein derived it differently i.e. assuming stationary independent increments). We refer to Fürth's note (13) in [6] (pp. 102-104) for experimental confirmations of these results.

4. *Remark*. Brownian particles move throughout the fluid because of the impacts made by fluid molecules. A possible interaction between Brownian particles in this process may be neglected as a cause of the motion (at least when one wants to study the motion of a single Brownian particle and think of N Brownian particles as N independent realisations of the same phenomenon). Thus it would be wrong to think that the force of pressure, which in the derivation above is exerted upon the cross-sectional surfaces S_1 and S_2 by means of Brownian particles, also acts upon every Brownian particle from the volume ΔV by means of other Brownian particles. A more correct view is obtained by realizing that each Brownian particle from ΔV receives impacts by fluid molecules from both sides (see *Figure 3*). The number of these impacts is enormous, and they tend to cancel each other but fail to do so in reality (due to the specific proportion in size between the Brownian particle and liquid molecules). When the *pushing* force prevails from the left-hand side, it is counteracted by the *damping* force from the right-hand side, both originating from the impacts made by fluid molecules. The exchange of winning sides happens very rapidly (at very low time scales) and along any line in the three-dimensional space (the cylindrical vessel of which is just a convenient idealisation). The force of pressure in the derivation above quantifies the average magnitude of the winning force having its cause in fluid molecules. It is in this point that the real power of the argument rests. The resulting dynamic equilibrium is illustrated in *Figure 3*.

4. Presence of external force

1. In this section we show how the Einstein argument (cf. Section 3) can be extended to yield the equation of motion of a Brownian particle that is under the influence of the external force:

(4.1) $$F_e \,=\, m\,A(t,x)$$

where m is the mass of the Brownian particle. The result obtained is completed in Section 6 below.

2. *Derivation*. As before, take a cylindrical vessel filled with a fluid and suspend N Brownian particles into the fluid at time $t = 0$, as shown on *Figure 1*. Due to the impacts by fluid molecules, Brownian particles will begin the process of diffusion (cf. Section 2). Assume moreover that each Brownian particle is under the influence of the external force (4.1).

Consider the state in the vessel at a time $t > 0$ later on. It follows, as in the derivation above (cf. Section 3), that each Brownian particle in the volume ΔV is being acted upon by the force

(4.2) $$F_p \,=\, -kT\,\frac{\nu_x}{\nu}$$

which is caused by the concentration difference (see *Figure 2*). This force is then being superposed with the force (4.1), imposing on each Brownian particle from ΔV a velocity v satisfying:

(4.3) $$F_p + F_e \,=\, m\beta v \,=\, m\beta\,\frac{\nu v}{\nu} \,=\, -m\beta\,\frac{\widetilde{D}\nu_x}{\nu}$$

where $\widetilde{D}$ is a diffusion coefficient corresponding to the given particle flow (recall (3.6)). Inserting (4.1) and (4.2) into (4.3), we obtain the following identity:

(4.4) $$\widetilde{D} \,=\, \frac{kT}{m\beta} - \frac{A}{\beta}\frac{\nu}{\nu_x}\ .$$

On the other hand, by the conservation of the number of particles law (and the divergence theorem), we find that ν and $\widetilde{D}$ solve the diffusion equation:

(4.5) $$\nu_t \,=\, div\,(\widetilde{D}\ grad\,\nu) \,=\, \widetilde{D}_x\nu_x + \widetilde{D}\nu_{xx}\ .$$

This argument is standard and goes as follows. From the definition of $\widetilde{D}$ in (4.3), i.e. Fick's law (2.4) with $\widetilde{D}$ in place of D , we see that

(4.6) $$\begin{aligned} -N = \int_{t_1}^{t_2} dt \int_S (\widetilde{D}\nu_x)(t,s)\,ds &= A\int_{t_1}^{t_2} dt\,\Big((\widetilde{D}\nu_x)(t,x+\Delta x) - (\widetilde{D}\nu_x)(t,x)\Big) \\ &= A\int_{t_1}^{t_2} dt \int_x^{x+\Delta x} (\widetilde{D}\nu_x)_x(t,x)\ dx \end{aligned}$$

represents the number of Brownian particles passing through $S := S_1 \cup S_2$ into ΔV during the time interval $[t_1, t_2]$. On the other hand, recalling the interpretation of (2.1), we know that

(4.7) $$\int_{\Delta V} \Big(\nu(t_2,z) - \nu(t_1,z)\Big)\,dz = \int_{t_1}^{t_2} dt \int_{\Delta V} \nu_t(t,z)\,dz = A\int_{t_1}^{t_2} dt \int_x^{x+\Delta x} \nu_t(t,x)\ dx$$

represents the difference between the number of Brownian particles in ΔV at times t_1 and t_2 . By the conservation of the number of particles law, the two numbers (4.6) and (4.7) must be equal. Hence $\nu_t = (\widetilde{D}\nu_x)_x$ or more generally $\nu_t = div\,(\widetilde{D}\,grad\,\nu)$ if one uses the divergence theorem in (4.6) (in the three-dimensional case for instance). This establishes (4.5).

Differentiating in (4.4) we find that

$$\widetilde{D}_x \,=\, -\frac{1}{\beta}\,\frac{A_x\nu\nu_x + A(\nu_x)^2 - A\nu\nu_{xx}}{(\nu_x)^2}\ . \tag{4.8}$$

Inserting (4.8) and (4.4) into (4.5) we obtain:

$$\nu_t = -\frac{1}{\beta}\,A_x\nu - \frac{1}{\beta}\,A\nu_x + \frac{1}{\beta}\,\frac{A\nu\nu_{xx}}{\nu_x} + \left(\frac{kT}{m\beta} - \frac{A}{\beta}\frac{\nu}{\nu_x}\right)\nu_{xx} = -\left(\frac{A}{\beta}\,\nu\right)_x + \frac{kT}{m\beta}\,\nu_{xx}\ . \tag{4.9}$$

Given that the position process $(X_t)_{t\geq 0}$ of (2.3) is a *Markov process*, we can now recognize (4.9) as a *Kolmogorov forward equation* with drift $\mu = A/\beta$ and diffusion coefficient $D = kT/m\beta$ (cf. [8], [22], [16]). It follows that the equation of motion is given by

$$dX_t \,=\, \frac{A(t,X_t)}{\beta}\ dt + \sqrt{2D}\ dB_t \tag{4.10}$$

where $D = kT/m\beta$, the process $(B_t)_{t\geq 0}$ is a standard Wiener process, and (4.10) is understood in Itô's sense (cf. [11], [12]). This completes the derivation.

3. *Remark*. The result of (4.9)-(4.10) is known as *the Smoluchowski approximation*. It has been derived by Smoluchowski [24] using different methods. Detailed discussions of the Smoluchowski approximation are given in [1] (Chapter II) and [19] (Section 10) offering conditions for (4.10) to be a valid approximation of the motion. Clearly, this is closer to the truth if the external force is slowly varying. Moreover, a breakdown of the Markov property (independent increments) for small time intervals, and likewise Fick's law (both implying non-differentiability of the sample paths), requires also that the time between two observations be large in comparison with the relaxation time $1/\beta$ if (4.10) is to be valid. We refer to [6] (pp. 34-35) for a simple argument in support of the latter fact. It also extends to the equations obtained in Sections 5 and 6 below.

5. Non-constant temperature

1. In this section we examine consequences of the Einstein argument (cf. Section 3) in the case when the temperature T of the fluid is not constant. Recalling the interpretation of the temperature as a measure of the average translational kinetic energy per fluid molecule (cf. (2.6)), it becomes clear that we must also account for the size of T_x if we want to describe the diffusion coefficient D of (2.4). This suggests that it is not sufficient to replace T in (3.8) by the function $T(t,x)$.

We will now derive the extension of the formula (3.8) in the case when the temperature

$$T \,=\, T(t,x) \tag{5.1}$$

of the fluid is a function of position and time.

2. *Derivation*. As before, take a cylindrical vessel filled with a fluid and suspend N Brownian particles into the fluid at time $t = 0$, as shown on *Figure 1*. Due to the impacts by fluid molecules, Brownian particles will begin the process of diffusion (cf. Section 2). Assume moreover that the temperature of the fluid is given by (5.1).

Consider the state in the vessel at a time $t > 0$ later on. It follows, as in the derivation above (cf. Section 3), that each Brownian particle in the volume ΔV is being acted upon by the force F_p satisfying (3.2), which is caused by the concentration difference (see *Figure 2*). The force F_p imposes on each Brownian particle from ΔV a velocity v satisfying (3.3). The pressure at a point of the liquid is again given by (3.4). Differentiating in (3.4), and using (3.2) and (3.3), we find by means of (3.6) that

$$\frac{\partial p}{\partial x} = kT\,\frac{\partial \nu}{\partial x} + k\nu\,\frac{\partial T}{\partial x} = -\nu F_p = -m\beta\nu v = m\beta\widetilde{D}\,\frac{\partial \nu}{\partial x}\ . \tag{5.2}$$

where $\widetilde{D}$ is a diffusion coefficient corresponding to the given particle flow. It follows from (5.2) that the following identity holds:

$$\widetilde{D} = \frac{kT}{m\beta} + \frac{kT_x}{m\beta}\frac{\nu}{\nu_x} \tag{5.3}$$

(cf. (4.4) above). Observe that (5.3) can be rewritten as follows:

$$\widetilde{D} = \frac{kT}{m\beta}\left(1 + \frac{(\log T)_x}{(\log \nu)_x}\right)\ . \tag{5.4}$$

On the other hand, by the conservation of the number of particles law (cf. (4.6)-(4.7)) we know that ν and $\widetilde{D}$ solve the diffusion equation:

$$\nu_t = div\,(\widetilde{D}\ grad\,\nu) = \widetilde{D}_x\nu_x + \widetilde{D}\nu_{xx}\ . \tag{5.5}$$

This equation should be coupled with the identity (5.4).

Thus, instead of the single formula (3.8) for the diffusion coefficient, we have obtained a system of two equations (5.4) and (5.5) with two unknowns ν and $\widetilde{D}$. We shall now proceed by giving a physical interpretation of the correction term $(\log T)_x/(\log \nu)_x$ appearing in (5.4).

3. Assume first that T is constant. Then it follows as in the derivation above (cf. Section 3) that

$$F_{p,c} = -kT\,\frac{\nu_x}{\nu} \tag{5.6}$$

is the force per Brownian particle due purely to the concentration difference (recall the final remark of Section 3). Hence we see that

$$v_{press} = -\frac{kT}{m\beta}\,\frac{\nu_x}{\nu} \tag{5.7}$$

is the velocity of a Brownian particle due purely to the concentration difference (as if the temperature were constant).

Assume next that ν is constant. Then it follows from (3.2) and (3.4) that

$$F_{p,t} = -kT_x \tag{5.8}$$

is the force per Brownian particle due purely to the temperature difference (recall the interpretation

of the temperature by (2.6)). Hence we see that

$$v_{temp} = -\frac{kT}{m\beta}\,\frac{T_x}{T} \tag{5.9}$$

is the velocity of a Brownian particle due purely to the temperature difference (as if the concentration were constant).

Using (5.7) and (5.9) we can now give the following form to (5.4):

$$\widetilde{D} = \frac{kT}{m\beta}\left(1 + \frac{v_{temp}}{v_{press}}\right) \tag{5.10}$$

where v_{press} and v_{temp} are velocities described above. When T is constant, then $v_{temp} = 0$, and (5.10) reduces to the Einstein relation (3.8). When $T_x < 0$ for example, then $v_{temp} > 0$, and since $v_{press} > 0$ too (see *Figure 2*), we see from (5.10) that $\widetilde{D} > kT/m\beta$ (cf. (3.8)). Thus, in the case when $T_x < 0$, the diffusion coefficient *is larger* than what would be predicted by (3.8). Note that this consequence is in agreement with intuition, since from $T_x < 0$ we expect that the impacts by fluid molecules on a Brownian particle are infinitesimally larger from the left-hand side than from the right-hand side, which makes it easier for the Brownian particle to "diffuse" to the right.

4. To find the equation of motion, note that from (5.3) we get:

$$\widetilde{D}_x = \left(\frac{1}{\beta}\right)_x\left(\frac{kT}{m} + \frac{kT_x}{m}\,\frac{\nu}{\nu_x}\right) + \left(\frac{1}{\beta}\right)\left(\frac{kT_x}{m} + \frac{k(T_x\nu)_x\nu_x - kT_x\nu\nu_{xx}}{m(\nu_x)^2}\right)\,. \tag{5.11}$$

Inserting (5.11) and (5.3) into (5.5), the latter notably simplifies as follows:

$$\frac{\partial\nu}{\partial t} = -\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x}\left(\frac{1}{\beta}\right)\frac{kT}{m}\,\nu\right) + \frac{\partial^2}{\partial x^2}\left(\frac{kT}{m\beta}\,\nu\right)\,. \tag{5.12}$$

Given that the position process $(X_t)_{t\geq 0}$ of (2.3) is a *Markov process*, we can now recognize (5.12) as a *Kolmogorov forward equation* with drift $\mu = (1/\beta)_x(kT/m)$ and diffusion coefficient $D = (kT/m\beta)$ (cf. [8], [22], [16]). It follows that the equation of motion is given by

$$dX_t = \left(\frac{\partial}{\partial x}\left(\frac{1}{\beta}\right)\frac{kT}{m}\right)(t, X_t)\,dt + \sqrt{2D(t, X_t)}\,dB_t \tag{5.13}$$

where $D(t,x) = (kT(t,x)/m\beta(t,x))$, the process $(B_t)_{t\geq 0}$ is a standard Wiener process, and (5.13) is understood in Itô's sense (cf. [11], [12]). This completes the derivation.

5. By *the Fourier law* and *the conservation of energy law* we know that $T = T(t,x)$ in (5.12)-(5.13) solves *the heat equation*:

$$c\rho T_t = div\,(\kappa\,grad\,T) \tag{5.14}$$

where $c = c(x)$ is the *specific heat* of the fluid, $\rho = \rho(x)$ is the *mass density* of the fluid, and $\kappa = \kappa(x,T)$ is the *thermal conductivity* of the fluid. Clearly, initial and boundary conditions in (5.14) should also be specified. Explicit expressions for κ in terms of T are given elsewhere

and can be found e.g. in [23] (pp. 478-483). Moreover, when the fluid is a gas it is known that

$$\kappa = c_1 \eta \tag{5.15}$$

where c_1 is a constant depending on the physical properties of the gas (see [3] Chapter 13).

6. The equation of motion (5.13) requires a knowledge of the friction coefficient β in terms of the temperature T. Such calculations have been carried out for gases, and the following facts are well-known. For most gases we have:

$$\eta = c_2 T^s \quad (s \geq 1/2) \tag{5.16}$$

where the constant c_2 depends on the physical properties of the gas (the radius and mass of a gas molecule), and the exponent s depends on the interaction between the gas molecules (e.g. $s = 1/2$ corresponds to a hard-sphere interaction with no repulsive or attractive forces). For more details see [3] (Chapters 10-12) and [23] (pp. 473-478 and pp. 544-545).

On the other hand, it is found in the Fürth's note (6) of [6] (pp. 92–96) that the Stokes formula (2.7) requires a correction when the fluid is a gas, but still reads:

$$\beta = c_3 \eta \tag{5.17}$$

where the constant c_3 depends on the radius r and mass m of the Brownian particle, and on the mean free path ℓ of the gas molecule, being a good approximation when r is comparable with ℓ.

Combining (5.16) and (5.17) we find:

$$\beta = c_4 T^s \quad (s \geq 1/2) \tag{5.18}$$

for some constant c_4 obtained as a product c_2 and c_3 above, and this relation is to hold for most gases when r is comparable with ℓ.

7. *The Enskog-Chapman effect.* Inserting (5.18) into (5.13) we see that the drift satisfies:

$$sign\left[\frac{\partial}{\partial x}\left(\frac{1}{\beta}\right)\frac{kT}{m}\right] = -sign\,(T_x) \quad \text{(in gases)}. \tag{5.19}$$

Thus, the equation (5.13) predicts a refinement of the Enskog-Chapman effect for a *Brownian particle* in the *gas* in the form of *a drift towards the colder regions* at *all* times (see the note of caution below). The phenomenon (*thermal diffusion in gases*) was first predicted theoretically by Enskog in 1911, and then independently by Chapman in 1916, and was experimentally verified for gas mixtures in 1917 (see [2] p. 35 for detailed references). Note, moreover, that (5.19) i.e. the equation (5.13) also predicts a drift towards the colder regions for a Brownian particle in a *Maxwellian gas* (when $s = 1$ in (5.16) and (5.18) above). This fact cannot be deduced from the argument used by Chapman [2] (p. 52), and did not show up in Enskog's work either. Chapman ([2] p. 52) concludes: "it is curious that in such a gas "Brownian" thermal diffusion ceases to operate just as does true gaseous diffusion". The fact predicted by the equation (5.13) that *a Brownian particle in the Maxwellian gas receives a drift towards the colder region at all times* would be therefore interesting to submit to experimental tests (see the note of caution below).

8. *The Ludwig-Soret effect.* In contrast to a gas, when the fluid is a liquid, it is well-known from experiments that viscosity η decreases with increasing temperature T, in some cases very rapidly. In view of the Stokes formula (2.7), the same fact is true for the friction coefficient β as a function of T. It follows therefore from (5.13) that the drift satisfies:

$$sign\left[\frac{\partial}{\partial x}\left(\frac{1}{\beta}\right)\frac{kT}{m}\right] = sign\,(T_x) \quad \text{(in liquids)}. \tag{5.20}$$

Thus, the equation (5.13) predicts a refinement of the Ludwig-Soret effect for a *Brownian particle* in the *liquid* in the form of *a drift towards the hotter regions* at *all* times (see the note of caution below). The phenomenon (*thermal diffusion in liquids*) was first described by Ludwig in 1856 and later independently by Soret in 1879 (see [2] p. 35 for references). Using the same argument as in the case of a gas, Chapman ([2] p. 52) concludes: "thus Brownian thermal diffusion is more powerful in liquids than in gases" implying also that "the grains will tend towards the cooler regions" ([2] p. 34). At first glance it seems that the equation (5.13) contradicts this prediction as by (5.20) we see that *a Brownian particle in the liquid receives a drift towards the hotter region at all times*, but this is a subtle point to which we devote a special note of caution below. Therefore, it would be interesting to test the latter experimentally.

Note that the predictions on the existence of a "negative" drift in *gases* and a "positive" drift in *liquids* just stated are in agreement with physical intuition, since the hotter region in a gas implies a *higher friction* in the sense that the Brownian particle will be hit "more and harder" by gas molecules from the direction in the hotter region, while the hotter region in a liquid implies a *lower friction* in the sense that the Brownian particle will have "more room" to "slide" through "more vibrant" and thus "less touching" liquid molecules from the direction in the hotter region.

9. *A note of caution.* Chapman's argument recalled twice above, and a similar argument used by many other authors, is based on the attempt to detect a steady state of the system (after enough time has elapsed so that the system approaches equilibrium). Within his model, and in our notation above, Chapman ([2] p. 52) found that in the steady state one has $\nu \sim 1/D$, and therefore using (3.9) and (5.16) it followed that $\nu \sim \eta/T = 1/T^{1-s}$. On the basis of this fact he then concluded ([2] p. 52) that "the grains would in the steady state be more concentrated in the colder regions of the gas" when $s < 1$ (and $s > 1/2$ in his case). The case of a Maxwellian gas corresponds to $s = 1$ and was therefore left uncovered by the argument, since in this case $\nu \sim constant$. As the viscosity η is known to be reversely proportional to the temperature T, the same argument indicated (as already quoted above) that the Brownian diffusion is more powerful in liquids.

The two predictions on the Enskog-Chapman and the Ludwig-Soret effects of the equation (5.13) stated above *are* however *of different nature*. These predictions express the existence of a definite (positive) drift towards the cold or the hot region at *all* times t (small as well). To see, moreover, that *the existence of such a drift does not contradict the steady-state conclusions* of Chapman quoted above, we shall proceed by determining a steady state of the process X solving (5.13).

For this, note (cf. [13]) that *the scale function* of X reads as follows:

$$S(x) = \int_0^x \beta\ dz \tag{5.21}$$

and *the speed measure* of X is given by

(5.22) $$m(dx) = \frac{1}{\beta D}\, dx = \frac{m}{kT}\, dx \ .$$

Hence we see that the invariant density of X must be of the following form:

(5.23) $$p = \frac{c}{T}$$

whenever a normalizing constant $c > 0$ exists (making the integral of p equal to one).

From (5.23) we now read, just as Chapman did, that in the (ultimate) steady state there is a tendency for Brownian particles to end up in the colder region (in both gases and liquids). Note, moreover, that this also holds for a Maxwellian gas. For liquids, however, this long-run tendency is counter-balanced by a definite (positive) drift towards the hotter region, and it is a matter of more detailed statistical analysis to decide which one of the two effects becomes more dominant during the course of observation. This problem is worthy of further consideration.

10. *Other works.* After I completed the first draft of the present paper, I became acquainted with several other works and historical facts that are related to assumptions and predictions of the theory presented above. These will be, at some moderate length, exposed here.

Perhaps Wereide [29] was the first to discuss two alternative theories of the Ludwig-Soret effect, one based on the work of Nernst and the other on the work of Einstein i.e. assuming that the solute molecules behave like Brownian particles. I am not familiar with the details of his work and it may be that the approach taken above is in some parts similar.

The statistical mechanics of Brownian motion, including the case where the temperature gradient is present, has been considered by several authors. I was told that two notable early papers of this kind are [20] and [31]. A closer examination shows that these authors derive more complicated Fokker-Planck equations in a fluid with a temperature gradient where "the medium is accounted for exactly" ([20] p. 1112). I know of no simple comparison between these equations and the equation (5.12), but their existence is by no means excluded.

Another way of looking at the result of the equation (5.12) is that under a temperature gradient there is a mean force of $-kT_x$ on the Brownian particle (recall (3.2), (3.5) and (5.2) above). Indeed, under this supposition, the equation (5.12) follows readily from a general diffusion equation, if of course one is willing to accept that the Einstein relation (3.8) extends unchanged to the case of non-constant temperature. Such forces have been suggested in the thermal diffusion literature (see [10] for a detailed analysis). These authors also state ([10] p. 85) that "the remarkable agreement between theoretical predictions and experimental data is good support for this interpretation of thermal diffusion". I am indebted to a reader for pointing out this reference.

An early paper [9] (and many later papers by the same author) questions the validity of a gas kinetic model as the starting point for a theory of thermal diffusion in liquids, and develops a "thermal-radiation-pressure theory of thermodiffusive phenomena". In this theory, the force from the temperature gradient is found to depend on the thermal conductivities of the solute particle and liquid, which is in line with the idea that one has to say something about thermophysical properties of the particle. (Such properties of the Brownian particle in the simple model above are completely neglected.) The paper ([9] p. 294) concludes by pointing out the "interesting feature" of the equation derived that "the Soret coefficient can be positive or negative" so that "macromolecular materials can be expected to migrate towards the hot or the cold wall". The paper then continues by stating

that "this is a fundamental feature of the theory, in contrast to all other theoretical predictions based on kinetic models". The simple equation (5.13) and its predictions on the two effects displayed above seem to contradict this view on kinetic models.

Van Kampen [15] shows that if one formally starts with the Kramers equation [17] (i.e. the Kolmogorov forward equation [16] associated with the two-dimensional Ornstein-Uhlenbeck position-velocity process ([18], [27]) where constant β and T are replaced by non-constant $\beta(x)$ and $T(x)$, and applies the standard method of reducing this equation to the one-dimensional Smoluchowski equation (by letting β be large), one arrives at the equation (5.12) in a steady-state. Despite the fact that he noted a predictive power of the equation obtained and exploited the latter to some extent, it is with regret to realize that he failed to explain the dynamics of the equation (see Section 5 in [15] pp. 110-111). He further points out in [14] that if the linear damping law (3.3) fails for v, then yet another additional term appears in the drift of the equation (5.12). This point is further elaborated in [30] (p. 458) where a necessity of the general gas law (3.4) was deduced. It should be noted that both these facts are completely transparent from the dynamic-equilibrium derivation given above: if either of the two laws (3.3) and (3.4) fails in the present form, then the equation (5.12) fails to hold in the present form as well. The power of the approach above, however, rests in the fact that the dynamic-equilibrium derivation can be repeated with the new laws (3.3) and (3.4) in place of the old ones, and this will lead to a correct form of the equation (5.12). This methodology is illustrated through one example in Section 7 below.

While it may appear that I was motivated by the development just described, this unfortunately was not the case. Nonetheless, since I have derived this equation from the other end (relying on a dynamic equilibrium between forces of pressure and friction i.e. the Einstein relation), the van Kampen result [15] can be combined with the result above to establish a correct form of the Kramers equation (this one is simply obtained by replacing the constant β and T with non-constant ones). The same of course is true of the general equation (6.3) below (the details of this will be omitted).

Recent paper [25] (see also [26]) studies a gas of Brownian particles in a fluid with a temperature gradient and derives Fokker-Planck equations by the methods of "statistical dynamics". Although the author states in another publication that "it is not a good model for a single Brownian particle", a closer comparison with the equations derived here may be nonetheless interesting.

6. Presence of external force at non-constant temperature

1. The two derivations presented in the previous two sections can be unified into a single derivation to yield the equation of motion of a Brownian particle that is under the influence of the external force (4.1) while the fluid temperature (5.1) is a function of position and time. The derivation is easily reconstructed and we only display the key points.

2. Using the same physical arguments as in (4.3) and (5.2) we find:

$$F_p + F_e = -kT\,\frac{\nu_x}{\nu} - kT_x + mA = m\beta v = m\beta\,\frac{\nu v}{\nu} = -m\beta\,\frac{\widetilde{D}\nu_x}{\nu}\ . \tag{6.1}$$

It follows from (6.1) that (4.4) and (5.3) extend as

(6.2) $$\widetilde{D} = \frac{kT}{m\beta} - \frac{A}{\beta}\frac{\nu}{\nu_x} + \frac{kT_x}{m\beta}\frac{\nu}{\nu_x} \ .$$

On the other hand, applying the conservation of the number of particles law (cf. (4.6)-(4.7)), and inserting (6.2) with its derivative into (4.5), it follows that (4.9) and (5.12) extend as

(6.3) $$\frac{\partial \nu}{\partial t} = -\frac{\partial}{\partial x}\left(\left(\frac{A}{\beta} + \frac{\partial}{\partial x}\left(\frac{1}{\beta}\right)\frac{kT}{m}\right)\nu\right) + \frac{\partial^2}{\partial x^2}\left(\frac{kT}{m\beta}\,\nu\right) \ .$$

Given that the position process $(X_t)_{t\geq 0}$ of (2.3) is a *Markov process*, we can now recognize (6.3) as a *Kolmogorov forward equation* with drift $\mu = (A/\beta) + (1/\beta)_x(kT/m)$ and diffusion coefficient $D = (kT/m\beta)$ (cf. [8], [22], [16]). It follows that the equation of motion is given by

(6.4) $$dX_t = \left(\frac{A}{\beta} + \frac{\partial}{\partial x}\left(\frac{1}{\beta}\right)\frac{kT}{m}\right)(t, X_t)\,dt + \sqrt{2D(t, X_t)}\,dB_t$$

where $D(t,x) = (kT(t,x)/m\beta(t,x))$, the process $(B_t)_{t\geq 0}$ is a standard Wiener process, and (6.4) is understood in Itô's sense (cf. [11], [12]).

It follows moreover by *the Fourier law* and *the conservation of energy law* that $T = T(t,x)$ in (6.3)-(6.4) solves *the heat equation* (5.14) where initial and boundary conditions should also be specified. Note that the equation (6.4) includes the equations (4.10) and (5.13) as special cases of constant T and zero A , respectively.

3. We shall conclude this section with three additional comments on the equation (6.4). First, the equation (6.4) may be viewed as an extension of the Smoluchowski approximation [24] (see the final remark of Section 4) to the case of non-constant temperature. Second, the equation (6.4) provides a clear physical interpretation of the stochastic differential equation:

(6.5) $$dX_t = \mu(t, X_t)\,dt + \sigma(t, X_t)\,dB_t$$

which is of interest for applications in diverse areas of science. The main novelty in this context is the fact that functions $\mu(t,x)$ and $\sigma(t,x)$ from (6.5) solve partial differential equations, so that the system of equations (with initial-boundary conditions) constitutes the equation of motion. Third, the physical case of a non-constant temperature provides a scholar example that clearly demonstrates the need for a stochastic integral.

7. Interacting Brownian particles

1. So far we have assumed that Brownian particles do not interact with each other no matter how large the number. In this section we shall examine changes in the diffusion coefficient where the equation of state of Brownian particles in the Einstein argument deviates from the general-gas law (2.5) to *the van der Waals equation*:

(7.1) $$\left(p + \frac{a}{\lambda^2}\right)(\lambda - b) = RT$$

where $\lambda = V/n$ is the molar volume. These deviations lead to an understanding of how the

methodology of using "count data" (based on the average number of Brownian particles cf. (2.1)) to make conclusions about the movement of a single Brownian particle can affect the diffusion coefficient. Yet we shall see that the approach leads to a *nonlinear* partial differential equation as an extension of the Fokker-Planck equation (6.3).

2. The equation (7.1) is an empirical equation, although with suitable approximations, it can also be derived from statistical mechanics upon making use of a *virial expansion*:

$$\frac{p}{kT} = \nu + B_2(T)\,\nu^2 + B_3(T)\,\nu^3 + \ \ldots \tag{7.2}$$

(see [23] pp. 424-425, 418-424, 426-428). The equation (7.1) is known to be approximately valid even at temperatures and molar volumes so low that the gas has become a liquid.

The constants a and b are subject to the best fit of (7.1) to the experimental data. These constants also have a simple interpretation in terms of the departure from the general-gas law (2.5). The term a/λ^2 represents the additional positive pressure of the gas molecules on the container walls that is influenced by other gas molecules (especially when the gas molecules are not widely separated and when they move at relatively low speeds). It is a consequence of *the long-range attractive forces* between gas molecules (having the same effect as a slight compression of the gas). On the other hand, there could also exist *the short-range repulsive forces* between the gas molecules that keep them sufficiently apart to prevent them from occupying the same volume at the same time. The constant b represents the volume occupied by the gas molecules, so that $\lambda - b$ represents the "*free volume*" within the container available to the gas molecules.

3. *Derivation*. As before, take a cylindrical vessel filled with a fluid and suspend N Brownian particles into the fluid at time $t = 0$, as shown on *Figure 1*. Due to the impacts by fluid molecules, Brownian particles will begin the process of diffusion (cf. Section 2). Assume moreover that the system of N Brownian particles satisfies the equation of state (7.1) where $n = N/N_0$.

Consider the state in the vessel at a time $t > 0$ later on. It follows, as in the derivation above (cf. Section 3), that F_p satisfying (3.2) is the force per Brownian particle in the volume ΔV , which is caused by the concentration difference (see *Figure 2*). The force F_p imposes on each Brownian particle from ΔV a velocity v satisfying (3.3).

It follows from (7.1) that

$$p = \frac{RT}{(\lambda - b)} - \frac{a}{\lambda^2} = \frac{\nu kT}{(1 - b_0\nu)} - a_0\nu^2 \tag{7.3}$$

where $a_0 = a/N_0^2$ and $b_0 = b/N_0$. Differentiating in (7.3), and using (3.2) and (3.3), we find easily by means of (3.6) that

$$\frac{\partial p}{\partial x} = kT\,\frac{\nu_x}{(1 - b_0\nu)^2} - 2a_0\nu\nu_x = m\beta\widetilde{D}\nu_x \tag{7.4}$$

where $\widetilde{D}$ is a diffusion coefficient corresponding to the given particle flow. It follows from (7.4) that the following identity holds:

$$\widetilde{D} = \frac{kT}{m\beta}\ \frac{1}{(1 - b_0\nu)^2} - \frac{2a_0}{m\beta}\,\nu\ . \tag{7.5}$$

On the other hand, by the conservation of the number of particles law (cf. (4.6)-(4.7)) we know that ν and $\widetilde{D}$ solve the diffusion equation:

$$\nu_t = div\,(\widetilde{D}\; grad\,\nu) = \widetilde{D}_x \nu_x + \widetilde{D}\nu_{xx}\ . \tag{7.6}$$

In this way we have obtained a system of two equations (7.5) and (7.6) with two unknowns ν and $\widetilde{D}$, and the derivation is complete.

4. We shall now treat two cases separately. First, consider the case when $a = 0$, i.e. when only short-range repulsive forces act between Brownian particles. Then (7.5) reads as follows:

$$\widetilde{D} = \frac{kT}{m\beta}\ \frac{N_0^2}{(N_0 - b\nu)^2}\ . \tag{7.7}$$

Observe that (7.7) defines an increasing function of b . This indicates that *under the presence of short-range repulsive forces between the Brownian particles, the count data tend to increase the diffusion coefficient in comparison with the data based on observations of a single Brownian particle*.

Second, consider the case when $b = 0$, i.e. when only long-range attractive forces act between Brownian particles. Then (7.5) reads as follows:

$$\widetilde{D} = \frac{kT}{m\beta} - \frac{2a}{m\beta N_0^2}\,\nu\ . \tag{7.8}$$

Observe that (7.8) defines a decreasing function of a . This indicates that *under the presence of long-range attractive forces between the Brownian particles, the count data tend to decrease the diffusion coefficient in comparison with the data based on observations of a single Brownian particle*.

It should be noted that the preceding two conclusions are in agreement with intuition. The case of general $\widetilde{D}$ from (7.5) is inconclusive: in some cases the count data may tend to increase the diffusion coefficient, in the others they may tend to decrease it. A simple comparison of the formulas (7.7) and (7.8) can be made to quantify such a conclusion, but we shall omit these details.

5. We shall conclude this section by deriving the extension of the Fokker-Planck equation (6.3) in the case when the interacting Brownian particles satisfy the equation of state (7.1). This corresponds to the physical picture of the interaction being caused by the long-range attractive forces (measured by a) and the short-range repulsive forces (measured by b) between Brownian particles.

To derive the equation we may first differentiate in (7.5) to find $\widetilde{D}_x$, and then insert both this $\widetilde{D}_x$ and $\widetilde{D}$ from (7.5) into (7.6). It is then a matter of routine to verify that this calculation leads to the following equation:

$$\nu_t = \left(\frac{kT}{m\beta}\,\frac{2b_0}{(1-b_0\nu)^3} - \frac{2a_0}{m\beta}\right)(\nu_x)^2 + \left(\frac{kT}{m\beta}\,\frac{1}{(1-b_0\nu)^2} - \frac{2a_0}{m\beta}\,\nu\right)\nu_{xx} \tag{7.9}$$

where $a_0 = a/N_0^2$ and $b_0 = b/N_0$. This is a nonlinear partial differential equation which in the limit for $a \downarrow 0$ and $b \downarrow 0$ reduces to the Fokker-Planck equation (6.3) when A is zero.

In the case when $a = 0$, i.e. when the interaction between Brownian particles is caused purely by the short-range repulsive forces, the equation (7.9) reads as follows:

$$\nu_t \,=\, \frac{2b_0 D}{(1-b_0\nu)^3}\,\big(\nu_x\big)^2 \,+\, \frac{D}{(1-b_0\nu)^2}\,\nu_{xx} \tag{7.10}$$

where $b_0 \,=\, b/N_0$ and $D \,=\, kT/m\beta$.

In the case when $b = 0$, i.e. when the interaction between Brownian particles is caused purely by the long-range attractive forces, the equation (7.9) reads as follows:

$$\nu_t \,=\, -C\,\big(\nu_x\big)^2 - \,\big(C\nu - D\big)\,\nu_{xx} \tag{7.11}$$

where $C \,=\, 2a/m\beta N_0^2$ and $D \,=\, kT/m\beta$.

Applying the same method in the case when the Brownian particles satisfying (7.1) are also under the influence of an external force and the fluid temperature is not necessarily constant, we obtain a more complicated nonlinear partial differential equation which further extends (7.9) but which we omit to state explicitly.

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