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On the Theory of Brownian Motion. II. Nonuniform Systems

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An equation of evolution for a heavy particle immersed in a solvent of lighter particles is derived for the case when the system suffers gradients of temperature composition, or velocity. The derivation unifies the theory by applying the same methods which have proved useful in the uniform case. The final equation contains some new terms due to concentration gradients in the solvent, and is applicable to the case when the heavy particles are present at finite concentration and interact with each other.

KEY WORDS: Brownian motion; Molecular theory; Nonuniform system; Gradients of temperature, velocity, concentration; Local equilibrium.

In recent years, the molecular theory of the Brownian motion of heavy particles in a fluid has been put on a firm footing.(1–3) In a preceding paper(4) (hereafter referred to as I), we showed how the methods used for the case of Brownian particles (henceforth called B-particles) at infinite dilution could be extended to cover the case of B-particles at finite concentration. In the present paper we wish to extend these same methods to the case of Brownian motion in a nonuniform medium where there may be gradients of temperature, concentration, or fluid velocity.

This problem has been treated by varying methods by Nicolis,(5) Misguich,(6) and Zubarev and Bashkirov(7) for the case of B-particles at infinite dilution. Our purpose is twofold; first, to unify the theory by treating the nonhomogeneous problem by the homogeneous case, and second to indicate how the theory may be extended to nonzero concentrations of B-particles.

The system under consideration is $N+1$ B-particles of mass M immersed in

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a medium of n lighter particles. The medium particles, henceforth called the solvent, may have various masses, charges, and interactions. It will be necessary to have these differences explicit in the notation at certain points, but whenever possible without risk of confusion we omit subscripts related to species labels. The Hamiltonian and Liouville operators are as given in I [Eqs. (2) and (3)]. The system may contain steady gradients of concentrations, temperature, and velocity.

As in I, we seek an equation for

$$\rho_1 = \int \rho_{N+n+1}\, d\{n\}\, d\{N\} \tag{1}$$

where the distribution function ρ_{N+n+1} satisfies

$$i\frac{\partial \rho_{N+n+1}}{\partial t} = L\rho_{N+n+1} \tag{2}$$

Exactly as in I, we define projection operators $\hat{P}$ and $\hat{Q} = 1 - \hat{P}$ by

$$\hat{P} = \lambda \int d\{n\}\, d\{N\} \tag{3}$$

where λ is a function which is independent of $\mathbf{P}_0$ and normalized to unity. Defining $f = \hat{P}\rho_{n+N+1}$, $g = \hat{Q}\rho_{N+n+1}$ we find [(8)]

$$i\frac{\partial f}{\partial t} = \hat{P}Lf + \hat{P}L\exp[-i\hat{Q}Lt]\, g(0) - i\hat{P}L\int_0^t \exp[-i\hat{Q}L(t-t')]\, \hat{Q}Lf(t')\, dt' \tag{4}$$

We must now choose λ to reflect the nonuniform nature of the system. Clearly the choice made in I and References 1–3 is inappropriate here. We choose λ to be the local equilibrium distribution function in the field of particle zero. Specifically,

$$\begin{aligned}\lambda = \frac{1}{Z_0}\exp\Bigg\{ &- \sum_{\alpha=1}^{\theta}\sum_{j=1}^{n_\alpha} \beta_j \frac{(\mathbf{P}_j - m_\alpha u_\alpha)^2}{2m_\alpha} \\ &- \tfrac{1}{2}\sum_{\alpha,\beta=1}^{\theta}\sum_{j=1}^{n_\alpha}\sum_{k=1}^{n_\beta} U_{\alpha\beta}(\mathbf{R}_{jk})\,\beta_j + \sum_{\alpha=1}^{\theta}\sum_{j=1}^{n_\alpha} \nu_\alpha(\mathbf{R}_j)\Bigg\}\end{aligned} \tag{5}$$

where Z_0 is a normalization factor and $\nu_\alpha(\mathbf{R}_j)$ is $\mu_\alpha(\mathbf{R}_j)\,\beta(\mathbf{R}_j)$. Greek letters label species while latin letters label particles. If the B-particles are present at finite concentration, then they must be counted as one of the species present. The interaction of the solvent particles with B-particle zero is included. That is, the potential energy sums involving the B-particles must start with $j = 0$. From here on, the main difference between the present development and that for homogeneous systems is that $L_F\lambda \neq 0$ for our choice of λ, i.e., local equilibrium is not a steady-state solution of the Liouville equation.

First of all, we choose $\rho_{n+N+1}(0)$ to be the local equilibrium distribution function for the entire system. As is well known, there are then no fluxes at time $t = 0$, but the fluxes will develop in a very short time. This is a very commonly used initial condition, and should certainly be entirely adequate for transport theory.

We now expand the exponential operator in (4) in powers of L_B, keeping only the lowest-order term. The justification for this has already been discussed in I. Noting that $f = \lambda\rho_1$ and that $\hat{P}L_F = 0$, we find that (4) reduces to

$$\frac{\partial\rho_1}{\partial t} + \frac{\mathbf{P}_0}{M}\cdot\nabla\rho_1 + \langle\mathbf{F}_0\rangle_l\cdot\frac{\partial\rho_1}{\partial\mathbf{P}_0} = -\lambda^{-1}\hat{P}L_B\int_0^t \exp[-i\hat{Q}L_F(t-t')]\,\hat{Q}L\lambda\rho_1(t')\,dt' \tag{6}$$

where $\langle\mathbf{F}_0\rangle_l$ is the mean force on particle zero computed with the local equilibrium distribution function λ; in true equilibrium, $\langle\mathbf{F}_0\rangle_l$ vanishes, of course. Since the $\mathbf{P}_0\cdot\nabla_0$ term in L_B commutes with $\hat{P}$ and since $\hat{P}\hat{Q} = 0$, only the $\mathbf{F}_0\cdot\partial/\partial P_0$ term in the leftmost L_B operator on the right of Eq. (6) is effective. Calling the left-hand member $\mathscr{D}_t\rho_1$, we have

$$\mathscr{D}_t\rho_1 = i\frac{\partial}{\partial\mathbf{P}_0}\cdot\int d\{n\}\,d\{N\}\,\mathbf{F}_0\exp[-iL_F(t-t')]\,\hat{Q}L\lambda\rho_1(t')\,dt' \tag{7}$$

It only remains to analyze the last $\hat{Q}L$ operator.

We first note that L_F does not operate on ρ_1, which depends on $\mathbf{R}_0$ and $\mathbf{P}_0$ only. Therefore we have

$$(L_B + L_F)\,\lambda\rho_1 = (L_F\lambda)\,\rho_1 + (L_B\lambda)\,\rho_1 + \lambda L_B\rho_1 \tag{8}$$

Furthermore,

$$\hat{Q}L_B\lambda = L_B\lambda = -i(\mathbf{P}_0/M)\cdot\nabla_0\lambda \tag{9}$$

since λ does not depend on $\mathbf{P}_0$. Also, by a direct computation

$$\hat{Q}\lambda L_B\rho_1 = -i(\mathbf{F}_0 - \langle\mathbf{F}_0\rangle_l)\cdot\partial\rho_1/\partial\mathbf{P}_0 \tag{10}$$

where $\langle\mathbf{F}_0\rangle_l$ has the same meaning as in Eq. (6).

We now have to compute $L_F\lambda$. This has, however, been done many times previously[2] and we need not repeat the calculation here. The result, to first order in gradients, is

$$\begin{aligned} iL_F\lambda = \int \beta(\mathbf{r})\Big\{&\mathbf{S} : \nabla\mathbf{u}(\mathbf{r}) + \tilde{\mathbf{Q}}\cdot\nabla\ln T(\mathbf{r}) \\ &+ \sum_{\alpha=1}^{\theta}\sum_{j=1}^{n_\alpha}\frac{\mathbf{P}_j{}'}{m_j}\nabla_T\nu_\alpha(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{R}_j)\Big\}\,\rho_{n+N+1}^{(\mathrm{eq})}\,d^3\mathbf{r} \\ &- \mathbf{u}_0\cdot\mathbf{F}_0\beta_0 - \mathbf{u}_0\cdot\sum_k \mathbf{R}_{k0}\nabla_k U_{k0}\cdot\nabla_0\beta \end{aligned} \tag{11}$$

Here $\beta = (kT)^{-1}$, $\tilde{\tilde{\mathbf{Q}}}$ is the energy flux vector, and $\mathbf{S}$ is the momentum flux tensor. The exact formulas for these quantities are of little concern. They are given for refer-

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[2] See, for example, Reference 10, Section 10.8. Although the method used there is perfectly valid, the detailed formulas of Section 10.8 cannot be trusted. The entire section is studded with sign errors.

ence in the Appendix. We emphasize that Eq. (11) is not exact but is limited to the terms in λ which are linear in the gradients. The only real novelty in Eq. (11) is the last three terms, which arise because there are no derivatives with respect to $\mathbf{R}_0$ and $\mathbf{P}_0$ in L_F.

Returning to Eq. (9), we see that by expanding Eq. (5) to terms linear in the gradients

$$\lambda = \rho^{(\mathrm{eq})}\left[1 + \mathbf{A}\cdot\nabla\beta + \mathbf{B} : \nabla\mathbf{u} + \sum_\alpha \mathbf{C}_\alpha \cdot \nabla_T \nu_\alpha\right] \tag{12}$$

$$\nabla_T = \nabla - \nabla T \frac{\partial}{\partial T}$$

so that

$$\begin{aligned}\nabla_0\lambda = {} & \beta\mathbf{F}_0\rho^{(\mathrm{eq})}\left(1 + \mathbf{A}\cdot\nabla\beta + \mathbf{B} : \nabla\mathbf{u} + \sum_\alpha \mathbf{C}_\alpha \cdot \nabla_T\nu_\alpha\right) \\ & + \rho^{(\mathrm{eq})}\left(\nabla_0\,\mathbf{A}\cdot\nabla\beta + \sum_\alpha \nabla_0\mathbf{C}_\alpha\cdot\nabla_T\nu_\alpha\right)\end{aligned} \tag{13}$$

where **A**, **B**, and **C** are functions of the phases of all the particles present, but **B** does not depend on $\mathbf{R}_0$. Putting this into Eq. (7), we see that we have to evaluate quantities such as

$$\langle \mathbf{F}_0(t)\,\mathbf{F}_0\mathbf{U}\rangle, \qquad \langle \mathbf{F}_0\nabla\mathbf{U}\rangle \tag{14}$$

where the brachets $\langle\cdots\rangle$ mean equilibrium average, and where **U** is **A**, **B**, or **C**. Since $\rho^{(\mathrm{eq})}$ describes a homogeneous isotropic system, the only one of these terms which need not vanish is

$$\langle \mathbf{F}_0(t)\,\mathbf{F}_0(0)\,\mathbf{B}\rangle : \nabla\mathbf{u} \tag{15}$$

since there are no isotropic numerical tensors of odd order. **B** is given by the formula

$$\mathbf{B} = \beta \sum_{j\neq 0} \mathbf{P}_j{}'\mathbf{R}_j/m_j \tag{16}$$

The term in **S** in Eq. (11) as well as the last term in this equation also give no contribution to Eq. (7) for the same reasons of isotropy. Therefore, putting Eqs. (9), (10), and (11) into (7), we obtain

$$\begin{aligned}\mathscr{D}_t\rho_1 = {} & \frac{\partial}{\partial\mathbf{P}_0}\cdot\int_0^t \left[\mathbf{G}(t-t_1)\cdot\left(\frac{\partial}{\partial\mathbf{P}_0} + \frac{(\mathbf{P}_0 - M u_0)}{MkT}\right)\right. \\ & \left. + \mathscr{H}(t-t')\cdot\frac{\nabla\beta}{\beta} + \sum_\alpha \mathbf{J}_\alpha(t-t')\cdot\nabla_T\nu_\alpha\right]\rho_1(t')\,dt'\end{aligned} \tag{17}$$

In Eq. (17)

$$\mathbf{G}(\tau) = \langle\mathbf{F}_0(\tau)\,\mathbf{F}_0(0)\rangle + \langle\mathbf{F}_0(\tau)\,\mathbf{F}_0(0)\,\mathbf{B}\rangle : \nabla\mathbf{u} \tag{18}$$

$$\mathscr{H}(\tau) = \beta\langle\mathbf{F}_0(\tau)\,\tilde{\mathbf{Q}}(0)\rangle \tag{19}$$

$$\mathbf{J}_\alpha(\tau) = \langle\mathbf{F}_0(\tau)\,\mathbf{j}_\alpha(0)\rangle \tag{20}$$

and $\mathbf{j}_\alpha$, the current density of component α, is given by

$$\mathbf{j}_\alpha(\mathbf{r}) = \sum_{k=1}^{n_\alpha} \frac{(\mathbf{P}_j - m_j \mathbf{u}_\alpha)}{m_\alpha} \, \delta(\mathbf{R}_j - \mathbf{r}) \tag{21}$$

In the limit of infinite dilution of B-particles $\mathbf{G}$, $\mathscr{H}$, and $\mathbf{J}_\alpha$ will be very rapidly decaying functions of τ, and one may write

$$\mathscr{D}_t \rho_1 = \frac{\partial}{\partial \mathbf{P}_0} \cdot \left(\zeta' \left(\frac{\partial}{\partial \mathbf{P}_0} + \frac{\mathbf{P}_0 - M\mathbf{u}_0}{MkT} \right) + \eta \frac{\nabla\beta}{\beta} + \sum_\alpha \phi_\alpha \nabla_T \nu_\alpha \right) \rho_1 \tag{22}$$

where ζ', η, and the ϕ_α are integrals of $\mathbf{G}$, $\mathscr{H}$, and $\mathbf{J}_\alpha$ respectively from 0 to ∞. We write them as scalars, now recognizing that they are equilibrium averages in an isotropic system. However, when account is taken of the interactions between B-particles, these functions may have a slowly varying component, in first approximation proportional to the concentration of the B-particles, rendering the reduction from Eq. (17) to (22) less accurate. This has been discussed in I.

Thus we see that the Fokker–Planck equation for nonuniform systems, Eq. (22), is distinguished from that for uniform systems by (a) the occurrence of new coefficients η and ϕ_α, and (b) by the fact that the friction coefficient ζ' has an extra term proportional to the velocity gradient $\nabla\mathbf{u}$. The streaming operator $\mathscr{D}_t$ contains a term $\langle \mathbf{F}_0 \rangle_l \cdot \partial/\partial \mathbf{P}_0$. $\langle \mathbf{F}_0 \rangle_l$ will again be linear in $\nabla\beta$ and $\nabla_T \nu_\alpha$. It will not depend on $\nabla\mathbf{u}$ for reasons of isotropy. It has been analyzed by Zubarev and Bashkirov,⁽⁷⁾ and Misguich.⁽⁶⁾

The additional term in the friction constant is the time integral of Eq. (15). We conjecture that it is not likely to be of much importance, for two reasons. First, it contains the small quantity $\nabla\mathbf{u}$ (small by hypothesis, so that linearization is valid). Second, the coefficient of $\nabla\mathbf{u}$ is a correlation function of four variables [cf. Eq. (16)] which vanishes for $t = 0$ and $t \to \infty$. Because it expresses a more complicated correlation than does $\langle \mathbf{F}_0(t)\, \mathbf{F}_0(0) \rangle$, it is never likely to become appreciable in size.

The term in Eq. (22) involving η agrees with that of Zubarev and Bashkirov.⁽⁷⁾ The terms in ϕ_α do not appear in their treatment because they have implicitly assumed a one-component solvent and have treated the B-particles at infinite dilution only.

Our equation is in agreement with that of Nicolis⁽⁵⁾ (given in full in his thesis, though not in the published paper), who does treat the case of a multicomponent solvent, though the B-particles are at infinite dilution.

The term in ζ' proportional to $\nabla\mathbf{u}$ appears to be stated explicitly here for the first time, though it is implicit in the works discussed above.

The theory presented here should be valid not only at infinite dilution, but for finite concentrations of the B-particles. It will be possible to derive density expansions for η and ϕ_α. We shall not carry out the expansion in detail since it is so similar to that carried out for ζ in I. Of course, when the B-particle concentration approaches that of the solvent, the expansion of the exponential in Eq. (4) in powers of L_B is no longer a good approximation. To draw an analogy with the theory of gases, one is leaving the regime of the Rayleigh gas and entering that of the Lorentz gas.

The main results of this paper are the derivation of Eq. (22) in a manner analogous to that used in the homogeneous case and the extension to the case of mixed solvents with possible diffusion fluxes. The theory is thus applicable when there is a nonvanishing concentration of B-particles.

APPENDIX

For the case of a system with no external fields and with pair forces V between the constituent molecules, the heat flow vector is given by

$$\tilde{\mathbf{Q}}(\mathbf{r}) = \sum_j \frac{\mathbf{P}_j'}{m_j} \cdot \left[\left\{ \frac{\mathbf{P}_j'^2}{2m_j} - h(\mathbf{R}_j) \right\} \mathbf{1} + \tfrac{1}{2} \sum_{j \neq k} (V_{kj}\,\mathbf{1} - \mathbf{R}_{jk} \nabla_{R_j} V_{jk}) + V_{0k}\,\mathbf{1} - \mathbf{R}_{j0} \nabla_j V_{j0} \right] \delta(\mathbf{R}_j - \mathbf{r}) \tag{A.1}$$

The momentum flux vector is given by

$$\mathbf{S} = \sum_j \left[\frac{\mathbf{P}_j'\mathbf{P}_j'}{m_j} - \tfrac{1}{2} \sum_{k \neq j} \mathbf{R}_{jk} \nabla_j V_{kj} - \mathbf{R}_{j0} \nabla_j V_{j0} \right] \delta(\mathbf{R}_j - \mathbf{r}) \tag{A.2}$$

In these formulas the sums are over all particles except particle 0.
For the diffusion flux of species we have

$$\mathbf{j}_\alpha = \sum_{k=1}^{n_\alpha} \frac{P_k'}{m_\alpha} \delta(\mathbf{R}_k - \mathbf{r}) \tag{A.3}$$

and, in all of these formulas

$$\mathbf{P}_i' = \mathbf{P}_i - m_i \mathbf{u}_i$$

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