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Theory of thermophoresis. I. General considerations and mode-coupling analysis

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The phenomenon of the motion of suspended particles induced by temperature gradients in fluids, known as thermophoresis, is considered. We show that thermophoresis is related to the Soret effect. The thermophoretic force acting on a particle immersed in a fluid which has a temperature gradient, $\vec{\nabla}T$, is given phenomenologically by $-\eta_T\vec{\nabla}T$. η_T is shown to be related to the thermal-diffusion ratio by $\eta_T=k_B(k_T-1)$. In the limit of a dilute suspension we find a molecular expression for k_T in terms of an equilibrium time-correlation function of the momentum of a suspended particle and the dissipative heat current. As a by-product, we also obtain the force acting on a such a particle due to a pressure gradient. We further show, using time-scale arguments, that a local-equilibrium calculation of the thermophoretic force cannot be adequate. Finally, we show, using a mode-coupling approach, that the *hydrodynamic contribution* to the thermophoretic force coefficient is negligible, unlike in the case of Stokes friction. We conclude that although thermophoresis is a macroscopic effect (not a fluctuating one) observed in fluids, it is not given by standard hydrodynamics. In a subsequent paper, with the use of kinetic theory, we identify the microscopic processes responsible for thermophoresis, calculate the thermophoretic force coefficient for moderately dense gases, and compare our results to experiment.

I. INTRODUCTION

The effort invested over many years in the investigation of simple nonequilibrium systems resulted in the construction of several powerful techniques: kinetic theory,[1] mode-coupling theory,[2] projection-operator techniques,[3] linear-[4] and nonlinear-[5] response theories, information theoretical approaches,[6] etc.[7] All these techniques have certainly improved our understanding of transport properties and nonequilibrium phenomena. There are still, however, many open problems and specific effects to be understood.

In particular, it is not at all clear that the existing approaches always yield equivalent results. It is therefore important to look for and explore simple nonequilibrium systems in order to develop our nonequilibrium understanding and intuition and check our theoretical tools.

In the past few years there has been progress in the understanding of simple nonequilibrium steady states.[8] It has been shown that the fluctuations in these states differ both qualitatively and quantitatively from those in equilibrium states, even if these steady states are close to equilibrium. The theoretical results[8–11] were obtained, using methods ranging from kinetic theory[8(b),9] to phenomenological fluctuating hydrodynamics.[10,11] Encouragingly, all these methods led to the same results. Moreover, they seem to be confirmed by experiments.[12]

In this series of papers we propose to examine another simple nonequilibrium situation known as thermophoresis. There exists a wealth of experimental and theoretical information related to this problem.[13] The reason for this situation is the relevance of thermophoresis to aerosol, dust and smoke dynamics, colloid chemistry, geophysics, astrophysics, and many areas of chemical engineering.

The thermophoretic effect is the motion of small (for example, 1 μm in size) but macroscopic particles suspended in a fluid which has a steady temperature gradient. Early observations of this effect were reported by Tyndall[14] in 1870 and an early theory,[15] due to Einstein, was proposed in 1924.

Most of the experimental work related to thermophoresis has been performed on aerosols. These experiments face many difficulties (e.g., it is difficult to create aerosol particles of uniform size and composition or to create electrically neutral particles). In spite of these problems, it seems that different experiments in which different techniques are used agree with each other. The interested reader is referred to some excellent reviews for details.[13(a),13(b)]

The theoretical situation is somewhat less satisfying. The successful theories seem to depend on a number of free parameters which makes their agreement with experiment somewhat questionable.

Naively speaking, one can explain thermophoresis as follows: A particle (to be called henceforth a "*B*" particle) suspended in a fluid which has a steady temperature gradient is hit by "hot" fluid particles on one side and "cooler" fluid particles on its other side. The result must be a net force leading the *B* particle towards the colder region. Such an approach was taken by Einstein,[15(a)] who also assumed that the mean-free path of the host fluid particles was much bigger than the size of the *B* particle.

Einstein's model tacitly assumed that the density of the host gas was uniform, which actually means he did not consider a steady state. In a steady state the pressure is uniform ($\rho \sim 1/T$) and a calculation similar to Einstein's would yield no net force. This should come as no surprise since the *total* force in a steady state vanishes. As has been noted by Chapman,[15(b)] mean-free-path theories (of which Einstein's is an example), may lead to manifestly wrong results when applied to a diffusion, and thermal-diffusion problems. He concludes that mean-free-path theory is "unsafe to use in searching for new phenomena and scarcely satisfactory to make it the basis of a theory even in cases where it gives approximately correct results—better no simple theory than one based on unsafe or erroneous arguments." In all fairness, Einstein's model is in qualitative agreement with experiment in the Knudsen regime.

A more successful theory was proposed by Waldmann. His theory, based on the Chapman-Enskog[1] approach to the Boltzmann equation, is restricted to the density region where the mean free path of the fluid particles is much larger than the size of the *B* particle. He took the host fluid to be a Maxwell gas and the *B* particle an infinitely massive sphere. In addition, he assumed that a fraction of the gas particles colliding with the sphere are thermalized. Similar assumptions were used in other kinetic approaches,[13] mainly for mathematical simplicity.

In contrast to the above microscopic approaches, which are, strictly speaking, restricted to low densities of the host fluid and ignore internal structure of the *B* particle(s), Epstein proposed a phenomenological theory.[16] He assumed that the host fluid was described by linear hydrodynamics. The boundary conditions he used at the sphere were not the standard free (slip) or rigid (stick) conditions. The latter imply zero thermophoretic force. Instead, Epstein assumed, on the basis of Maxwell's kinetic approach,[17] that the velocity of the fluid at the *B* particles (which was taken to be a sphere, as in all other theories) had a tangential component proportional in size to the temperature gradient. This assumption led to an expression for the velocity of the *B* particle and for the thermophoretic force (known as "Epstein's formula") which are in reasonable agreement with experiment for poorly conducting *B* particles in fairly dilute host gases. Brock,[18] still using the hydrodynamic approach, employed more sophisticated boundary conditions and achieved a very good fit to experimental data. The weakness of his theory, from a practical point of view, is the fact he had four free parameters. Although these parameters are, in principle, measurable in separate experiments, they rarely are.

A different point of view in treating the problem was put forward in the work of Mason and Chapman.[19] Instead of concentrating on a single "large" particle fixed in a fluid, they regarded the suspended particles as a dilute second component. This approach is justified by the understanding that the only difference between the usual dilute solution and the present case is the size of the solute molecules. Employing the Chapmann-Enskog technique, they obtained results that are qualitatively similar to Waldman's[20] (they differ in overall prefactors of order unity). Unlike the phenomenological approaches, it is difficult to include internal properties of the *B* particles (e.g., heat conductivity) in the Mason-Chapmann approach, or for that matter in the other kinetic theories.

In addition to the theories mentioned above, there are many other works.[13,21,22] One of them, due to Zubarev and Bashkirov[22] is referred to in Sec. II.

To summarize this short (and incomplete) review we feel that the following several points should be stressed.

(1) There is no microscopic theory of thermophoresis that is valid over a wide region of densities of the host fluid.

(2) The phenomenological hydrodynamic theories employ boundary conditions that are taken from a dilute kinetic regime, where hydrodynamics may not apply. This makes their validity questionable.

(3) From a purely hydrodynamic point of view (employing free or rigid boundary conditions), a particle in a fluid with a temperature gradient does

not move. As is shown in Landau and Lifshitz[23] the full nonlinear Navier-Stokes equation for a fluid containing a stationary spherical particle, with slip or stick boundary conditions and having an asymptotically constant temperature gradient, admit the following solution: velocity $\equiv 0$ everywhere with the pressure constant. The temperature profile is determined by the heat-conduction equation. This immediately implies that the thermophoretic force corresponding to this solution vanishes. This conclusion remains valid for any boundary conditions as long as they do *not* directly couple velocity and temperature gradients at the particle's surface. In addition, it can be shown that the above solution is stable for an incompressible fluid. Compressibility allows for sound modes in the fluid. Both mode-coupling calculations (see below) and an application of a generalized Faxen's theorem[24] show that the latter are irrelevant for thermophoresis.

(4) In constructing a theory of thermophoresis one may employ either the single-particle point of view (e.g., Waldmann) or the dilute solution approach (e.g., Mason and Chapmann).

(5) Most of the above theories have not addressed themselves to the relation of thermophoresis to Brownian motion. After all, typical Brownian particles are of the same size as typical aerosols or dust particles which are dealt with in the theories of thermophoresis.

(6) Most theories, with the exception of Brock's, do not compare well with experiments in moderately dense gases.

In this series of papers, we study some of the theoretical problems described so far. We believe that we have a qualitative understanding of thermophoresis as well as quantitative results to be compared with experiment. Our approach can be classified as a dilute solution theory. The two main theoretical points we make are that the thermophoretic effect is of nonhydrodynamic origin and that thermophoresis is closely related, both qualitatively and quantitatively, to the Soret[25] effect.

The paper is organized as follows. In Sec. II, we employ microscopic considerations to derive a formula for the average force acting on a B particle. These considerations are very general, and in particular, do not assume anything about the density of the host fluid. The latter could be a dilute gas, a dense gas, or a liquid. It is shown, that due to the fact that Brownian (or momentum relaxation) time scales are very fast compared to typical thermophoresis time scales, there is no separate "local-equilibrium" contribution to thermophoresis (in distinction to the Zubarev-Bashkirov approach). In addition, a simple connection between the Soret coefficient and the thermophoretic force coefficient is derived. Thus, it suffices to calculate the Soret coefficient for a dilute suspension.

Section III is devoted to hydrodynamic calculation of the Soret coefficient in the following sense: It is well known[26] that the Stokes-Einstein diffusion coefficient can be derived from mode-coupling theory by assuming a *small "bare"* diffusion coefficient and attributing the observed values of that coefficient to a "renormalization" due to the nonlinear terms in the Navier-Stokes equations. Thus, Stokes-type diffusion is regarded as being of hydrodynamic origin. A similar calculation performed for the Soret or thermal-diffusion coefficient is presented in Sec. III. The result is that the *part* of the Soret coefficient which is due to mode-coupling or hydrodynamic effects is negligibly small. Soret diffusion is a nonhydrodynamic (bare) effect. The basic reason for this is the absence of a coupling of the heat flux to momentum in hydrodynamics. This is why the hydrodynamic solution contained in Landau and Lifshitz is stable. It is worthwhile mentioning that unlike the theories of fluctuations in simple nonequilibrium steady states,[8-12] different approaches (e.g., mode coupling versus kinetic theory) are not equally useful. The reason is that the mode-coupling calculations show that the quantity of interest is determined entirely by its bare part. This cannot be calculated using mode-coupling techniques.

Section IV offers a short summary of this paper. In the next paper in this series we employ some modern techniques of kinetic theory to calculate the Soret coefficient. It turns out that the necessary couplings are of nonhydrodynamic nature and depend strongly on the details of the B fluid interaction. It is well known from the Chapmann-Enskog kinetic theory that the Soret coefficient is highly sensitive to details as well as to mathematical approximations (unlike, e.g., the viscosity) in molecular mixtures. It should thus come as no surprise that the same is true when one of the species becomes macroscopic in size. The resulting formulas compare well with experiments for both dilute and dense gases.

II. CONNECTION TO SORET AND DUFOUR PHENOMENA

A. General considerations

It is well known that mixtures subjected to temperature gradients will respond by establishing concentration diffusion fluxes. This effect is known as the Soret effect (the opposite effect, i.e., heat flux caused by concentration gradients, is called the Dufour effect). Phenomenologically, for small enough temperature and concentration gradients, the mass flux $\vec{j}_i$ corresponding to species "i" can be written as

$$\vec{j}_i = -\sum_j L_{ij}\vec{\nabla}(\beta\mu_j) + L_{i,T}\vec{\nabla}\beta\ , \tag{2.1}$$

where the sum is over all different species, L_{ij} are the Onsager diffusion coefficients, $L_{i,T}$ is the Soret coefficient, β is $1/k_BT$ (k_B is the Boltzmann constant and T is temperature), and $\{\mu_j\}$ are the chemical potentials per unit mass. The L_{ij}'s are not independent because of Onsager's reciprocal relations and the fact that $\sum_i L_{ij}=0$. (Note that our definition of the Soret coefficient is somewhat different from that in Ref. 25. The connection between the two definitions is trivial.)

The Soret phenomenon can be thought of as thermophoresis on a molecular level, i.e., the only real difference between a fluid mixture and a fluid with macroscopic particles immersed in it is basically the size of the "solute" particles. Unfortunately, Eq. (2.1) cannot be directly applied to the problem of thermophoresis. This is so because the chemical potential for a single macroscopic particle in a fluid is not known. To overcome this difficulty, we shall derive an expression for the thermophoretic force, which, when combined with Eq. (2.1), does not contain the chemical potential of the large particle. To do so, we employ a microscopic approach.

The thermophoretic force is related to the nonequilibrium mean force felt by the large particle. That is,

$$\vec{F}_{\mathrm{NE}}(\vec{R},t) \equiv \frac{\left\langle \sum_j \vec{F}_j \delta(\vec{R}-\vec{r}_j)\right\rangle_{\mathrm{NE}(t)}}{\left\langle \sum_j \delta(\vec{R}-\vec{r}_j)\right\rangle_{\mathrm{NE}(t)}}\ , \tag{2.2}$$

where $\vec{F}_j$ is the total force felt by the jth particle at position $\vec{r}_j$, and $\langle\ \rangle_{\mathrm{NE}}(t)$ is a nonequilibrium ensemble average at time t and where the sums over j include only the large particles. Note that $\vec{F}_{\mathrm{NE}}(\vec{R},t)$ is the total force felt, on the average, by a particle at position $\vec{R}$ and thus contains frictional as well as thermophoretic effects. In steady state, this force vanishes in the absence of external fields. We seek an expression for $\vec{F}_{\mathrm{NE}}$ in terms of the state variables of the nonequilibrium system.

Before continuing, it must be stressed that Eq. (2.2) defines the average force felt by a particle at point $\vec{R}$. In order to use this force to determine the motion of any one particle, fluctuations must be small and/or quickly average to zero. This is quite reasonable for a large enough particle. On the other hand, in molecular systems, the force fluctuations are expected to be relatively large and their time scale comparable to that of the molecular motion. Thus, the use of Eq. (2.2) in a one-particle equation of motion for a microscopic particle would be quite meaningless.

For this work we assume that the macroscopic state of the system is specified by the averages of the densities of the conserved (i.e., "slow") quantities. We denote the corresponding phase functions as $\underline{A}(\vec{r},t)$. More specifically, when the solvent consists of a single component, the $\underline{A}(\vec{r},t)$ consists of $N^f(\vec{r},t)$, $N^B(\vec{r},t)$, $\vec{P}(\vec{r},t)$, $E(\vec{r},t)$, the fluid mass density, the large-particle mass density, the total momentum density, and the energy density at a point $\vec{r}$ at time t, respectively. The microscopic definitions of these densities are given by

$$N^f(\vec{r},t) \equiv \sum_{j\in f} m\delta(\vec{r}-\vec{r}_j(t))\ , \tag{2.3a}$$

$$N^B(\vec{r},t) \equiv \sum_{j\in B} M\delta(\vec{r}-\vec{r}_j(t))\ , \tag{2.3b}$$

$$\vec{P}(\vec{r},t) \equiv \sum_j \vec{p}_j(t)\delta(\vec{r}-\vec{r}_j(t))\ , \tag{2.3c}$$

and

$$E(\vec{r},t) \equiv \sum_j \delta(\vec{r}-\vec{r}_j(t)) \times \left[p_j^2/2m_j + \tfrac{1}{2}\sum_{j'\neq j} u(jj') \right] . \tag{2.3d}$$

In the above definitions, m and M are the solvent and large-particle masses, respectively, $\vec{p}_j$ is the momentum of the jth particle, $m_j \in \{m,M\}$ is its mass, and the sums on j include both types unless otherwise noted. f denotes the set of j's corresponding to fluid particles and B to large particles. In Eq. (2.3d), we have assumed pairwise additive potentials $u(jj')$ for concreteness. This assumption is not needed in this section.

In order to compute the nonequilibrium averages appearing in Eq. (2.2), we use a generalization of response theory.[27] The main result of this approach is that

$$\langle B(\vec{r})\rangle_{\mathrm{NE}}(t)=\langle B(\vec{r})\rangle_{\mathrm{hom}}(\vec{r},t)+\int d\vec{r}_1 d\vec{r}_2 \langle B(\vec{r},t)\underline{\hat{A}}(\vec{r}_1)\rangle_{\mathrm{hom}}(\vec{r},t)\cdot\langle \underline{\hat{A}}(\vec{r}_1,t)\underline{\hat{A}}(\vec{r}_2)\rangle^{-1}_{\mathrm{hom}}(\vec{r},t)(\vec{r}_2-\vec{r})\cdot\vec{\nabla}\underline{a}(\vec{r},t)\ , \tag{2.4}$$

where $a(\vec{r},t)\equiv\langle A(\vec{r})\rangle_{\mathrm{NE}}(t)$ and $\langle B(\vec{r})\rangle_{\mathrm{NE}}(t)$ is the nonequilibrium average of a dynamical variable $B(\vec{r})$. In Eq. (2.4), the symbol $\langle\ \rangle_{\mathrm{hom}}(\vec{r},t)$ denotes an equilibrium grand-canonical average where the equilibrium average values of the $\underline{A}$'s are chosen to coincide with the actual ones at the point $\vec{r}$ and time t,

$$\underline{\hat{A}}(\vec{r}\,',t)\equiv\underline{A}(\vec{r}\,',t)-\langle\underline{A}(\vec{r}\,')\rangle_{\mathrm{hom}}(\vec{r},t) \tag{2.5}$$

and

$$\int d\vec{r}_1\langle\underline{\hat{A}}(\vec{r},t)\underline{\hat{A}}(\vec{r}_1)\rangle_{\mathrm{hom}}\cdot\langle\underline{\hat{A}}(\vec{r}_1,t)\underline{\hat{A}}(\vec{r}\,')\rangle^{-1}_{\mathrm{hom}}\equiv\underline{1}\,\delta(\vec{r}-\vec{r}\,')\ , \tag{2.6}$$

defines the inverse $\langle\underline{\hat{A}}(\vec{r},t)\underline{\hat{A}}(\vec{r}\,')\rangle^{-1}_{\mathrm{hom}}$ with $\underline{1}$ a unit matrix. Equation (2.4) neglects nonlinear terms in $\vec{\nabla}\underline{a}$ as well as terms in $\vec{\nabla}\,\vec{\nabla}\underline{a}$, etc. Thus, this result is valid for systems where the average spatial nonuniformity is small. The "hom" averages simply account for the local-equilibrium state. We remark that if Eq. (2.4) is linearized around full equilibrium, then the usual linear-response theory is obtained. Since we consider only systems which are translationally invariant when in equilibrium, all the hom correlation functions appearing in Eq. (2.4) depend only on differences in the spatial coordinates inside the average.

The mean force vanishes in equilibrium; therefore,

$$\left\langle\sum_j\vec{F}_j\delta(\vec{r}-\vec{r}_j)\right\rangle_{\mathrm{hom}}(\vec{r},t)=0 \tag{2.7}$$

and hence to linear order in the gradients

$$\vec{F}_{\mathrm{NE}}(\vec{r},t)=\int d\vec{r}_1 d\vec{r}_2\left\langle\sum_{j\in B}\vec{F}_j(t)\delta(\vec{r}-\vec{r}_j(t))\underline{\hat{A}}(\vec{r}_1)\right\rangle_{\mathrm{hom}}(\vec{r},t)\cdot\langle\underline{\hat{A}}(\vec{r}_1,t)\underline{\hat{A}}(\vec{r}_2)\rangle^{-1}_{\mathrm{hom}}(\vec{r},t)\times(\vec{r}_2-\vec{r})\cdot\vec{\nabla}\underline{a}(\vec{r},t)\Bigg/\left\langle\sum_{j\in B}\delta(\vec{r}-\vec{r}_j)\right\rangle_{\mathrm{hom}}(\vec{r},t)\ . \tag{2.8}$$

The denominator on the right-hand side (rhs) of Eq. (2.8) is the local number density of large particles which we write as $\rho_B(\vec{r},t)/M$. Note that space and time, in general, appear both explicitly inside the averages as well as implicitly in the definition of the hom distribution function. The latter is not a dynamical dependence and is completely parametric. Consequently, we can treat the averages appearing in Eq. (2.8) as full equilibrium averages and at the last step replace the chemical potentials, temperature, and velocity by their nonequilibrium values at the point $\vec{r}$ at time t. We exploit this property and rewrite Eq. (2.8) in Fourier representation, namely,

$$\frac{\vec{F}_{\mathrm{NE}}(\vec{r},t)\rho_B(\vec{r},t)}{M}=\left[-\frac{\partial}{\partial i\vec{k}}\left[\left\langle\sum_{j\in B}\vec{F}_j(t)e^{i\vec{k}\cdot\vec{r}_j(t)}\underline{\hat{A}}_{-\vec{k}}\right\rangle\cdot\langle\underline{\hat{A}}_{\vec{k}}(t)\underline{\hat{A}}_{-\vec{k}}\rangle^{-1}\right]_{\vec{k}=0}\right]_{\mathrm{hom}}(\vec{r},t)\cdot\vec{\nabla}\underline{a}(\vec{r},t)\ . \tag{2.9}$$

The Fourier transform is defined by

$$f_{\vec{k}}\equiv\int d\vec{r}e^{i\vec{k}\cdot\vec{r}}f(\vec{r})\ . \tag{2.10}$$

Noting that

$$\vec{F}_j(t)=\frac{d\vec{P}_j(t)}{dt}\equiv\dot{\vec{P}}_j(t) \tag{2.11}$$

and using the "dot-switching" property of equilibrium averages (i.e., stationarity) gives

$$\vec{F}_{\mathrm{NE}}(\vec{r},t)\rho_B(\vec{r},t)/M=\left[\left[\left\langle\sum_{j\in B}\vec{P}_j(t)\vec{P}_j(t)\underline{\hat{A}}_T\right\rangle\Big/M-\left\langle\sum_{j\in B}\vec{P}_j(t)\underline{\hat{J}}_T\right\rangle\right]\cdot\langle\underline{\hat{A}}_T\underline{\hat{A}}_T\rangle\right]_{\mathrm{hom}}(\vec{r},t)\cdot\vec{\nabla}\underline{a}(\vec{r},t)\ , \tag{2.12}$$

where we have performed the $\vec{k}$ derivative, set $\vec{k}=0$ in the result, and used the conservation laws, namely,

$$\dot{\underline{A}}_{\vec{k}} \equiv i\vec{k}\cdot\underline{\vec{J}}_{\vec{k}} \,. \tag{2.13}$$

The quantities $\underline{\vec{J}}$ are the fluxes corresponding to the A's. Lastly, the subscript T denotes the $\vec{k}=0$ value (i.e., total).

Since the A's are conserved, the first average in Eq. (2.12) is time independent. The flux appearing in Eq. (2.12) contains two parts: a slow part proportional to $\hat{\underline{A}}$ and the rest. More specifically, we write

$$\underline{\vec{J}}_T \equiv \underline{\vec{I}}_T + \langle \underline{\vec{J}}_T \hat{\underline{A}}_T \rangle \langle \hat{\underline{A}}_T \hat{\underline{A}}_T \rangle^{-1} \cdot \hat{\underline{A}}_T \,, \tag{2.14}$$

where the "dissipative flux" $\vec{I}_T$ has been made orthogonal to the A's (in the sense of projection operator theories).[3] Thus,

$$\vec{F}_{NE}(\vec{r},t)\frac{\rho_B(\vec{r},t)}{M} = \left[\left\langle \sum_{j\in B} \frac{\vec{P}_j\vec{P}_j}{M}\hat{\underline{A}}_T \right\rangle - \left\langle \sum_{j\in B} \vec{P}_j \hat{\underline{A}}_T \right\rangle \cdot \langle \hat{\underline{A}}_T \hat{\underline{A}}_T \rangle^{-1} \cdot \langle \hat{\underline{A}}_T \underline{\vec{J}}_T \rangle - \left\langle \sum_{j\in B} \vec{P}_j(t) \underline{\vec{I}}_T \right\rangle \right]_{\text{hom}} (\vec{r},t)$$

$$\cdot \langle \hat{\underline{A}}_T \hat{\underline{A}}_T \rangle^{-1}_{\text{hom}} (\vec{r},t) \cdot \vec{\nabla} \underline{a}(\vec{r},t) \,. \tag{2.15}$$

The only time dependence in the coefficient of $\vec{\nabla} a$ (ignoring that associated with hom) comes from the correlation function

$$\overleftrightarrow{\underline{C}}(t) \equiv \left\langle \sum_{j\in B} \vec{P}_j(t) \underline{\vec{I}}_T \right\rangle \,. \tag{2.16}$$

Roughly speaking, there are three characteristic time scales associated with $\overleftrightarrow{C}(t)$: (1) microscopic times $\tau_m \sim 10^{-12}$ sec; (2) intermediate times related to the Brownian motion of the large particle $\tau_B \sim (\xi_B/M)^{-1}$; ξ_B is the friction constant. For aerosol particles, $\tau_B \sim 10^{-6}$ sec. (3) Hydrodynamic times. Since the correlation function $\overleftrightarrow{C}(t)$ is a correlation between quantities orthogonal to the hydrodynamic variables, it should, barring nonlinear effects, decay on the τ_B time scale. This is considerably shorter than relevant experimental times and thus

$$\vec{F}_{NE}(\vec{r},t)\frac{\rho_B(\vec{r},t)}{M} = \left[\left\langle \sum_{j\in B} \frac{\vec{P}_j\vec{P}_j}{M}\hat{\underline{A}}_T \right\rangle - \left\langle \sum_{j\in B} \vec{P}_j \underline{\vec{A}}_T \right\rangle \cdot \langle \underline{\vec{A}}_T \underline{\vec{A}} \rangle^{-1} \cdot \langle \hat{\underline{A}}_T \underline{\vec{J}}_T \rangle \right]_{\text{hom}} \cdot \langle \hat{\underline{A}}_T \hat{\underline{A}}_T \rangle^{-1} \cdot \vec{\nabla} \underline{a}(\vec{r},t) \tag{2.17}$$

on the experimental time scale. For what follows we choose a frame of reference where the average velocity at point $\vec{r}$ and time t vanishes. The equilibrium averages appearing in Eq. (2.17) are easily calculable. Using the definitions of the A's easily gives

$$\left\langle \sum_{j\in B} \vec{P}_j \hat{\underline{A}}_T \right\rangle \cdot \langle \hat{\underline{A}}_T \hat{\underline{A}}_T \rangle^{-1} \cdot \langle \hat{\underline{A}}_T \underline{\vec{J}}_T \rangle = \frac{\rho_B}{\rho_B + \rho_F} \cdot \langle \vec{P}_T \vec{J}_T \rangle \,, \tag{2.18}$$

where ρ_F is the mass density of solvent particles. Note that stationarity (dot switching) implies that

$$i\vec{k} \cdot \langle \overleftrightarrow{\tau}_{\vec{k}} \hat{\underline{A}}_{-\vec{k}} \rangle = \langle \vec{P}_{\vec{k}} \underline{\vec{J}}_{-\vec{k}} \rangle \cdot i\vec{k} \,, \tag{2.19}$$

where $\overleftrightarrow{\tau}_{\vec{k}}$ is the stress tensor (momentum flux). These correlation functions are either rank two tensors or vanish due to time reversal (i.e., for $A = P$). As such, they must be proportional to the unit tensor at $\vec{k}=0$, and therefore,

$$\langle \overleftrightarrow{\tau}_T \hat{\underline{A}}_T \rangle = \tfrac{1}{3} \operatorname{Tr} \langle \overleftrightarrow{\tau}_T \hat{\underline{A}}_T \rangle = \langle \vec{P}_T \hat{\underline{J}}_T \rangle \,. \tag{2.20}$$

Combining Eqs. (2.18), (2.20), and (2.17) yields

$$\vec{F}_{NE}(\vec{r},t)\frac{\rho_B(\vec{r},t)}{M} = \left\langle \left[\sum_{j\in B} \frac{\vec{P}_j\vec{P}_j}{M} - \frac{1}{3}\frac{\rho_B}{(\rho_B+\rho_F)} \operatorname{Tr}\overleftrightarrow{\tau}_T \right] \hat{\underline{A}}_T \right\rangle_{\text{hom}} (\vec{r},t) \cdot \langle \hat{\underline{A}}_T \hat{\underline{A}}_T \rangle^{-1}_{\text{hom}} (\vec{r},t) \cdot \vec{\nabla} \hat{\underline{a}}(\vec{r},t) \,. \tag{2.21}$$

Finally, equilibrium fluctuation theory allows us to rewrite Eq. (2.21) as (V is the system's volume)

$$\vec{\mathrm{F}}_{\mathrm{NE}}(\vec{\mathrm{r}},t)\rho_B(\vec{\mathrm{r}},t)/M=\left[\frac{\partial}{\partial \underline{a}}\left[\left\langle\sum_{j\in B}\vec{\mathrm{P}}_j\vec{\mathrm{P}}_j\Big/MV\right\rangle\right]-\frac{\rho_B}{3(\rho_B+\rho_F)}\frac{\partial}{\partial \underline{a}}\left[\frac{\langle \mathrm{Tr}\vec{\mathrm{r}}\overleftrightarrow{\tau}_T\rangle}{V}\right]\right]_{\mathrm{hom}}(\vec{\mathrm{r}},t)\cdot\vec{\nabla}\underline{a}(\vec{\mathrm{r}},t)$$

$$=\vec{\nabla}\cdot\left\langle\sum_{j\in B}\vec{\mathrm{P}}_j\vec{\mathrm{P}}_j\Big/(MV)\right\rangle_{\mathrm{hom}}(\vec{\mathrm{r}},t)-\frac{\rho_B(\vec{\mathrm{r}},t)}{3[\rho_B(\vec{\mathrm{r}},t)+\rho_F(\vec{\mathrm{r}},t)]}\cdot\vec{\nabla}\langle\mathrm{Tr}(\overleftrightarrow{\tau}_T/V)\rangle_{\mathrm{hom}}(\vec{\mathrm{r}},t)\,. \tag{2.22}$$

Of course,

$$\left\langle\sum_{j\in B}\vec{\mathrm{P}}_j\vec{\mathrm{P}}_j\Big/(MV)\right\rangle=\overleftrightarrow{1}\rho_B k_B T/M \tag{2.23a}$$

and

$$\langle \tfrac{1}{3}\mathrm{Tr}\vec{\mathrm{r}}\overleftrightarrow{\tau}_T/V\rangle=p_h\,, \tag{2.23b}$$

where p_h is the hydrostatic pressure. Inserting Eqs. (2.23) into (2.22) gives

$$\vec{\mathrm{F}}_{\mathrm{NE}}(\vec{\mathrm{r}},t)=\frac{1}{\rho_B(\vec{\mathrm{r}},t)}\vec{\nabla}[\rho_B(\vec{\mathrm{r}},t)k_BT(\vec{\mathrm{r}},t)]-\frac{M}{[\rho_B(\vec{\mathrm{r}},t)+\rho_F(\vec{\mathrm{r}},t)]}\vec{\nabla}p_h(\vec{\mathrm{r}},t)\,. \tag{2.24}$$

Notice that Eq. (2.24) reduces to the usual expression for the mean force in equilibrium (T and p_h are both constant).

Since ρ_B appears explicitly in (2.24), it is still not straightforward to find out what happens to a single large particle. We will eliminate ρ_B using Eq. (2.1) which, for the present case, may be rewritten in the familiar form

$$\vec{\mathrm{j}}_D(\vec{\mathrm{r}},t)=-\rho_BD(\vec{\nabla}\ln\rho_B+k_T\vec{\nabla}\ln T+k_p\vec{\nabla}\ln p_h)\,, \tag{2.25}$$

where the diffusion constant is given by

$$\rho_BD\equiv L_{BB}\left[\frac{\partial\beta(\mu_B-\mu_f)}{\partial\ln\rho_B}\right]_{p_h,T}\,, \tag{2.26a}$$

the barodiffusion ratio,

$$k_p\equiv-p_h\left[\frac{\partial\ln\rho_B}{\partial p_h}\right]_{T,(\mu_B-\mu_f)}\,, \tag{2.26b}$$

and the thermal-diffusion ratio,

$$k_T\equiv\frac{L_{BT}}{L_{BB}}\left[\frac{\partial\ln\rho_B}{\partial(\mu_B-\mu_f)}\right]_{T,p_h}-T\left[\frac{\partial\ln\rho_B}{\partial T}\right]_{p_h,(\mu_B-\mu_f)/T} \tag{2.26c}$$

(where for a binary mixture, $L_{BB}=-L_{BF}$). Moreover, the diffusion flux is nothing more than

$$\vec{\mathrm{j}}_D(\vec{\mathrm{r}},t)\equiv\rho_B(\vec{\mathrm{r}},t)\vec{\mathrm{v}}_B(\vec{\mathrm{r}},t)\,, \tag{2.26d}$$

where $\vec{\mathrm{v}}_B(\vec{\mathrm{r}},t)$ is the mean [in the sense of Eq. (2.2)] large-particle velocity.

We now substitute Eq. (2.26) into Eq. (2.25), solve for $\vec{\nabla}\ln\rho_B$ and use the result in Eq. (2.24), thus obtaining

$$\vec{\mathrm{F}}_{\mathrm{NE}}(\vec{\mathrm{r}},t)=-\frac{k_BT}{D}\vec{\mathrm{v}}_B(\vec{\mathrm{r}},t)+(1-k_T)\vec{\nabla}(k_BT)-\left[\frac{M}{(\rho_B+\rho_f)}p_h+k_BTk_p\right]\vec{\nabla}\ln p_h\,. \tag{2.27}$$

As is well known, the friction coefficient ξ is related to D by

$$\xi=k_BT/D \tag{2.28}$$

and thus, in the laboratory frame [$\vec{\mathrm{v}}(\vec{\mathrm{r}},t)$ is the total mass average velocity]

$$\vec{\mathrm{F}}_{\mathrm{NE}}(\vec{\mathrm{r}},t)=-\xi[\vec{\mathrm{v}}_B(\vec{\mathrm{r}},t)-\vec{\mathrm{v}}(\vec{\mathrm{r}},t)]+(1-k_T)\vec{\nabla}[k_BT(\vec{\mathrm{r}},t)]-\left[\frac{M}{(\rho_B+\rho_F)}+\frac{k_BT}{p_h}k_p\right]\vec{\nabla}p_h(\vec{\mathrm{r}},t)\,. \tag{2.29}$$

The first term on the right-hand side (rhs) of Eq. (2.29) is the drag force felt by a particle moving with velocity $\vec{\mathrm{v}}_B$ relative to the fluid moving with velocity $\vec{\mathrm{v}}$. The third term is the barophoretic force. Notice that the barophoretic force constant is given solely in terms of thermodynamic derivatives (i.e., not in terms of kinetic coefficients). Finally, the second term is the thermophoretic force. Notice, that the only assumption used so far was that spatial gradients be small. In particular, we did not assume that ρ_B or ρ_F were small or that the B particles were large. Thus Eq. (2.29) should hold for molecular systems as well as suspensions of macroscopic particles. This does not mean that Eq. (2.29) can be used in calculating a single-particle trajectory for small particles. As mentioned after Eq. (2.2), the mean force equals, to a good approximation, the actual average force felt by a single particle when fluctuations are small. This is not the case for very small particles. Thus, the validity of (2.29) is very general but its usefulness when the motion of a single particle is of interest is limited to the regimes where fluctuations in $\vec{F}_{NE}$ can be neglected. Most important, the thermophoretic force constant n_T [the coefficient of $-\nabla T$ in Eq. (2.29)] is given by

$$\eta_T = k_B(k_T - 1)\ . \tag{2.30}$$

Consequently, irrespective of densities, etc., the thermophoretic force constant and "molecular" thermal-diffusion ratio are trivially related. In the remainder of this work we specialize in the case where the B species is very dilute.

B. Dilute suspensions

In the limit of high dilution of the B particles, one can easily calculate the thermodynamic quantities that appear in the preceding section. Since in actuality, the experiments probing thermophoresis are performed on dilute suspensions, this limit is appropriate. To leading order in ρ_B we use ideal solution theory.

First, we calculate the barophoretic force coefficient. From Eq. (2.26b) and the Gibbs-Duhem equation [i.e., $dp_h = (\rho_B + \rho_f)d\mu_f$ at constant T and $\mu_B - \mu_f$] it follows that

$$\frac{k_B T}{p_h} k_p = -\frac{1}{(\rho_B + \rho_f)} \left[\frac{\partial \ln \rho_B}{\partial \beta \mu_f} \right]_{T, \mu_B - \mu_f} = -\frac{1}{(\rho_B + \rho_f)\rho_B} \left[\left[\frac{\partial \rho_B}{\partial \beta \mu_f} \right]_{T, \mu_B} + \left[\frac{\partial \rho_B}{\partial \beta \mu_B} \right]_{T, \mu_f} \right] . \tag{2.31}$$

The thermodynamic derivatives appearing in Eq. (2.31) are easily related to the $\langle \hat{N}_B^2 \rangle$ and $\langle \hat{N}_B \hat{N}_f \rangle$ static correlation functions.[28] These in turn may be expressed in terms of pair-correlation functions. Carrying this out in Eq. (2.31) gives

$$-\left[\frac{M}{(\rho_B + \rho_f)} + k_p \frac{k_B T}{p_h} \right] = \frac{1}{(\rho_B + \rho_f)} \left[\rho_B \int d\vec{r}\,[g^{BB}(\vec{r}) - 1] + \rho_f \int d\vec{r}\,[g^{Bf}(\vec{r}) - 1] \right] , \tag{2.32}$$

where g^{BB} and g^{Bf} are the pair-correlation functions for a B-B and B-fluid pair of particles, respectively. The coefficient of the $O(\rho_B)$ term on the rhs of Eq. (2.32) is (up to a factor of -2) the second osmotic virial coefficient. For dilute suspensions (assuming no long-range interactions) this term is negligible. The remaining term on the rhs of Eq. (2.32), when used in Eq. (2.29), yields for the barophoretic force

$$\vec{F}_{NE}(\vec{r},t) = \int d\vec{r}\,[g^{BF}(\vec{r}) - 1]\vec{\nabla} p_h + O(\rho_B) \tag{2.33a}$$

$$\approx -\mathcal{V}_B \vec{\nabla} p_h\ , \tag{2.33b}$$

where $\mathcal{V}_B$ is the volume of the B particle. The second expression follows by assuming that outside the B particle g^{Bf} vanishes on a distance which is much smaller than the size of B. This of course precludes long-range forces. The force given by Eq. (2.33b) is exactly the force acting on a body immersed in a constant pressure gradient—as calculated from the usual Navier-Stokes hydrodynamics (see, e.g., Ref. 23).

In the same fashion it is easily shown that

$$\rho_B D = L_{BB}/M + O(\rho_B^2) \tag{2.34}$$

[cf. Eq. (2.26a)]. Finally, in order to evaluate the thermodynamic quantities appearing in k_T, we note that

$$\frac{d\rho_B}{M} = (e_0 + p_h)d\beta - \rho_{F,0} d\beta\mu_F + O(\rho_B^2) \quad (p_h \text{ const})\ , \tag{2.35a}$$

where $\rho_{F,0}$ and e_0 are the mass and energy densities of pure solvent at chemical potential $\beta\mu_F$ and temperature T. Also, using the Gibbs-Duhem equation gives

$$d\beta\mu_F = \frac{h}{(\rho_B + \rho_F)} d\beta\ [p_h, \beta(\mu_B - \mu_F) \text{ const}]\ , \tag{2.35b}$$

where h is the enthalpy per unit volume. Combining Eqs. (2.35a) and (2.35b) thus yields

$$T\left[\frac{\partial \ln\rho_B}{\partial T}\right]_{p_h,\beta(\mu_B-\mu_F)} = \frac{M}{\rho_F k_B T}\left[h\left[\frac{\rho_{F,0}-\rho_F}{\rho_B}-1\right]+\frac{\rho_{F,0}}{\rho_B}(e-e_0)\right] + O(\rho_B)\ . \tag{2.36}$$

In addition, it is easy to show that

$$\frac{e-e_0}{\rho_B}=\frac{1}{M}(\langle E\rangle_1-\langle E\rangle_0)+O(\rho_B)\equiv\Delta E/M \tag{2.37a}$$

and

$$\frac{\rho_F-\rho_{F,0}}{\rho_B}=\frac{1}{M}(\langle N_F\rangle_1-\langle N_F\rangle_0)+O(\rho_B) \equiv \Delta N_F/M\ , \tag{2.37b}$$

where $\langle\ \rangle_i$ is a semigrand-ensemble average[26] containing "i" B particles with solvent at temperature T and chemical potential μ_F. Alternately, the rhs of Eqs. (2.37) can be expressed in terms of β and $\beta\mu_F$ derivatives of the osmotic pressure.

To make further progress we need the explicit Green-Kubo relations for L_{BB} and L_{BT}.[1,7] These are

$$L_{BB}=\frac{\rho_B}{M}\int_0^\infty dt\langle\vec{\mathrm{P}}_B(t)\vec{\mathrm{P}}_B(0)\rangle+O(\rho_B^2) \tag{2.38a}$$

and

$$L_{BT}=\frac{\rho_B}{M}\int_0^\infty dt\langle\vec{\mathrm{P}}_B(t)\vec{\mathrm{I}}_{E,T}(0)\rangle+O(\rho_B^2)\ , \tag{2.38b}$$

where $\vec{\mathrm{P}}_B$ is the momentum of a B particle and where the dissipative energy current

$$\vec{\mathrm{I}}_{E,T}\equiv\vec{\mathrm{J}}_{E,T}-\frac{h}{\rho_F}\vec{\mathrm{P}}_T\ . \tag{2.39}$$

Thus, combining Eqs. (2.36)–(2.39) and (2.26c) gives

$$k_T=\frac{\rho_B}{L_{BB}k_BT}\int_0^\infty dt\left\langle\vec{\mathrm{P}}_B(t)\left\{\vec{\mathrm{I}}_{E,T}-\left[\frac{h}{\rho_F}\left[\frac{\rho_{F,0}-\rho_F}{\rho_B}-1\right]+\frac{(e-e_0)}{\rho_B}\right]\vec{\mathrm{P}}_B(0)\right\}\right\rangle\ . \tag{2.40}$$

Moreover, taking the internal degrees of freedom for the B particle to be separable from the rest, allows us to write

$$\begin{aligned}\vec{\mathrm{I}}_{E,T}=&\sum_{j\in F}\left[\frac{p_j^2}{2m}-\frac{mh}{\rho_F}+\tfrac{1}{2}\sum_{j\neq j'}[u(jj')+\vec{\mathrm{r}}_{jj'}\vec{\mathrm{F}}_{jj'}]\right]\cdot\frac{\vec{\mathrm{p}}_j}{m}\\ &+\left[\frac{P_B^2}{2M}+H_{\mathrm{int}}-\frac{Mh}{\rho_F}+\tfrac{1}{2}\sum_{j\in F}[u(B,j)+\vec{\mathrm{r}}_{Bj}\vec{\mathrm{F}}_{Bj}]\right]\cdot\frac{\vec{\mathrm{P}}_B}{M}\ ,\end{aligned} \tag{2.41}$$

where H_{int} is internal Hamiltonian for the B particles. As we shall discuss below, this decoupling of the internal degrees of freedom limits the applicability of the theory. Inserting Eq. (2.41) in (2.40) gives

$$\begin{aligned}k_T=\frac{\rho_B}{L_{BB}k_BT}\int_0^\infty dt\Bigg\langle\vec{\mathrm{P}}_B(t)\Bigg\{\vec{\mathrm{I}}_{E,F}+&\left[\frac{P_B^2}{2M}+\langle H_{\mathrm{int}}\rangle-\frac{hM}{\rho_F}\left[\frac{\rho_{F,0}-\rho_F}{\rho_B}\right]-\frac{(e-e_0)}{\rho_B}M\right.\\ &\left.+\tfrac{1}{2}\sum_{j\in F}[u(Bj)+\vec{\mathrm{r}}_{Bj}\vec{\mathrm{F}}_{Bj}]\right]\cdot\frac{\vec{\mathrm{P}}_B}{M}\Bigg\}\Bigg\rangle\ ,\end{aligned} \tag{2.42}$$

where $\vec{\mathrm{I}}_{E,F}$ corresponds to the terms in p_j in Eq. (2.41).

Some of the terms in Eq. (2.42) are negligible in the limit of large M/m. To see that we rewrite $\langle E\rangle_1$ and $\langle N_f\rangle_1$ appearing in Eq. (2.37) as follows:

$$\langle E\rangle_1=\langle H_{\mathrm{int}}\rangle+\tfrac{3}{2}k_BT+Se_s+(\langle E\rangle_0-\mathcal{V}_Be_0)\ , \tag{2.43a}$$

$$\langle N_F\rangle_1=\langle N_F\rangle_0-\mathcal{V}_B\rho_F+\rho_{f,s}S\ , \tag{2.43b}$$

where S is the surface area of the B particle, $\mathcal{V}_B$ its volume, e_s the surface energy density, and $\rho_{f,s}$ the Gibbs excess mass density. Both e_s and $\rho_{f,s}$ can be of either sign. Using (2.37) and (2.43), the expression inside the square bracket in (2.42) can be rewritten as

$$\left[\ \right]=\frac{P_B^2}{2M}-\tfrac{3}{2}k_BT-S\left[e_s-\frac{h}{\rho_F}\rho_{f,s}\right]-p_h\mathcal{V}_B$$
$$+\tfrac{1}{2}\sum_{j\in F}[u(Bj)+\vec{\mathrm{r}}_{Bj}\vec{\mathrm{F}}_{Bj}]\ . \qquad (2.43\mathrm{c})$$

Note that the internal energy $\langle H_{\mathrm{int}}\rangle$ has disappeared. This cancellation is exact only when the internal degrees of freedom of the B particle are rigorously decoupled from all the other degrees of freedom.

All the terms in (2.43) contribute negligibly to k_T. To see this we estimate the contribution of the terms in the square bracket and compare to the size of $\vec{\mathrm{I}}_{E,F}$ terms. On the average, the largest terms in Eq. (2.43c) are of the order of $k_BT\rho_F\mathcal{V}_B/m$ (consider, e.g., an ideal system). On the other hand, $\vec{\mathrm{I}}_{E,F}$ contains the effects of fluid particles, many of them, typically ρ_FSl/m, will correlate with $\vec{\mathrm{P}}_B(t)$ (l is the mean free path). The energy flux associated with each fluid particle is $O(k_BTc)$, where c is the mean fluid particle speed. Noting that

$$P_B/m\sim(m/M)^{1/2}c \qquad (2.44)$$

gives for the ratio of these two contributions

$$\frac{\mathcal{V}_B}{Sl}\left[\frac{m}{M}\right]^{1/2}\approx\frac{R}{l}\left[\frac{m}{M}\right]^{1/2}$$
$$\approx\frac{R}{l}\left[\frac{r}{R}\right]^{3/2}=\left[\frac{r}{R}\right]^{1/2}\frac{r}{l}\ , \qquad (2.45)$$

where R is the typical linear dimension of the B particle and r of the host-fluid particle. The above estimate assumes the density of the B particle is of the order, or more than the "density" of a fluid particle. This is certainly true for all cases of interest. Since obviously $r/l<1$, the ratio of the contributions is at most $(r/R)^{1/2}$. Typically, $r\sim1$ Å and $R\sim1$ μm, hence, $(r/R)^{1/2}\approx10^{-2}$, so to the accuracy of a few percent the terms in the square brackets make a negligible contribution. To summarize Sec. II B, we have shown that the thermal-diffusion ratio for a large B particle is

$$k_T=\frac{1}{MDk_BT}\int_0^\infty dt\langle\vec{\mathrm{P}}_B(t)\vec{\mathrm{I}}_{E,F}\rangle\ . \qquad (2.46)$$

The calculation of (2.46) is undertaken in the remainder of this work. Once k_T is obtained, the thermophoretic force constant follows from Eq. (2.30).

C. Local-equilibrium limit

Zubarev[22] calculated the thermophoretic force assuming an initial local-equilibrium distribution function for the host fluid (his local equilibrium differs from the hom average used here).

To see the connection to Zubarev's theory we rewrite Eq. (2.16) as

$$\overleftrightarrow{C}(t)=\overleftrightarrow{C}(0)+\int_0^t\dot{\overleftrightarrow{C}}(t')dt'$$
$$=\left\langle\sum_{j\in B}\vec{\mathrm{p}}_j\underline{\vec{\mathrm{I}}}_T\right\rangle+\int_0^t dt_1\left\langle\sum_{j\in B}\vec{\mathrm{F}}_j(t_1)\underline{\vec{\mathrm{I}}}_T\right\rangle\ , \qquad (2.47)$$

where $\vec{\mathrm{F}}_j$ is the total force acting on the jth particle. Moreover, if the correlation function decays quickly, then the limit of integration may be extended to infinity. Using Eq. (2.47) in (2.15) results in

$$\vec{\mathrm{F}}_{\mathrm{NE}}(\vec{\mathrm{r}},t)\frac{\rho_B(\vec{\mathrm{r}},t)}{M}$$
$$=\left[\left\langle\sum_{j\in B}\frac{\vec{\mathrm{P}}_j\vec{\mathrm{P}}_j}{M}\underline{\hat{A}}_T\right\rangle-\left\langle\sum_{j\in B}\vec{\mathrm{P}}_j\underline{\vec{\mathrm{J}}}_T\right\rangle\right.$$
$$\left.-\int_0^\infty dt_1\left\langle\sum_{j\in B}\vec{\mathrm{F}}_j(t_1)\underline{\vec{\mathrm{I}}}_T\right\rangle\right]_{\mathrm{hom}}(\vec{\mathrm{r}},t)$$
$$\cdot\langle\underline{\hat{A}}_T\underline{\hat{A}}_T\rangle_{\mathrm{hom}}^{-1}(\vec{\mathrm{r}},t)\cdot\vec{\nabla}\underline{a}(\vec{\mathrm{r}},t)\ , \qquad (2.48)$$

where Eq. (2.14) has been employed in obtaining this expression.

Using the dot-switching property allows us to rewrite the first two terms on the rhs of Eq. (2.48) as

$$-\frac{\partial}{\partial i\vec{\mathrm{k}}}\left\langle\sum_{j\in B}e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}_j}\vec{\mathrm{F}}_j\underline{\vec{\mathrm{A}}}_{-\vec{\mathrm{k}}}\right\rangle\bigg|_{\vec{\mathrm{k}}=0}\ . \qquad (2.49)$$

This when used in Eq. (2.48) results in the ∇a term obtained by expanding the local-equilibrium average. The time integral in Eq. (2.48) is estimated in Zubarev's theory. In our notation this corresponds to letting (est is estimate)

$$\overleftrightarrow{C}(t)\approx\overleftrightarrow{C}(0)+\mathrm{est}\ . \qquad (2.50)$$

On the other hand, we have argued that $\overleftrightarrow{C}(t)$ vanishes on the Brownian-motion time scale; a time scale much shorter than the duration of the experiment. Hence, Eq. (2.50) is invalid for the size of particles used in experiments. For very large particles (i.e., $6\pi\eta R/M \sim 1\ \text{sec}^{-1}$, η is the viscosity) Eq. (2.50) may be valid, although the inertial terms in the equation of motion would make the observation of the thermophoretic force quite difficult.

D. Summarizing remarks

In this section, we have established a general connection between the phenomena associated with molecular diffusion (and of course the associated cross effects) and the forces felt by a large particle in a nonequilibrium system. In doing so we have established an almost trivial connection between the thermal-diffusion ratio and the thermophoretic force constant, the former simplifying for a large, massive particle. We reiterate that the only significant approximation so far has been the separability of the internal and external degrees of freedom of the large particle. This should be most justified for poor heat conductors. The case of good conductors must be considered separately, a point to which we will return later.

III. MODE-COUPLING ANALYSIS

The main aim of this section is to show that thermophoresis is not a purely hydrodynamic effect in the sense that Stokes friction is.

Mode-coupling theories are usually employed to calculate the influence of the nonlinear couplings among fluctuating linear hydrodynamic modes on the observed values of the various transport coefficients. A typical result for an Onsager (transport) coefficient would consist of the bare coefficient and its renormalization. In many cases, the hydrodynamic renormalization term is much bigger than the bare coefficient. In this fashion, Keyes and Oppenheim[26] derived the Stokes-Einstein expression for the self-diffusion constant. As will be shown, the renormalization of the Soret coefficient and thus of the thermophoretic force constant is negligibly small. The significance of this result will be discussed below.

A. Main ingredients of mode-coupling theory

The basic input of mode-coupling theory is a nonlinear Langevin equation for the hydrodynamic variables. In practice only reversible quadratic nonlinearities are included (which results in the usual Navier-Stokes fluctuating hydrodynamics). Moreover, it is normally assumed that the random fluxes are δ correlated in time and have Gaussian statistics. In the standard notation,[2] the basic nonlinear equation of motion is

$$\begin{aligned}\dot{A}_{\alpha,\vec{\mathrm{k}}}(t)=M_{\alpha\beta}(\vec{\mathrm{k}})A_{\beta,\vec{\mathrm{k}}}(t)&+\int\frac{d\vec{\mathrm{k}}'}{(2\pi)^3}V^{\alpha\beta\gamma}_{\vec{\mathrm{k}};\vec{\mathrm{k}}-\vec{\mathrm{k}}',\vec{\mathrm{k}}'}A_{\beta,\vec{\mathrm{k}}-\vec{\mathrm{k}}'}(t)\\&\times A_{\gamma,\vec{\mathrm{k}}'}(t)+F_{\alpha,\vec{\mathrm{k}}}(t)\ ,\end{aligned}\tag{3.1}$$

where A_α are the different hydrodynamic variables indexed by α. In Eq. (3.1), the matrix M is the linear (bare) hydrodynamic matrix, V is the bare vertex function, and F is the random force.

The nonlinear term in Eq. (3.1) is usually treated perturbatively. The resulting expression for $\underline{A}(t)$ is multiplied by $\underline{A}(t=0)\langle\underline{A}\underline{A}\rangle^{-1}$ and averaged. Subsequently, standard resummation techniques are employed and the renormalization of the transport coefficients is identified. The general result is[2]

$$k^2L_{\alpha\beta}(\vec{\mathrm{k}})=k^2L^{(0)}_{\alpha\beta}+4\int\frac{d\vec{\mathrm{k}}'}{(2\pi)^3}\int_0^\infty dt\ V^{\alpha\epsilon\gamma}_{\vec{\mathrm{k}};\vec{\mathrm{k}}-\vec{\mathrm{k}}',\vec{\mathrm{k}}'}G^{\epsilon\delta}_{\vec{\mathrm{k}}-\vec{\mathrm{k}}'}(t)U^{\gamma\sigma}_{\vec{\mathrm{k}}'}(t)V^{\delta,\sigma,\phi}_{\vec{\mathrm{k}}-\vec{\mathrm{k}}';-\vec{\mathrm{k}}',\vec{\mathrm{k}}}\frac{\langle\underline{A}_{\vec{\mathrm{k}}}\underline{A}_{-\vec{\mathrm{k}}}\rangle^{\phi,\beta}}{V}\ ,\tag{3.2}$$

where the correlation function

$$\underline{U}_{\vec{\mathrm{k}}}(t)\equiv\frac{\langle\underline{A}_{\vec{\mathrm{k}}}(t)\underline{A}_{-\vec{\mathrm{k}}}\rangle}{V}\ ,\tag{3.3a}$$

$$\underline{G}_{\vec{\mathrm{k}}}(t)\equiv\langle\underline{A}_{\vec{\mathrm{k}}}(t)\underline{A}_{-\vec{\mathrm{k}}}\rangle\cdot\langle\underline{A}_{\vec{\mathrm{k}}}(0)\underline{A}_{-\vec{\mathrm{k}}}\rangle^{-1}\ ,\tag{3.3b}$$

and where the vertex function was taken to be symmetric, i.e.,

$$V^{\alpha\beta\gamma}_{\vec{\mathrm{k}};\vec{\mathrm{k}}-\vec{\mathrm{k}}',\vec{\mathrm{k}}'}=V^{\alpha\gamma\beta}_{\vec{\mathrm{k}};\vec{\mathrm{k}}',\vec{\mathrm{k}}-\vec{\mathrm{k}}'}\ .\tag{3.3c}$$

From stationarity it follows that

$$\tilde{V}^{\alpha\beta\gamma}_{\vec{k};\vec{k}',\vec{k}''}+\tilde{V}^{\beta\gamma\alpha}_{\vec{k}';\vec{k}'',\vec{k}}+\tilde{V}^{\gamma\alpha\beta}_{\vec{k}'';\vec{k},\vec{k}'}=0\ , \tag{3.4a}$$

where

$$\tilde{V}^{\alpha\beta\gamma}_{\vec{k};\vec{k}-\vec{k}',\vec{k}'}\equiv V^{\alpha\beta'\gamma'}_{\vec{k};\vec{k}-\vec{k}',\vec{k}'}\langle A_{\beta',\vec{k}-\vec{k}'}A_{\beta,\vec{k}'-\vec{k}}\rangle\langle A_{\gamma',\vec{k}'}A_{\gamma,-\vec{k}'}\rangle/V^2\ . \tag{3.4b}$$

Note that $\tilde{V}^{\beta\gamma\alpha}$ is symmetric in $\beta\gamma$ in the same way as V [cf. Eq. (3.3c)]. Using Eq. (3.4) one can easily show that

$$k^2L_{\alpha\beta}(\vec{k})=k^2L^{(0)}_{\alpha\beta}(\vec{k})-2\int_0^{\infty}dt\int\frac{d\vec{k}_1}{(2\pi)^3}V^{\alpha\gamma\delta}_{\vec{k};\vec{k}-\vec{k}_1,\vec{k}_1}G^{\gamma\phi}_{\vec{k}-\vec{k}_1}(t_1)G^{\delta\sigma}_{\vec{k}_1}(t_1)\tilde{V}^{\beta\sigma\phi}_{\vec{k};\vec{k}_1,\vec{k}-\vec{k}_1}\ . \tag{3.5}$$

Equation (3.5) is the starting point for our calculation of the renormalization of the Soret coefficient. We remark that, strictly speaking, Eq. (3.4) is valid only for Gaussian statistics. Nonetheless, Eq. (3.5) can still be obtained using some simple aspects of non-Gaussian statistics combined with N-ordering arguments. This brief introduction has omitted practically all details. The interested reader is referred to the review by Keyes.[2]

B. Mode-coupling theory for the Soret coefficient

As in Sec. II, the variables $\underline{A}$ are the densities of the host fluid and the B particles, the momentum density, and the energy density. For convenience, we transform to a set of variables in which the total mass density replaces the fluid mass density.

The nonlinear hydrodynamic equations describing such a system are well known, see, e.g., De Groot and Mazur.[25] The bare vertices in hydrodynamics (small-k limit) can be written as

$$V^{\alpha\beta\gamma}_{\vec{k};\vec{k}-\vec{k}',\vec{k}'}=\tfrac{1}{2}i\vec{k}\cdot\frac{\partial\langle J^{\alpha}\rangle}{\partial a^{\gamma}\partial a^{\beta}}\ . \tag{3.6}$$

If (3.6) is used only in its $k\to 0$ limit, one has to cut off the resulting k integrals in Eq. (3.2).

Keyes and Oppenheim have considered Eq. (3.5) for $\alpha=\beta$ corresponding to ρ_B (self-diffusion). We need $\alpha=\rho_B$ and $\beta=E$, corresponding to the Soret coefficient. In addition, we need the propagators. The easiest way to find both the vertices and the propagators is to read them off the nonlinear Navier-Stokes equations for binary mixtures[25]:

$$\delta\dot{\rho}_{\vec{k}}(t)=i\vec{k}\cdot\vec{p}_{\vec{k}}(t)\ , \tag{3.7a}$$

$$\begin{aligned}\delta\dot{\rho}_{B,\vec{k}}(t)={}&i\vec{k}\cdot\int\frac{d\vec{k}_1}{(2\pi)^3}\frac{\vec{p}_{\vec{k}_1}}{\rho}\left[\delta\rho_{B,\vec{k}-\vec{k}_1}-\frac{\rho_B}{\rho}\delta\rho_{\vec{k}-\vec{k}_1}\right]+i\vec{k}\cdot\vec{p}_{\vec{k}}\rho_B/\rho\\&-k^2L_{BB}\left[\left[\frac{\partial\beta\mu}{\partial\rho_B}\right]_{\rho,e}\delta\rho_{B,\vec{k}}+\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{\rho_B,e}\delta\rho_{\vec{k}}+\left[\frac{\partial\beta\mu}{\partial e}\right]_{\rho_B,\rho}\delta e_{\vec{k}}\right]\\&+k^2L_{BT}\left[\left[\frac{\partial\beta}{\partial\rho_B}\right]_{\rho,e}\delta\rho_{B,\vec{k}}+\left[\frac{\partial\beta}{\partial\rho}\right]_{\rho_B,e}\delta\rho_{\vec{k}}+\left[\frac{\partial\beta}{\partial e}\right]_{\rho_B,\rho}\delta e_{\vec{k}}\right]\ ,\end{aligned} \tag{3.7b}$$

$$\dot{\vec{p}}_{\vec{k}}=i\vec{k}\left[\left[\frac{\partial p_h}{\partial\rho_B}\right]_{e,\rho}\delta\rho_{B,\vec{k}}+\left[\frac{\partial p_h}{\partial\rho}\right]_{\rho_B,e}\delta\rho_{\vec{k}}+\left[\frac{\partial p_h}{\partial e}\right]_{\rho_B,\rho}\delta e_{\vec{k}}\right]-k^2\nu_t\vec{p}_{\vec{k}}-\vec{k}\,\vec{k}(\nu_l-\nu_t)\cdot\vec{p}_{\vec{k}}\ , \tag{3.7c}$$

and

$$\delta\dot{e}_{\vec{k}}=i\vec{k}\cdot\int\frac{d\vec{k}_1}{(2\pi)^3}\vec{p}_{\vec{k}_1}\left[\left[\frac{\partial\overline{H}}{\partial\rho_B}\right]_{\rho,e}\delta\rho_{B,\vec{k}-\vec{k}_1}+\left[\frac{\partial\overline{H}}{\partial\rho}\right]_{\rho_b,e}\delta\rho_{\vec{k}-\vec{k}_1}+\left[\frac{\partial\overline{H}}{\partial e}\right]_{\rho_B,\rho}\delta e_{\vec{k}-\vec{k}_1}\right]$$
$$+i\vec{k}\cdot\vec{p}_{\vec{k}}\overline{H}+k^2L_{EE}\left[\left[\frac{\partial\beta}{\partial\rho_B}\right]_{\rho,e}\delta\rho_{B,\vec{k}}+\left[\frac{\partial\beta}{\partial\rho}\right]_{\rho_B,e}\delta\rho_{\vec{k}}+\left[\frac{\partial\beta}{\partial e}\right]_{\rho_B,\rho}\delta e_{\vec{k}}\right]$$
$$-k^2L_{BT}\left[\left[\frac{\partial\beta\mu}{\partial\rho_B}\right]_{\rho,e}\delta\rho_{B,\vec{k}}+\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{\rho_B,e}\delta\rho_{\vec{k}}+\left[\frac{\partial\beta\mu}{\partial e}\right]_{\rho_B,\rho}\delta e_{\vec{k}}\right]. \tag{3.7d}$$

In writing out the hydrodynamic equations, *only* the quadratic terms needed in the renormalization of the Soret coefficient [cf. Eq. (3.5)] have been included. In addition, we have expressed fluctuations in the chemical potentials (via $\beta\mu$), inverse temperature β, pressure and enthalpy per unit mass ($\overline{H}$) in terms of the variables $\delta\rho_B$, $\delta\rho$, and δe. (δ denotes the deviation from equilibrium.) The dissipative coefficients have their standard meaning and

$$\mu\equiv\mu_B-\mu_F\ . \tag{3.8}$$

Their relevant vertex functions are trivially obtained from the first terms on the rhs of Eqs. (3.7b) and (3.7d). Physically, the mode-coupling terms account for convective transport of the B particles and heat convection.

Not all of the terms appearing in Eq. (3.7) are required in our calculation, since we need the Soret coefficient only to linear order in ρ_B. (As mentioned before, we need the limit $\rho_B\to 0$.) With the use of (3.7a) and (3.7b) it is easy to see that

$$G_{\vec{k}}^{B,\alpha}(t)-\frac{\rho_B}{\rho}G_{\vec{k}}^{\rho,\alpha}(t)=e^{Dk^2t}\left[\delta_{\alpha,B}-\frac{\rho_B}{\rho}\delta_{\alpha,\rho}\right]$$
$$-k^2\int_0^t dt_1 e^{-Dk^2(t-t_1)}\left\{L_{BB}\left[\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{\rho_B}G_{\vec{k}}^{\rho,\alpha}(t_1)+\left[\frac{\partial\beta\mu}{\partial e}\right]_{\rho,\rho_B}G_{\vec{k}}^{E,\alpha}(t_1)\right]\right.$$
$$-L_{BT}\left[\left[\frac{\partial\beta}{\partial\rho_B}\right]_{\rho,e}G_{\vec{k}}^{B,\alpha}(t_1)+\left[\frac{\partial\beta}{\partial\rho}\right]_{\rho_B}G_{\vec{k}}^{\rho,\alpha}(t_1)\right.$$
$$\left.\left.+\left[\frac{\partial\beta}{\partial e}\right]_{\rho,\rho_B}G_{\vec{k}}^{e,\alpha}(t_1)\right]\right\}, \tag{3.9}$$

where D is given by Eq. (2.26a). Note that all terms but the first on the rhs of Eq. (3.9) are $O(\rho_B)$ as $\rho_B\to 0$. In addition, using Eq. (3.7b) to find the vertices and Eq. (3.5) gives

$$k^2(L_{BT}-L_{BT}^{(0)})=-\frac{2}{\rho}\int_0^\infty dt\int_{k_1<k_c}\frac{d\vec{k}_1}{(2\pi)^3}i\vec{k}\cdot G_{\vec{k}-\vec{k}_1}^{\vec{P}\alpha}(t)\left[G_{\vec{k}_1}^{B,\gamma}(t)-\frac{\rho_B}{\rho}G_{\vec{k}}^{\rho\gamma}(t)\right]\tilde{V}_{\vec{k};\vec{k}-\vec{k}_1,\vec{k}_1}^{E\alpha\gamma}\ , \tag{3.10}$$

where we have used the fact that B vertex must involve momentum and either of ρ or ρ_B. The combination of propagators appearing in the square brackets is exactly what appears on the rhs of Eq. (3.9). Thus there are only two possibilities: (1) $\gamma=B$ for which (see below) $\tilde{V}^{A\alpha B}=\delta_{\alpha\vec{P}}O(\rho_B)$ or (2) $\gamma\neq B$ in which case the propagators in square brackets are $O(\rho_B)$. To linear order in ρ_B, we can now write

$$
\begin{aligned}
&k^2(L_{BT}-L_{BT}^{(0)})\\
&\quad=-\frac{2}{\rho}\int_0^\infty dt\int_{k_1<k_c}\frac{d\vec{k}_1}{(2\pi)^3}\Bigg[i\vec{k}\cdot G^{\vec{P}\vec{P}}_{\vec{k}-\vec{k}_1}(t)e^{-Dk_1^2t}\left[\tilde{V}^{E,P,B}_{\vec{k},\vec{k}-\vec{k}_1,\vec{k}_1}-\frac{\rho_B}{\rho}\tilde{V}^{E,P,P}_{\vec{k},\vec{k}-\vec{k}_1,\vec{k}_1}\right]\\
&\qquad -i\vec{k}\cdot G^{\vec{P}\alpha}_{\vec{k}-\vec{k}_1}(t)k_1^2\int_0^t dt_1e^{-Dk_1^2(t-t_1)}\Bigg\{\left[L_{BB}\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{\rho_B,e}-L_{BT}\left[\frac{\partial\beta}{\partial\rho}\right]_{\rho_B,e}\right]G^{\rho\gamma}_{\vec{k}_1}(t_1)\\
&\qquad\qquad +\left[L_{BB}\left[\frac{\partial\beta\mu}{\partial e}\right]_{\rho,\rho_B}-L_{BT}\left[\frac{\partial\beta}{\partial e}\right]_{\rho,\rho_B}\right]G^{E\gamma}_{\vec{k}_1}(t_1)\Bigg\}\\
&\qquad \times\tilde{V}^{E\alpha\gamma}_{\vec{k},\vec{k}-\vec{k}_1,\vec{k}_1}\Bigg]+O(\rho_B^2)\,,
\end{aligned}
\tag{3.11}
$$

where the term resulting from that containing $L_{BT}(\partial\beta/\partial\rho_B)G^{B\alpha}$ on the rhs of Eq. (3.9) has been dropped since its contribution is $O(\rho_B^2)$. This follows from the fact that the term would involve the vertex with $\gamma=B$, this supplying an additional factor of ρ_B. For similar reasons, in the sums over α and γ in Eq. (3.11) we can omit those terms for which α or γ equals B. The remaining propagators involve only the solvent variables and can thus be evaluated at $\rho_B=0$. The explicit evaluation of the propagators for a pure fluid is straightforward, tedious, and the result appears in Appendix A. In addition, the explicit forms of the remaining vertices follow from Eqs. (3.6) and (3.7), yielding

$$
\tilde{V}^{E,P,\alpha}_{k;k-k_1,k_1}=\tilde{V}^{E,\alpha,P}_{k;k_1,k-k_1}=\begin{cases}\dfrac{i\vec{k}}{2}\rho k_BT\left[\dfrac{\partial\bar{H}}{\partial a_{\alpha_1}}\right]\dfrac{\langle\hat{A}_{\alpha_1}\hat{A}_\alpha\rangle}{V}, & \alpha\neq P\\ 0, \ \text{otherwise}\end{cases}
\tag{3.12}
$$

where the small-k (hydrodynamic) approximation has been used. The susceptibilities can be expressed as thermodynamic derivatives, thereby obtaining

$$
\tilde{V}^{EP\rho}=\tilde{V}^{E\rho P}=\tfrac{1}{2}i\vec{k}\rho k_BT\left[\frac{\partial\bar{H}}{\partial\beta\mu_F}\right]_{\beta,\beta\mu}\,,
\tag{3.13a}
$$

$$
\tilde{V}^{EPE}=\tilde{V}^{PEP}=\tfrac{1}{2}i\vec{k}\rho k_BT\left[\frac{\partial\bar{H}}{\partial-\beta}\right]_{\beta\mu,\beta\mu_F}\,,
\tag{3.13b}
$$

and

$$
\tilde{V}^{EPB}=\tilde{V}^{EBP}=\tfrac{1}{2}i\vec{k}\rho k_BT\left[\frac{\partial\bar{H}}{\partial\beta\mu}\right]_{\beta,\beta\mu_F}\,.
\tag{3.13c}
$$

We now have all the information needed to evaluate Eq. (3.11). The integrations are straightforward and the result is

$$
\begin{aligned}
(L_{BT}-L_{BT}^{(0)})=\frac{k_ck_BT}{3\pi^2\rho(\nu_t+D)}&\Bigg\{\Bigg[\left[\left[\frac{\partial\bar{H}}{\partial\beta\mu}\right]_{\beta,\beta\mu_F}-\frac{\rho_B}{\rho}\left[\frac{\partial\bar{H}}{\partial\beta\mu_F}\right]_{\beta,\beta\mu}\right]\rho-\rho\left[\bar{H}\left[\frac{\partial\bar{H}}{\partial\beta\mu_F}\right]_{\beta\rho_B}+\left[\frac{\partial\bar{H}}{\partial\beta}\right]_{\beta\mu_F,\rho_B}\right]\\
&\times\left[L_{BB}\left[\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{e,\rho_B}\left[\frac{\partial p_h}{\partial e}\right]_{\rho,\rho_B}-\left[\frac{\partial\beta\mu}{\partial e}\right]_{\rho,\rho_B}\left[\frac{\partial p_h}{\partial\rho}\right]_{e,\rho_B}\right]\right.\\
&\left.-L_{BT}\left[\left[\frac{\partial\beta}{\partial\rho}\right]_{e,\rho_B}\left[\frac{\partial p_h}{\partial e}\right]_{\rho,\rho_B}-\left[\frac{\partial\beta}{\partial e}\right]_{\rho,\rho_B}\left[\frac{\partial p_h}{\partial\rho}\right]_{e,\rho_B}\right]\right]\Bigg]\Bigg/[(\nu_t+\Gamma_T)c_0^2]\Bigg\}\,,
\end{aligned}
\tag{3.14}
$$

where unless stated otherwise the thermodynamic quantities are taken to be functions of ρ, ρ_B, and e. In deriving Eq. (3.14) terms $O(k_c\nu_t/c_0)$ were omitted. As defined in Appendix A, c_0 is the adiabatic sound speed, Γ_T is the heat mode damping constant, and $\bar{C}_p$ is the heat capacity at constant pressure per unit mass. With the use of thermodynamic identitites, contained in Appendix B, Eq. (3.14) can be written as

$$(L_{BT}-L_{BT}^{(0)})=\frac{k_c k_B T\rho_B}{3\pi^2\rho(\nu_t+D)}\left[[\Delta E-\bar{H}(\Delta N_F+M)]\left[1+\frac{D}{(\nu_t+\Gamma_T)}\right]+k_BT^2\gamma_T-\frac{L_{BT}}{\rho_B(\nu_t+\Gamma_T)}\right], \tag{3.15}$$

where γ_T is the thermal-expansion coefficient and where Eqs. (2.37) and (2.34) have been used. This equation must be solved for L_{BT}; the result is

$$L_{BT}=\left\{\frac{k_c k_B T\rho_B}{3\pi^2\rho(\nu_t+D)}\left[[\Delta E-\bar{H}(\Delta N_F+M)]\left[1+\frac{D}{\nu_t+\Gamma_T}\right]+k_BT^2\gamma_T\right]+L_{BT}^{(0)}\right\}\Bigg/\left[1+\frac{k_c k_B T}{3\pi^2\rho(\nu_t+D)(\nu_t+\Gamma_T)}\right]. \tag{3.16}$$

Before we calculate the thermal-diffusion ratio k_T and the thermophoretic force constant η_T, we need the mode-coupling result for the diffusion constant. In the same way we obtained L_{BT}, it follows[25] that

$$D-D_0=\frac{k_c k_B T}{3\pi^2\rho(\nu_t+D)}. \tag{3.17}$$

What is usually assumed is that D_0 is negligible and that $k_c\sim O(R^{-1})$, i.e., the inverse-particle radius. If this is justified, then D has the Stokes-Einstein form (ignoring the small differences arising from different boundary conditions). Moreover, $D\ll(\nu_t+\Gamma_T)$ and thus

$$L_{BT}\approx L_{BT}^{(0)}+\rho_B D\{[\Delta E-\bar{H}(\Delta N_F+M)]+k_BT^2\gamma_T\}. \tag{3.18}$$

With the use of Eqs. (3.16), (3.17), (2.36), (2.37), and (2.26c) it is easily shown that

$$k_T=\left[\frac{L_{BT}^{(0)}}{k_BT\rho_BD}+T\gamma_T\right]\Bigg/\left[1+\frac{D}{\nu_t+\Gamma_T}\right] \tag{3.19}$$

and consequently, it follows [cf. Eq. (2.30)] that

$$\eta_T=\left[\frac{L_{BT}^{(0)}}{T\rho_BD}+k_B(T\gamma_T-1)\right], \tag{3.20}$$

where the term $O[D/(\nu_t+\Gamma_T)]$ was dropped.

The second terms explicitly proportional to k_B in Eq. (3.20) are far too small to explain the observed values of η_T; in fact, for a gas $\gamma_T\approx 1/T$ and thus they drop out all together. For a liquid $T\gamma_T\ll 1$ and hence the resulting contribution to the thermophoretic force is $+k_B\vec{\nabla}T$, again negligible for macroscopic particles. This implies that the dominant contribution to η_T is

$$\eta_T\approx\frac{L_{BT}^{(0)}}{\rho_BTD}=\xi\frac{L_{BT}^{(0)}}{\rho_Bk_BT^2},$$

where the second equality follows from the definition of the friction constant ξ [cf. Eq. (2.28)]. Thus, the mode coupling has renormalized the friction (diffusion) constant and nothing more. Moreover, the thermophoretic velocity in steady state $(-\eta_T/\xi\nabla T)$ would involve only bare quantities. Hence, unlike the case of the diffusion constant, here, neglecting the bare quantities makes the thermophoretic force too small. Mode coupling, as used above, provides no information about "bare" transport coefficients and is not useful in calculating the thermophoretic force. It does show that the source of the effect is of nonhydrodynamic or bare nature. As we show in the next paper, the cancellation of the hydrodynamic part of the Soret coefficient (i.e., the renormalization) in the thermophoretic force constant also occurs when kinetic theory is used. The result will be of exactly the same form as Eq. (2.31), although kinetic theory gives us the bare quantities.

It should not come as a surprise that the mode-coupling approach presented above does not renormalize η_T. One of the main ingredients of the mode-coupling theory was the convective nonlinear couplings in the energy-transport equation. From Eqs. (3.13) and Appendix B we see that the required vertex functions involve ΔE, the energy increase when one B particle is added to the fluid. This energy has contributions from degrees of freedom which are almost perfectly separable from the translational degrees of freedom (e.g., nuclear forces). Nonetheless, this energy is convected along and thus appears in the vertex function. The final results must, of course, be independent of this kind of internal energy and thus the cancellation which did occur should indeed be expected.

In conclusion, we have shown that mode coupling, (i.e., nonlinear fluctuating hydrodynamics) does not lead to any significant renormalization of the thermophoretic force coefficient. This is somewhat of a surprise since even the crudest mode-coupling theories (at least qualitatively) describe the renormalization of the diffusion coefficients. The thermophoretic force constant is essentially a Soret coefficient. In gases it is well known that Soret coefficients are extremely sensitive to details, e.g., potential form, unlike quantities like the viscosity and diffusion coefficients. Consequently, a good theory of thermophoresis must include much more microscopic information.

IV. SUMMARY

This paper contains two main results. First, we have established a connection between the Soret and Dufour phenomena and that of the thermophoresis. This connection is given quantitatively by Eq. (2.30) and it serves as a basis for the rest of our work. Our second result, which follows from the mode-coupling calculation (Sec. III), is that the usual nonlinear hydrodynamic couplings cannot possibly be responsible for the observed size of thermophoretic force. Indeed, their contribution is negligible. We conclude from these results that unlike, e.g., the Stokes-Friction phenomenon, thermophoresis cannot be explained or calculated on the basis of a purely hydrodynamic theory. This is somewhat surprising since the thermophoresis is really a *macroscopic* effect, i.e., in experiments the sizes of the "moving" particles are of the order of μm—and unlike Brownian motion, this is not a fluctuating phenomenon. Moreover, it is easy to show that a hydrodynamic solution in which a B particle has zero velocity (and thus one solves only the Fourier heat equations) is linearly stable for an incompressible fluid. Taking into account compressibility will not change the result.

The results of this paper are valid as long as

(i) Linear-response theory holds.

(ii) The Brownian motion time scale is short enough.

(iii) The particle is sufficiently large such that fluctuations can be neglected in using a mean force.

If these hold, then the formalism developed here should be valid for arbitrary densities of the host fluid and for a wide range of particle sizes. The assumption of the separability of the B internal degrees of freedom does not affect the connection to the thermal-diffusion ratio or the mode-coupling calculation.

As mentioned in the Introduction, hydrodynamic theories yielding thermophoretic forces do exist, but they assume *special* boundary conditions that, strictly speaking, are adequate only in the kinetic domain and therefore there is no obvious reason why they should be applicable in dense hydrodynamic regimes. It is worthwhile noting, based on the mode-coupling calculation, that no significant long-time tail phenomena are expected for the thermal-diffusion ratio.

It remains, therefore, to show the true source of thermophoresis. In the next paper in this series, the thermophoretic source is shown to follow, at least in a moderately dense gas, from kinetic processes that occur basically at the surface of the B particle and are not of hydrodynamic origin. The results obtained from a resummed kinetic theory compare well with experiments and thus will substantiate the main conclusions of this paper.

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APPENDIX A: HYDRODYNAMIC PROPAGATOR

The hydrodynamic matrix for a simple fluid $\underline{M}_k$ is given by

$$M_{\vec{x}} = \left\{ \begin{array}{ccccc} 0 & 0 & ik & 0 & 0 \\ -k^2\kappa_\rho & -k^2\kappa_e & ikh/\rho & 0 & 0 \\ ik\chi_\rho & ik\chi_e & -k^2\nu_l & 0 & 0 \\ 0 & 0 & 0 & -k^2\nu_t & 0 \\ 0 & 0 & 0 & 0 & -k^2\nu_t \end{array} \right\}, \tag{A1}$$

where the hydrodynamic variables are the mass, energy, and momentum densities. The quantities in the matrix are defined through

$$\chi_\rho \equiv \left(\frac{\partial p_h}{\partial \rho} \right)_e, \quad \chi_e \equiv \left(\frac{\partial p_h}{\partial e} \right)_\rho ,$$
$$\kappa_\rho \equiv \lambda \left(\frac{\partial T}{\partial \rho} \right)_e, \quad \kappa_e \equiv \lambda \left(\frac{\partial T}{\partial e} \right)_\rho , \tag{A2}$$
$$\nu_l \equiv (\zeta + \tfrac{4}{3}\eta)/\rho, \quad \nu_t \equiv \eta/(\rho) ,$$

where h is the enthalpy density, ρ is the mass density, and λ, ζ, and η are the thermal conductivity and bulk and shear viscosities, respectively. e, T, and p_n are energy density, temperature, and hydrostatic pressure, respectively.

The corresponding longitudinal block propagator is given by

$$\exp(M_k^l \sigma)$$
$$= \frac{1}{2c_0^2} \begin{pmatrix} (e^{\xi_+\sigma} + e^{\xi_-\sigma})\chi_n/m + 2e^{\xi_T\sigma}\chi_e h/mn, & \chi_e(e^{\xi_+\sigma} + e^{\xi_-\sigma} - 2e^{\xi_T\sigma})/m, & c_0(e^{\xi_+\sigma} - e^{\xi_-\sigma})/m \\ \chi_n h(e^{\xi_+\sigma} + e^{\xi_-\sigma} - 2e^{\xi_T\sigma})/mn, & \chi_e h(e^{\xi_+\sigma} + e^{\xi_-\sigma})/mn + 2\chi_n^{\xi_T\sigma}/m, & c_0 h(e^{\xi_+\sigma} - e^{\xi_-\sigma})/mn \\ c_0\chi_n(e^{\xi_+\sigma} - e^{\xi_-\sigma}), & c_0\chi_e(e^{\xi_+\sigma} - e^{\xi_-\sigma}), & c_0^2(e^{\xi_+\sigma} + e^{\xi_-\sigma}) \end{pmatrix} , \tag{A3}$$

where c_0 is the adiabatic speed of sound,

$$\Gamma_s = \frac{1}{2} \left[\left(\frac{c_p}{c_v} - 1 \right) \Gamma_T + \nu_l \right]$$

is the sound damping coefficient, $\Gamma_T = \lambda/\rho c_p$ is the thermal damping coefficient, c_p is the specific heat at constant pressure, c_v is the specific heat at constant volume, and $\bar{c}_p$ is c_p per unit mass. The qualities $\xi_\pm, \xi_T$ are defined through

$$\xi_\pm(k) \sim \pm ikc_0 - k^2\Gamma_s ,$$
$$\xi_T(k) \sim -k^2\Gamma_T . \tag{A4}$$

APPENDIX B: SOME THERMODYNAMIC RELATIONS

In this appendix we derive the thermodynamic expressions appearing in Eq. (3.14). Unless explicitly stated, we use relations for a single component fluid: (i)

$$\left(\frac{\partial \beta}{\partial \rho} \right)_e \left(\frac{\partial p_h}{\partial e} \right)_\rho - \left(\frac{\partial \beta}{\partial e} \right)_\rho \left(\frac{\partial p_h}{\partial \rho} \right)_e$$
$$= - \left(\frac{\partial \beta}{\partial e} \right)_\rho \left[\left(\frac{\partial p_h}{\partial \rho} \right)_e - \left(\frac{\partial p_h}{\partial e} \right)_\rho \left(\frac{\partial e}{\partial \rho} \right)_\beta \right]$$
$$= - \left(\frac{\partial \beta}{\partial e} \right)_\rho \left(\frac{\partial p_h}{\partial \rho} \right)_\beta = \frac{1}{k_B T^2 C_v \rho \gamma_p} , \tag{B1}$$

where γ_p is the compressibility.

(ii) Let $\bar{H}$ be the enthalpy per unit mass, $\bar{S},\bar{V},\bar{N}$ the entropy, volume, and number per unit mass. With the use of standard thermodynamic identities (for constant particle number)

$$d\bar{H} = T\,d\bar{S} + \bar{V}\,dp = \bar{e}_p dT + \bar{V}(1 - T\gamma_T)dp , \tag{B2}$$

where

$$\gamma_T \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p_h}$$

is the expansion coefficient and

$$\bar{H}\frac{dT}{T^2} - \bar{V}\frac{dp}{T} + d\left(\frac{\mu}{T} \right) = 0 , \tag{B3}$$

it follows that

$$d\bar{H} = \left(\bar{C}_p + \frac{\bar{H}}{T}(1 - T\gamma_T) \right) dT$$
$$+ T(1 - T\gamma_T) d\left(\frac{\mu}{T} \right) . \tag{B4}$$

Consequently,

$$\bar{H} \left(\frac{\partial \bar{H}}{\partial \beta\mu} \right)_\beta - \left(\frac{\partial \bar{H}}{\partial -\beta} \right)_{\beta\mu}$$
$$= k_B \left[\bar{H}T(1 - T\gamma_T) - T^2 \left(\bar{C}_p + \frac{\bar{H}}{T}(1 - T\gamma_T) \right) \right]$$
$$- k_B T^2 \bar{C}_p . \tag{B5}$$

(ii) We have then

$$\frac{\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{e,\rho_B}\left[\frac{\partial p_h}{\partial e}\right]_{\rho,\rho_B}-\left[\frac{\partial\beta\mu}{\partial e}\right]_{\rho,\rho_B}\left[\frac{\partial p_h}{\partial\rho}\right]_{e,\rho_B}}{\left[\frac{\partial(-\beta)}{\partial\rho}\right]_{e,\rho_B}\left[\frac{\partial p_h}{\partial e}\right]_{\rho,\rho_B}-\left[\frac{\partial(-\beta)}{\partial e}\right]_{\rho,\rho_B}\left[\frac{\partial p_h}{\partial\rho}\right]_{e,\rho_B}}$$

$$=\frac{\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{e,\rho_B}-\left[\frac{\partial\beta\mu}{\partial e}\right]_{\rho,\rho_B}\left[\frac{\partial e}{\partial\rho}\right]_{\rho_B p_h}}{\left[\frac{\partial(-\beta)}{\partial p}\right]_{e\rho_B}-\left[\frac{\partial(-\beta)}{\partial e}\right]_{\rho,\rho_B}\left[\frac{\partial e}{\partial\rho}\right]_{\rho_B p_h}}$$

$$=\frac{\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{p_h,\rho_B}}{\left[\frac{\partial-\beta}{\partial\rho}\right]_{p_h,\rho_B}}\ . \tag{B6}$$

(iv) As is well known,[26] the chemical potential μ_B for the solute particles, in the limit of high dilution is given by

$$M\beta\mu_B=\ln n_B-\ln\frac{\Xi^{(1)}}{V\Xi^0}+O(n_B)\ , \tag{B7}$$

where $\Xi^{(1)}$ is the semigrand partition function for one solute particle and Ξ^0 for the pure fluid. Hence,

$$M\,d\beta\mu_B=\frac{dn_B}{n_B}-\Delta E d(-\beta)-\Delta N_f d\beta\mu_F$$

$$+O(n_B)\ , \tag{B8}$$

where $\Delta E\equiv\langle E\rangle_1-\langle E\rangle_0$ is the difference in total energy between the system with one solute particle and pure fluid and $\Delta N_f\equiv\langle N_f\rangle_1-\langle N_f\rangle_0$ has a similar definition. Thus, for constant ρ_B (or n_B):

$$0=M\,d\beta\mu+\Delta E d(-\beta)+(\Delta N_f+M)d\beta\mu_F\ , \tag{B9}$$

where M is the mass of the B particle.

Substituting (B9) into (B6) we obtain

$$\frac{\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{p_h,\rho_B}}{\left[\frac{\partial(-\beta)}{\partial\rho}\right]_{p_h,\rho_0}}=-\frac{1}{M}\frac{\left[\Delta E\left[\frac{\partial(-B)}{\partial\rho}\right]_{\rho_B,p_h}+(\Delta N_f+M)\left[\frac{\partial\beta\mu_F}{\partial\rho}\right]_{\rho_B,p_h}\right]}{\left[\frac{\partial(-\beta)}{\partial\rho}\right]_{\rho_B,p_h}}$$

$$=-\frac{1}{M}\left[\Delta E+(\Delta N_f+M)\left[\frac{\partial\beta\mu_F}{\partial-\beta}\right]_{p_h,\rho}\right]\ . \tag{B10}$$

Using

$$\left[\frac{\partial\beta\mu_F}{\partial\beta}\right]_{p_h,\rho}=-\bar{H}\ , \tag{B11}$$

we finally obtain

$$\frac{\left[\frac{\partial\beta\mu}{\partial\rho}\right]_{p_h,\rho_B}}{\left[\frac{\partial(-\beta)}{\partial\rho}\right]_{p_h,\rho_B}}=-\frac{1}{M}[\Delta E-(\Delta N_f+M)\bar{H}]\ . \tag{B12}$$

(v) Next, we wish to calculate $(\partial H/\partial\beta\mu)_{\beta,\beta\mu_F}$ to linear order to the B-particle number n_B:

$$n_f=n_f^0+n_B\Delta N_f\ , \tag{B13a}$$

$$e=e_0+n_B\Delta E\ , \tag{B13b}$$

$$p_h=p_0+k_BTn_B\ , \tag{B13c}$$

where p_0,n_f^0,e_0 are pressure, number, and energy densities of the pure fluid. Thus, the enthalpy is given by

$$h=h_0+n_B(\Delta E+k_BT) \tag{B13d}$$

and the enthalpy per unit mass $\bar{H}$ is given by

$$\bar{H}=\bar{H}_0+\left[\frac{\Delta E+k_BT}{M}-\bar{H}_0(\Delta N_f/M+1)\right]\frac{\rho_B}{\rho_F^0}\ . \tag{B14}$$

Using (B7), we find

$$\begin{aligned}\left(\frac{\partial \bar{H}}{\partial \beta\mu}\right)_{\beta\mu_F,\beta} &= \left(\frac{\partial \bar{H}}{\partial \beta\mu_B}\right)_{\beta\mu_F,\beta} \\ &= \left(\frac{\partial \bar{H}}{\partial n_B}\right)_{\beta\mu_F,\beta}\left(\frac{\partial n_B}{\partial \beta\mu_B}\right)_{\beta\mu_F,\beta} \\ &= \left(\frac{\partial \bar{H}}{\partial n_B}\right)_{\beta\mu_F,\beta} M n_B = M\left(\frac{\partial \bar{H}}{\partial \rho_B}\right)_{\beta\mu_F}\rho_B\ .\end{aligned} \tag{B15}$$

Now , with the use of (B14)

$$\begin{aligned}\left(\frac{\partial \bar{H}}{\partial \beta\mu}\right)_{\beta\mu_F,\beta} &= M(\bar{H}-\bar{H}_0) \\ &= [\Delta E + k_B T - \bar{H}_0(\Delta N_f + M)]\frac{\rho_B}{\rho_F}\ .\end{aligned} \tag{B16}$$

Next using

$$\left(\frac{\partial \bar{H}}{\partial \beta\mu_F}\right)_{\beta} = k_B T(1 - T\gamma_T)\ . \tag{B17}$$

we find

$$\begin{aligned}\left(\frac{\partial \bar{H}}{\partial \beta\mu}\right)_{\beta\mu_F,\beta} - \frac{\rho_B}{\rho}\left(\frac{\partial \bar{H}}{\partial \beta\mu_F}\right)_{\beta,\beta\mu} &= [\Delta E + k_B T - \bar{H}(\Delta N_f + M) \\ &\quad - k_B T(1 - T\gamma_T)]\frac{\rho_B}{\rho_F}\ .\end{aligned} \tag{B18}$$

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