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Phoretic forces on convex particles from kinetic theory and nonequilibrium thermodynamics

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In this article we derive the phoretic forces acting on a tracer particle, which is assumed to be small compared to the mean free path of the surrounding nonequilibrium gas, but large compared to the size of the surrounding gas molecules. First, we review and extend the calculations of Waldmann [Z. Naturforsch. A **14A**, 589 (1959)] using half-sphere integrations and an accommodation coefficient characterizing the collision process. The presented methodology is applied to a gas subject to temperature, pressure, and velocity gradients. Corresponding thermophoretic, barophoretic, and rheophoretic forces are derived, and explicit expressions for spherical particles are compared to known results. Second, nonequilibrium thermodynamics is used to join the diffusion equation for the tracer particle with the continuum equations of nonisothermal hydrodynamics of the solvent. So doing, the distinct origin of the thermophoretic and barophoretic forces is demonstrated. While the latter enters similarly to an interaction potential, the former is given by flux-flux correlations in terms of a Green-Kubo relation, as shown in detail. © 2006 American Institute of Physics.
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I. INTRODUCTION

Phoretic forces on a tracer particle are caused by inhomogeneities in the properties of the solvent, e.g., temperature, pressure, and velocity field, giving rise to thermo-, baro-, and rheophoresis, respectively. Thermophoretic forces caused by a temperature gradient give rise to dust structures, are of central interest in the scavenging of aerosol particles in clouds, when droplets and/or ice crystals grow or evaporate, during the fall of hydrometeors,^{1,2} and have been discussed in the context of nonequilibrium thermodynamics,^{3,4} and in terms of a kinetic description, leading to a stochastic differential equation for a tracer particle in a solvent.⁵ In contrast to thermophoretic forces, barophoretic effects caused by pressure gradients⁶ and rheophoretic forces caused by velocity field gradients have been considered less frequently and not yet elaborated in an extensive, complete, or unifying fashion. The same is true concerning dielectrophoresis and photophoresis.^{7,8} A recent review on experimental results and theoretical approaches towards thermophoresis can be found in Ref. 2.

Inspired by a “first-principles” approach involving half-sphere integrations put forward by Waldmann,⁹ in this article we will demonstrate how the diverse phoretic forces on a dissolved tracer can be obtained in a conceptually simple manner for particles of arbitrary convex shape and for arbitrary solvent velocity distribution functions. The simultaneous incorporation of thermo-, baro-, and rheophoresis is complete in the sense that it accounts for inhomogeneities in all of the independent field variables of a nonisothermal hydrodynamic description of the solvent.

The manuscript is organized as follows. In Sec. II we derive the force acting on a surface element of a tracer particle by half-sphere integrations over solvent distribution functions before and after a collision with the tracer particle. All results will contain an accommodation coefficient a characterizing the collision process (elastic versus diffusive, $0 \leq a \leq 1$). In Sec. III, the general expressions for the phoretic and friction forces are evaluated for a spherical tracer particle. The resulting forces will be used to write down both the Langevin dynamics and the Fokker-Planck equation (FPE) for the tracer particle, suitable for immediate numerical implementation, complementing direct simulation Monte Carlo methods.^{10,11} In Sec. IV, the dynamics of the tracer particle is embedded in a wider description that encompasses also the continuum equations for the nonisothermal hydrodynamics of the solvent. Nonequilibrium thermodynamics is used to examine the phoretic effects from a nonkinetic perspective.

II. KINETIC THEORY

The point of departure is the Boltzmann equation for the velocity distribution function of solvent particles subjected to temperature and flow gradients in a reference frame where the mean velocity vanishes. By solving the Boltzmann equation for a rarefied gas one finds that the velocity distribution function $f(\mathbf{c})$ in its 13th moment approximation, which is equivalent with a second-order orthonormal Sonine polynomial expansion,¹² holds as approximate asymptotic solution,

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$$f(\mathbf{c}) = f_0(\mathbf{c}) \left[1 + \frac{4}{5} \left\langle \tilde{\mathbf{c}} \left(\tilde{c}^2 - \frac{5}{2} \right) \right\rangle_f \cdot \left(\tilde{\mathbf{c}} \left(\tilde{c}^2 - \frac{5}{2} \right) \right) + 2 \left\langle \tilde{\mathbf{c}}\tilde{\mathbf{c}} - \frac{\tilde{c}^2}{3} \mathbf{1} \right\rangle_f : \left(\tilde{\mathbf{c}}\tilde{\mathbf{c}} - \frac{\tilde{c}^2}{3} \mathbf{1} \right) \right],$$

$$f_0(\mathbf{c}) = n_s (\beta/\pi)^{3/2} e^{-\tilde{c}^2}, \quad (1)$$

where the averages are calculated using f itself; \mathbf{c} is the peculiar velocity, i.e., solvent particle velocity relative to the locally averaged, “macroscopic,” and eventually inhomogeneous flow velocity \mathbf{v} of solvent particles, $\beta \equiv m_s/(2k_B T)$ is used to define the dimensionless velocity $\tilde{\mathbf{c}}$ via $\tilde{\mathbf{c}} = \sqrt{\beta} \mathbf{c}$, the quantities n_s and m_s denote number density and mass of the solvent molecules, respectively, and f_0 is Maxwell’s isotropic velocity distribution function. Both distribution functions f and f_0 are normalized as $\langle 1 \rangle = n_s^{-1} \int f(\mathbf{c}) d^3c = 1$. In particular, $\sqrt{\beta} \langle \mathbf{c} \rangle_f = \mathbf{0}$, $\beta \langle c^2 \rangle_f = 3/2$, and $\beta \langle c^2 \rangle_f^2 = 4/\pi$, unaffected by the anisotropy of f . This feature, in turn, suffices to motivate the expansion chosen in (1) using orthonormal Sonine polynomials.¹³ The approach followed in this manuscript goes beyond a 13th moment approximation. With the help of Appendix B higher-order terms can be evaluated along the lines indicated in this manuscript, and the results will not depend on any approximation such as the hydrodynamic approximation. However, this limit had been often used. Next, we introduce it; results will be stated in the later sections.

The expansion coefficients in (1) were related to microscopic expressions for heat flux \mathbf{q} and anisotropic friction pressure tensor $\bar{\mathbf{p}}$ by Maxwell,^{9,14}

$$\left\langle \mathbf{c} \left(\tilde{c}^2 - \frac{5}{2} \right) \right\rangle_f = \frac{1}{p} \mathbf{q}, \quad (2)$$

$$2 \langle \tilde{\mathbf{c}}\tilde{\mathbf{c}} \rangle_f = \frac{1}{p} \bar{\mathbf{p}}. \quad (3)$$

The symbol $\bar{\mathbf{a}}$ denotes the symmetric traceless part of a tensor \mathbf{a} , i.e., $\bar{\mathbf{a}} = \frac{1}{2}(\mathbf{a} + \mathbf{a}^T) - \frac{1}{3} \text{Tr}(\mathbf{a}) \mathbf{1}$, and $p = \frac{1}{3} \text{Tr}(\mathbf{p})$ is the hydrostatic pressure. In the hydrodynamic approximation^{9,14,15}

$$\mathbf{q} = -\lambda \nabla T, \quad \lambda = \frac{15}{4} \frac{k_B}{m_s} \eta, \quad (4)$$

$$\bar{\mathbf{p}} = -2\eta \bar{\nabla} \mathbf{v}, \quad (5)$$

where η stands for the (Newtonian) viscosity of the pure solvent, \mathbf{q} denotes the heat flux, and $\bar{\mathbf{p}}$ the friction pressure tensor. For an ideal gas made of rigid spheres of diameter d , the viscosity is explicitly given as $\eta \propto \sqrt{m_s k_B T} / \pi d^2$ with a prefactor of $5/16$,^{13,15,16} and $p = n_s k_B T$. With or without hydrodynamic approximation, we will make use of the distribution function (1) to calculate a pressure tensor, phoretic forces, etc., for second-order Sonine polynomials below. The extension to higher-order Sonine polynomials does not require any additional tools.

A. Alternate notations

We mention two alternate notations of the distribution function (1) supplemented with (2)–(5).

- (i) In view of connecting the distribution function of solvent molecules with macroscopically observed gradients of intensive variables, one inserts Eqs. (2)–(5) into (1) to recover the notation preferred in Refs. 5, 14, and 17,

$$f(\mathbf{c}) = f_0(\mathbf{c}) \Phi(\tilde{\mathbf{c}}),$$

$$\Phi(\tilde{\mathbf{c}}) = 1 - \Theta \cdot \tilde{\mathbf{c}} \left(\tilde{c}^2 - \frac{5}{2} \right) - \Gamma : \tilde{\mathbf{c}}\tilde{\mathbf{c}}, \quad (6)$$

where the nondimensional temperature gradient Θ and the nondimensional, symmetrized, and traceless velocity-gradient tensor Γ —hopefully these newly chosen symbols help us to remember their physical meaning throughout the manuscript—are given by

$$\Theta = \frac{3\eta}{2p} \frac{1}{\sqrt{\beta}} \nabla \ln T = -\frac{4}{5p} \sqrt{\beta} \mathbf{q}, \quad (7)$$

$$\Gamma = \frac{2\eta}{p} \bar{\nabla} \mathbf{v} = -\frac{1}{p} \bar{\mathbf{p}}. \quad (8)$$

- (ii) For convenience, in the remainder of this manuscript we are going to deal with a distribution function normalized to unity, and to perform integrations over dimensionless quantities. We still have $\tilde{\mathbf{c}} = \sqrt{\beta} \mathbf{c}$ to define a reduced velocity $\tilde{\mathbf{c}}$. The dimensionless distribution function $f^*(\tilde{\mathbf{c}})$, with $\int f^*(\tilde{\mathbf{c}}) d^3\tilde{c} = 1$, therefore reads

$$f^*(\tilde{\mathbf{c}}) = \frac{f(\mathbf{c})}{n_s \beta^{3/2}} = f_0^*(\tilde{c}) \Phi(\tilde{\mathbf{c}}), \quad (9)$$

where $\Phi(\tilde{\mathbf{c}}) \neq 1$ characterizes (anisotropic) deviations from the isotropic, dimensionless, Maxwell distribution $f_0^*(\tilde{c}) = e^{-\tilde{c}^2} / \pi^{3/2}$. The scalar function $\Phi(\tilde{\mathbf{c}})$ is expanded into powers of $\tilde{\mathbf{c}}$ as

$$\Phi(\tilde{\mathbf{c}}) = \sum_{m=0}^{\infty} \Phi_m(\tilde{c}) \odot^m (\otimes^m \tilde{\mathbf{c}}),$$

$$= \Phi_0(\tilde{c}) + \Phi_1(\tilde{c}) \cdot \tilde{\mathbf{c}} + \Phi_2(\tilde{c}) : \tilde{\mathbf{c}}\tilde{\mathbf{c}} + \dots, \quad (10)$$

where $(\otimes^m \tilde{\mathbf{c}})$ denotes the m -fold dyadic product of $\tilde{\mathbf{c}}$, and $\tilde{c} = |\tilde{\mathbf{c}}|$. Writing this series in terms of Sonine polynomials¹⁵ instead, as in (1), offers some mathematical beauty, such that the coefficients F_m become “moments” of f^* , but for the present purpose, the notation (10) will be useful. While the isotropic Maxwell distribution is trivially recovered for $\Phi_0 = 1$ and $\Phi_{m>0} = 0$, the distribution (1) transforms into (9) and (10) with $\Phi_0 = 1$, $\Phi_1(\tilde{c}) = -\Theta(\tilde{c}^2 - 5/2)$, and $\Phi_2(\tilde{c}) = -\Gamma = \bar{\Phi}_2$, as we read off from (6).

B. Forces on surface elements of convex particles

For a quiescent solvent, Waldmann⁹ calculated the stress tensor $\mathbf{\Pi}$ at any surface position of a quiescent tracer particle in a straightforward manner. The related force $d\mathbf{F}$ on a surface element dS —whose normal \mathbf{n} points into the gas—of the tracer particle is $d\mathbf{F} = -\mathbf{\Pi}(\mathbf{n}) \cdot \mathbf{n} dS$. In order to rederive and extend his results we start from the kinetic pressure tensor

$$\mathbf{\Pi}(\mathbf{n}) = \int_{\mathbf{c} \cdot \mathbf{n} < 0} m_s \mathbf{c} \mathbf{c} f^-(\mathbf{c}) d^3c + \int_{\mathbf{c} \cdot \mathbf{n} > 0} m_s \mathbf{c} \mathbf{c} f^+(\mathbf{c}) d^3c, \quad (11)$$

where it is assumed that the rebound of the tracer particle upon collision can be neglected due to the assumed large mass disparity between tracer and solvent particles. In terms of sizes, this assumption means that the diameter of the tracer particle must be at least an order of magnitude larger than that of the solvent molecules, resulting in a mass disparity of three orders of magnitudes. In (11), $f^-(\mathbf{c})$ and $f^+(\mathbf{c})$ denote the velocity distribution functions for the gas particles approaching to, and—after colliding—departing from the tracer particle, respectively. Under the assumptions made in Ref. 9, one uses $f^-(\mathbf{c}) = f(\mathbf{c})$ with f the velocity distribution function of the pure gas at the position of the dissolved tracer. This implies the assumption that the velocity distribution of the solvent is disturbed only marginally by the presence of the tracer particle, which is satisfied if the tracer particle size is substantially smaller than the mean free path in the solvent, a regime often termed “large Knudsen number” or “free-molecule” limit. For the outgoing particles one makes the plausible ansatz $f^+(\mathbf{c}) = (1-a)f(\mathbf{c}') + a(n^+/n_s)f_0$, with $\mathbf{c}' = \mathbf{c} - 2\mathbf{c} \cdot \mathbf{nn}$ the velocity of the reflected gas particle, the Maxwell’s equilibrium distribution f_0 (1), and further involving a coefficient $0 < a < 1$ quantifying the amount of diffusively (versus elastically, purely elastic for $a=0$) reflected gas atoms. By making use of the uncrossability of the tracer particle, $(\int_{\mathbf{c} \cdot \mathbf{n} < 0} \mathbf{c} f^- d^3c + \int_{\mathbf{c} \cdot \mathbf{n} > 0} \mathbf{c} f^+ d^3c) \cdot \mathbf{n} = 0$, one can immediately evaluate $n^+ = 2n_s \sqrt{\pi} Z_0(\mathbf{n})$ and express $\mathbf{\Pi}$ and $d\mathbf{F}$ as follows:

$$\frac{\mathbf{\Pi}(\mathbf{n})}{p} = 4(1-a)\mathbf{Z}_1(\mathbf{n}) \cdot \mathbf{nnn} + 2a\mathbf{Z}_1(\mathbf{n})\mathbf{n} - a\sqrt{\pi}Z_0(\mathbf{n})\mathbf{1} + \dots (\mathbf{1} - \mathbf{nn}),$$

$$\frac{\mathbf{\Pi}(\mathbf{n})}{p} \cdot \mathbf{n} = 4(1-a)\mathbf{Z}_1(\mathbf{n}) \cdot \mathbf{nn} + 2a\mathbf{Z}_1(\mathbf{n}) - a\sqrt{\pi}Z_0(\mathbf{n})\mathbf{n}, \quad (12)$$

in terms of two dimensionless “projected moments” Z_0 and \mathbf{Z}_1 , with the k th rank tensor

$$\mathbf{Z}_k = \mathbf{n} \cdot \int_{\tilde{\mathbf{c}} \cdot \mathbf{n} < 0} (\otimes^{k+1} \tilde{\mathbf{c}}) f^*(\tilde{\mathbf{c}}) d^3\tilde{c}. \quad (13)$$

Now we use our notations (9) and (10) and introduce spherical coordinates to split \mathbf{Z}_k for all $k=0, 1, \dots$, into integrals over radial and angle coordinates as

$$\mathbf{Z}_k(\mathbf{n}) \equiv \frac{1}{\sqrt{\pi}} \sum_{m=0}^{\infty} \mathbf{R}_{m,k} \odot^m \mathbf{\Omega}_{k+m}(\mathbf{n}), \quad (14)$$

$$\mathbf{R}_{m,k} \equiv \int_0^{\infty} x^{3+m+k} e^{-x^2} \Phi_m(x) dx, \quad (15)$$

$$\mathbf{\Omega}_k(\mathbf{n}) \equiv -\frac{1}{\pi} \int_{\mathbf{y} \cdot \mathbf{n} < 0} (\otimes^k \mathbf{y})(\mathbf{n} \cdot \mathbf{y}) d^2y. \quad (16)$$

Using the methods of Ref. 18 and with the help of Appendix A, we obtain $\mathbf{\Omega}_0 = \mathbf{1}$, $\mathbf{\Omega}_1 = -(2/3)\mathbf{n}$, $\mathbf{\Omega}_2 = (1/4)(\mathbf{1} + \mathbf{nn})$, etc., cf. Appendix B. In Ref. 9, the force has been calculated for a distribution function of the form (1). To summarize, once a distribution function f or f^* for the gas particles in the absence of a suspended particle is given, we can immediately identify the coefficients Φ_m in (10) and evaluate the force on a surface element of a suspended object of arbitrary shape (surface S) via the surface integral $\mathbf{F} = \int_S d\mathbf{F} = -\int_S \mathbf{\Pi} \cdot \mathbf{n} dS$ with $\mathbf{Z}_k(\mathbf{n})$ from (14) needed to evaluate $\mathbf{\Pi} \cdot \mathbf{n}$ from (12). Since the problem of the half-sphere integration of definition (16) is solved, the remaining operation is the simple one-dimensional radial integration in (15).

For the important case that $\Phi_m(\tilde{c})$ in (9) has a polynomial form and is symmetric in \tilde{c} , i.e.,

$$\Phi_m(\tilde{c}) = \sum_{i=0}^{\infty} \alpha_{m,i} \tilde{c}^{2i}, \quad (17)$$

we can explicitly evaluate also the radial integral,

$$\begin{aligned} \mathbf{R}_{m,k} &= \sum_{i=0}^{\infty} \alpha_{m,i} \int_0^{\infty} x^{3+m+k+2i} e^{-x^2} dx, \\ &= \sum_{i=0}^{\infty} \frac{\alpha_{m,i}}{2} \Gamma\left(2+i+\frac{m+k}{2}\right), \end{aligned} \quad (18)$$

involving the gamma function with $\Gamma(1)=1$, $\Gamma(1/2)=\sqrt{\pi}$, and $\forall_{n>1} \Gamma(n+1)=n\Gamma(n)$.

C. Summary of results for surface elements

For a solvent velocity distribution function of the form

$$f(\mathbf{c}) = f_0(\mathbf{c}) \sum_i \sum_m \tilde{c}^{2i} \alpha_{m,i} \odot^m (\otimes^m \tilde{\mathbf{c}}), \quad (19)$$

where \tilde{c} is the norm of the dimensionless peculiar velocity $\tilde{\mathbf{c}} = \sqrt{\beta} \mathbf{c}$ of a gas particle, and f_0 Maxwell’s distribution (1), $\beta = m_s / (2k_B T)$, and with the abbreviation

$$\lambda_x \equiv (i+x)! \equiv \Gamma(i+x+1), \quad (20)$$

we arrive at expressions for Z_0 and \mathbf{Z}_1 directly in terms of given α ’s (17), known $\mathbf{\Omega}$ ’s (B2) carrying the surface element normal \mathbf{n} , and numerical factors λ_{\dots} (20),

$$\mathbf{Z}_k = \sum_{i=0}^{\infty} \sum_{m=0}^{\infty} \frac{1}{2\sqrt{\pi}} \frac{\lambda_{2+k+m}}{2} \alpha_{m,i} \odot^m \mathbf{\Omega}_{m+k}. \quad (21)$$

Inserting (21) into (12) yields

$$\frac{\mathbf{\Pi}}{p} \cdot \mathbf{n} = \sum_{i=0}^{\infty} \sum_{m=0}^{\infty} \alpha_{m,i} \odot^m \left[\frac{2(1-a)}{\sqrt{\pi}} \lambda_{\frac{3+m}{2}} \mathbf{\Omega}_{m+1} \cdot \mathbf{nn} + \frac{a}{\sqrt{\pi}} \lambda_{\frac{3+m}{2}} \mathbf{\Omega}_{m+1} - \frac{a}{2} \lambda_{\frac{2+m}{2}} \mathbf{\Omega}_m \mathbf{n} \right]. \quad (22)$$

These are the main results of this section and $d\mathbf{F} = -\mathbf{\Pi} \cdot \mathbf{n} dS$ the final expression for the force on a surface element. The results are therefore valid for arbitrarily convex-shaped tracer particles. For even more explicit expressions for Z_0 , Z_1 , and $\mathbf{\Pi} \cdot \mathbf{n}$, see Appendix C.

As side results, we can also evaluate the anisotropy of the “technical” density n^+ and the distribution function $f^+(\mathbf{c})$ of gas particles just after colliding with the tracer particle at its surface normal \mathbf{n} . According to Sec. II B we have $f^+(\mathbf{c}) = (1-a)f(\mathbf{c}-2\mathbf{c} \cdot \mathbf{nn}) + 2a\sqrt{\pi}Z_0(\mathbf{n})f_0(\mathbf{c})$ where $\sqrt{\pi}Z_0(\mathbf{n})$ is given by (21) for $k=0$ or (C1). Integrating $f^+(\mathbf{c})$ over the tracer particle’s surface allows us to discuss the net effect of a tracer onto the solvent within a distance below the mean free path of gas particles.

III. APPLICATION OF KINETIC THEORY TO SPHERICAL TRACER PARTICLE

For the case of a spherical tracer particle with radius R the force \mathbf{F}_\circ exerted by the solvent on the tracer particle becomes, upon essentially integrating (22) over the unit sphere (S_1),

$$\begin{aligned} \mathbf{F}_\circ &= - \int_{\circ} \mathbf{\Pi} \cdot \mathbf{n} dS = -R^2 \int_{S_1} \mathbf{\Pi} \cdot \mathbf{n} d^2n \\ &= R^2 \sum_{i,m} \alpha_{m,i} \odot^m \left[\frac{2(1-a)}{\sqrt{\pi}} \lambda_{\frac{3+m}{2}} \int p \mathbf{\Omega}_{m+1} \cdot \mathbf{nn} d^2n + \frac{a}{\sqrt{\pi}} \lambda_{\frac{3+m}{2}} \int p \mathbf{\Omega}_{m+1} d^2n - \frac{a}{2} \lambda_{\frac{2+m}{2}} \int p \mathbf{\Omega}_m \mathbf{n} d^2n \right]. \end{aligned} \quad (23)$$

The formula is valid inside and outside mechanical equilibrium, i.e., for arbitrary $p=p(\mathbf{n})$, and with or without hydrodynamic approximation. Most of the occurring integrals are tabulated in Appendix B. If p is insensitive to \mathbf{n} , the resulting force solely depends on the coefficients $\Phi_{1,3,5,\dots}$ of the unperturbed distribution function because of the property $\mathbf{\Omega}_m(-\mathbf{n}) = (-1)^m \mathbf{\Omega}_m(\mathbf{n})$, and since integrals over odd “powers” of \mathbf{n} vanish for symmetry reasons. A sample expression for the force (23) can be found in Appendix C.

In order to apply all the above results, to recover some known formulas, and to generalize the treatment by Waldmann⁹ who considered a temperature gradient, let us take into account temperature, flow, and pressure gradients (Fig. 1) of the gas, and switch to a reference frame of an unperturbed gas moving with a laboratory speed $\mathbf{v}_T = \mathbf{c}_T + \mathbf{v}$ of the tracer particle (at the location of the tracer). The distribution function of the gas to be used for the calculation of the force on the tracer reads

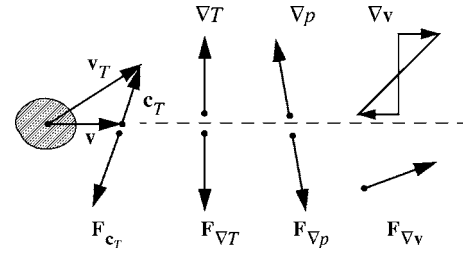


FIG. 1. Illustration of symbols used in the text. The solvent and the tracer velocity are given by \mathbf{v} and \mathbf{v}_T , respectively, and $\mathbf{c}_T = \mathbf{v}_T - \mathbf{v}$. The subscript of the forces indicates their physical origin, namely, friction and gradients in temperature, pressure, and velocity.

$$f^*(\tilde{\mathbf{c}} - \tilde{\mathbf{c}}_T) = f_0^*(\tilde{\mathbf{c}}) \Phi(\tilde{\mathbf{c}}), \quad (24)$$

with $\Phi(\tilde{\mathbf{c}})$ from (6). Assuming, as in Ref. 9, a tracer particle peculiar velocity small compared with the peculiar velocity of gas particles, $c_T \ll c$, i.e., by neglecting second- and higher-order terms in $\tilde{\mathbf{c}}_T$,

$$f^*(\tilde{\mathbf{c}}) = \int_0^* (\tilde{\mathbf{c}} + \tilde{\mathbf{c}}_T) \Phi(\tilde{\mathbf{c}} + \tilde{\mathbf{c}}_T) = f_0^*(\tilde{\mathbf{c}}) (1 - 2\tilde{\mathbf{c}} \cdot \tilde{\mathbf{c}}_T) \Phi(\tilde{\mathbf{c}} + \tilde{\mathbf{c}}_T). \quad (25)$$

This is an explicit expression for f^* upon replacing Φ from (6) and casts f^* into the form (19). By comparing (25) with (19) we read off the following coefficients needed to apply the general formulas of Sec. II C:

$$\begin{aligned} \alpha_{0,0} &= 1 + \frac{5}{2} \Theta \cdot \tilde{\mathbf{c}}_T, & \alpha_{0,1} &= -\Theta \cdot \tilde{\mathbf{c}}_T, \\ \alpha_{1,0} &= \frac{5}{2} \Theta - 2\tilde{\mathbf{c}}_T - 2\Gamma \cdot \tilde{\mathbf{c}}_T, & \alpha_{1,1} &= -\Theta, \\ \alpha_{2,0} &= -\Gamma - 7\Theta \tilde{\mathbf{c}}_T, & \alpha_{2,1} &= 2\Theta \tilde{\mathbf{c}}_T, \\ \alpha_{3,0} &= 2\Gamma \tilde{\mathbf{c}}_T. \end{aligned} \quad (26)$$

Only the symmetric parts of the α 's will actually enter the calculation. According to Sec. II, prior applying the hydrodynamic approximations (7) and (8) in the next section, Γ and Θ are self-consistently related to the expansion coefficients of the Sonine polynomial by

$$\Gamma = -2 \langle \tilde{\mathbf{c}}^2 \tilde{\mathbf{c}} \rangle_{f^*}, \quad \Theta = \frac{4}{5} \langle \tilde{\mathbf{c}} \left(\frac{5}{2} - \tilde{c}^2 \right) \rangle_{f^*}, \quad (27)$$

with f^* given by (25).

When calculating the force on the tracer particle in terms of the surface integral of $\mathbf{\Pi} \cdot \mathbf{n}$ given by Eq. (23), in the case of nonuniform situations attention must be paid to where the position-dependent quantities are evaluated. In principle, all contributions to $\mathbf{\Pi} \cdot \mathbf{n}$ should be evaluated at the surface position $\mathbf{r}_n \equiv \mathbf{r} + R\mathbf{n}$, rather than at the particle center \mathbf{r} . In the following, this procedure is applied not to all space-dependent terms in the expression for $\mathbf{\Pi} \cdot \mathbf{n}$, but rather only to the pressure p appearing therein, since it is assumed that higher than first-order space derivatives are negligible for simplicity.

For a spherical tracer particle with radius R , we now insert (26) into (23), write $p(\mathbf{n}) = p + R\mathbf{n} \cdot \nabla p$ with p the hydrostatic solvent pressure evaluated at the center of the tracer particle, and use several of the formulas collected in Appen-

dices B and C to obtain thermophoretic ($\propto \nabla T$), resistive ($\propto \tilde{\mathbf{c}}_T$), rheophoretic ($\propto \nabla \mathbf{v}$), and barophoretic ($\propto \nabla p$) forces,

$$\mathbf{F}_O = \mathbf{F}_{\nabla T} + \mathbf{F}_{\mathbf{c}_T} + \mathbf{F}_{\nabla \mathbf{v}} + \mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T} + \mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T}, \quad (28)$$

$$\mathbf{F}_{\nabla T} = -\frac{\tilde{\zeta}_O}{4} \Theta, \quad (29)$$

$$\mathbf{F}_{\mathbf{c}_T} = -\tilde{\zeta} \tilde{\mathbf{c}}_T, \quad (30)$$

$$\mathbf{F}_{\nabla \mathbf{v}} = \frac{1}{5} \tilde{\zeta}_O \left(1 + \frac{5\pi}{4} a\right) \Gamma \cdot \tilde{\mathbf{c}}_T, \quad (31)$$

$$\mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T} = -V_O \nabla p + \frac{6}{5} V_O \left(1 + \frac{a}{3}\right) \Gamma \cdot \nabla p, \quad (32)$$

$$\mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T} = \frac{a}{20} V_O (\tilde{\mathbf{c}}_T \Theta + \Theta \tilde{\mathbf{c}}_T + \tilde{\mathbf{c}}_T \cdot \Theta \mathbf{1}) \cdot \nabla p, \quad (33)$$

with surface area $A_O = 4\pi R^2$, volume $V_O = A_O R/3$, coefficient $\tilde{\zeta}$ with dimension of force,

$$\tilde{\zeta} = \frac{4}{3\sqrt{\pi}} p A_O \left(1 + \frac{\pi}{8} a\right), \quad (34)$$

and coefficient $\tilde{\zeta}_O$ for the special case of purely elastic collisions,

$$\tilde{\zeta}_O \equiv \lim_{a \rightarrow 0} \tilde{\zeta} = \frac{4}{3\sqrt{\pi}} p A_O. \quad (35)$$

These coefficients are proportional to the surface area of the tracer under consideration. The force contribution due to pressure gradients has been split into a $\tilde{\mathbf{c}}_T$ -dependent term, $\mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T}$, and a $\tilde{\mathbf{c}}_T$ -independent term, $\mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T}$. One should notice that only the terms $\alpha_{m,i}$ with odd m contribute to $\mathbf{F}_{\nabla T}$, $\mathbf{F}_{\mathbf{c}_T}$, and $\mathbf{F}_{\nabla \mathbf{v}}$, only the even m contribute to $\mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T}$, and that only the forces $\mathbf{F}_{\mathbf{c}_T}$ and $\mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T}$ are affected by the accommodation coefficient.

The density deviation becomes upon inserting the above α 's into (21) with $k=0$,

$$\frac{n^+ - n_s}{n_s} = 2n_s \sqrt{\pi} Z_0 = \sqrt{\pi} \tilde{\mathbf{c}}_T \cdot \mathbf{n} - \frac{1}{2} (\Gamma + \tilde{\mathbf{c}}_T \Theta) : \mathbf{nn}, \quad (36)$$

which we can average over the sphere of radius R to obtain

$$\int_{S_R} \frac{n^+ - n_s}{n_s} d^2 n = -\frac{2\pi}{3} \Theta \cdot \tilde{\mathbf{c}}_T, \quad (37)$$

which noticeably does not vanish; n^+ is actually smaller than n_s if $\mathbf{c}_T = \mathbf{v}_T - \mathbf{v}$ and ∇T point in the same direction, and larger n_s in the opposite limit. With (37) at hand the distribution function $f^+(\mathbf{c})$ is immediately written down.

A. Rarefied gas in the hydrodynamic approximation

In order to appreciate the correspondence of parts of these results with known formulas for rarefied gases, where $p = n_s k_B T$ holds, we use the hydrodynamic expressions for Θ

and Γ as well as the one for the heat conduction coefficient λ from Eqs. (4), (7), and (8), to rewrite Eqs. (29)–(34) in a dimensional form,

$$\mathbf{F}_{\nabla T} = -2 \sqrt{\frac{2\pi k_B T}{m_s}} R^2 \eta \nabla \ln T = -\alpha_0 k_B T \nabla \ln T, \quad (38)$$

$$\mathbf{F}_{\mathbf{c}_T} = -\zeta \mathbf{c}_T, \quad (39)$$

$$\mathbf{F}_{\nabla \mathbf{v}} = \frac{16}{15} \sqrt{\frac{2\pi m_s}{k_B T}} R^2 \eta \left(1 + \frac{5\pi}{4} a\right) \nabla \mathbf{v} \cdot \mathbf{c}_T, \quad (40)$$

$$\mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T} = -V_O \nabla p + \frac{12}{5} V_O \left(1 + \frac{a}{3}\right) \eta \nabla \mathbf{v} \cdot \nabla \ln p, \quad (41)$$

$$\mathbf{F}_{\nabla p}^{\tilde{\mathbf{c}}_T} = \frac{3a}{40} V_O \eta [\mathbf{c}_T (\nabla \ln T) + (\nabla \ln T) \mathbf{c}_T + \mathbf{c}_T \cdot (\nabla \ln T) \mathbf{1}] \cdot \nabla \ln p, \quad (42)$$

with friction coefficient ζ and thermodiffusion coefficient α_0 given by

$$\zeta = \sqrt{\beta} \tilde{\zeta} = \frac{8}{3} R^2 n_s \sqrt{2\pi m_s k_B T} \left(1 + \frac{\pi}{8} a\right), \quad (43)$$

$$\alpha_0 = \frac{5}{4\sqrt{2}} \left(\frac{R}{d}\right)^2 \approx 0.88 \left(\frac{R}{d}\right)^2. \quad (44)$$

Notice that α_0 is not sensitive to the collision parameter a , in contrast to ζ .

For $a=0$ we obtain the results for the case of purely elastic collision processes between tracer and gas particles, and for $a=1$ the purely diffusive limit, where the reflected gas particles “equilibrate” during the collision. The expressions for these forces hold for any ratio c_T/v or v/c with macroscopic flow strength $v=|\mathbf{v}|$, as long as $c_T \ll c$.

Equation (38) coincides with Epstein's result,¹⁹ and Ref. 20 upon replacing η by the translational contribution to the heat conduction coefficient λ given by Eq. (4). The thermophoretic force (38) agrees also with the result of Fernandez de la Mora and Mercer⁵ under the assumption that (i) the solvent particles are significantly smaller and lighter than the tracer particle and (ii) the differential cross section for solvent-tracer collisions is a constant. It may be a surprise that this (contribution to the) thermophoretic force is independent of a ; we could have chosen $f^+(\mathbf{c})=f^-(\mathbf{c}')$ in (11) to arrive at (38). Reference 21 allowed the treatment of the molecular scattering at the particle surface in apparently more detail, taking into account tangential and normal momentum accommodation coefficients, but observations are consistent with the result (38), see also Ref. 2. Mason and Chapman²² showed that the free-molecule thermophoretic force could also be obtained from the dusty-gas model. Their result was different from Waldmann's (38) by a factor of constant because they only considered elastic collisions. However, Monchick *et al.*²³ later showed that the dusty-gas model agrees with (38) if inelastic collision is correctly accounted for. In a large Knudsen number or free-molecule limit, the

thermophoretic velocity is insensitive to particle radius, as confirmed experimentally, and with decreasing Knudsen numbers it is known to decrease, cf. Ref. 24.

The friction force and coefficient ζ given in (39) and (43) are identical with the results of Epstein²⁵ and Waldmann,⁹ Eq. (3.8), and Ref. 20. Notice the sensitivity of the friction coefficient on the coefficient a characterizing the collision process. Smallest friction comes together with purely elastic collisions ($a=0$); it considerably increases with the amount of diffusively reflected gas particles ($0 < a \leq 1$). The friction coefficient (34) evaluated for $a=0$ agrees with the result of Fernandez de la Mora and Mercer⁵ under the same assumptions [aforementioned items (i) and (ii)].

The incorporation of the force proportional to the pressure gradient (barophoretic) is noteworthy in view of linking the tracer particle FPE with the nonisothermal hydrodynamic description of the solvent in the next section. The continuum hydrodynamics is captured in terms of the velocity field \mathbf{v} , the pressure p , and the temperature T of the solvent. Therefore, inhomogeneities in all of these hydrodynamic variables contribute to the force on the tracer particle. It is interesting to note that the dominant contribution to the barophoretic force, $-V_{\circ}\nabla p$, does not depend on kinetic coefficients, contrary to all other force contributions. A similar observation has been made in a slightly different context.⁶ The barophoretic force derived here in terms of solvent pressure differs from force expressions derived in Refs. 26 and 27, where the average pressure of multicomponent mixtures or multiphase fluids is used.

In the absence of pressure gradients, the stationary peculiar velocity of the spherical tracer particle achieved in the force-free state, using $\mathbf{F}_{\circ}=\mathbf{0}$ in (28), reads

$$\begin{aligned} \mathbf{c}_T &= -\frac{1}{4\sqrt{\beta}} \left[\left(1 + \frac{\pi}{8}a\right) \mathbf{1} - \frac{1}{5} \left(1 + \frac{5\pi}{4}a\right) \boldsymbol{\Gamma} \right]^{-1} \cdot \boldsymbol{\Theta} \\ &= -\frac{\lambda}{5} \left[\left(1 + \frac{\pi}{8}a\right) p \mathbf{1} + \frac{1}{5} \left(1 + \frac{5\pi}{4}a\right) \bar{\mathbf{p}} \right]^{-1} \cdot \nabla T, \end{aligned} \quad (45)$$

with λ specified by (4). Einstein²⁸ calculated the velocity of a spherical tracer in the absence of pressure ($\nabla p=0$) and velocity gradients ($\boldsymbol{\Gamma}=\mathbf{0}$), assuming elastic collisions by different arguments, and obtained $\mathbf{c}_T=-\lambda\nabla T/(4p)$ which differs from (45) evaluated at $a=0$ exactly by a factor of 5/4. However, our result (45)—for the special case just mentioned—simplifies to the one later derived by Waldmann⁹ and with early experimental data.^{29,30} The larger a , the smaller will be the magnitude of \mathbf{c}_T . Our equation (45) generalizes these results to the case of nonvanishing flow gradient. We refrain from writing down the generalization to nonvanishing pressure gradient because it is given by the expression for $\mathbf{F}_{\nabla p}^{\tilde{c}_T}$ above.

As will be shown elsewhere, a cube and a sphere experience exactly the same thermophoretic force $\mathbf{F}_{\nabla T}$ per surface area, and $\mathbf{F}_{\nabla v}$ is proportional to the surface area, in general. For elastic collisions ($a=0$), the same holds for the frictional force. The orientation of the cube just enters the viscous force where flow gradient and peculiar velocity couple. The driving force $\mathbf{F}_{\nabla p}^{\tilde{c}_T}$, however, is proportional to volume rather than to the surface area, independent of geometry of the

tracer particle. All except the “volume forces” $\mathbf{F}_{\nabla p}^{\tilde{c}_T}$ can be considered as originated from surface effects, and the acceleration of the tracer particle of course depends on the ratio between surface area or volume and mass of the tracer particle.

B. Fokker-Planck equation for thermophoresis

A particle suspended in an (inhomogeneous) heat bath does not only experience the forces as described by Eq. (28). In addition, there are Brownian forces related to the friction force by way of the fluctuation-dissipation theorem (FDT). Furthermore, there may be additional potential forces (e.g., gravitational and buoyancy), which we like to capture by incorporating a term of the form $-\nabla\varphi_{(t)}$, where $\varphi_{(t)}$ is the corresponding potential for interaction with the tracer particle. According to Eqs. (28)–(33), the force can be split into a term independent of peculiar velocity $\tilde{\mathbf{c}}_T$, denoted as $\mathbf{F}_{\circ}^{\tilde{c}_T}$, and a friction term as

$$\begin{aligned} \mathbf{F}_{\circ} &= \mathbf{F}_{\circ}^{\tilde{c}_T} - \boldsymbol{\zeta} \cdot \mathbf{c}_T, \\ \boldsymbol{\zeta} &= \boldsymbol{\zeta} \left[\mathbf{1} - \frac{1}{5} \left(\frac{1 + (5\pi/4)a}{1 + (\pi/8)a} \right) \boldsymbol{\Gamma} \right] \\ &\quad - \frac{aV_{\circ}\sqrt{\beta}}{20} \left[\boldsymbol{\Theta} \cdot (\nabla p) \mathbf{1} + \boldsymbol{\Theta} (\nabla p) + (\nabla p) \boldsymbol{\Theta} \right], \end{aligned} \quad (46)$$

$$\mathbf{F}_{\circ}^{\tilde{c}_T} = \mathbf{F}_{\nabla T} + \mathbf{F}_{\nabla p}^{\tilde{c}_T} - \nabla\varphi_{(t)}, \quad (47)$$

with symmetric friction tensor $\boldsymbol{\zeta}$. For a spherical particle, in the relaxed momentum approximation ($\mathbf{F}_{\circ} \approx \mathbf{0}$, thus $\mathbf{c}_T \approx \boldsymbol{\zeta}^{-1} \cdot \mathbf{F}_{\circ}^{\tilde{c}_T}$) the change in particle position $d\mathbf{r}$ over a time interval dt is given by the Itô-type stochastic differential equation (SDE)

$$d\mathbf{r} = \left(\mathbf{v} + \boldsymbol{\zeta}^{-1} \cdot \mathbf{F}_{\circ}^{\tilde{c}_T} \right) dt + (\nabla \cdot \mathbf{D}) dt + \mathbf{B} \cdot d\mathbf{W}, \quad (48)$$

with $\mathbf{B} \cdot \mathbf{B}^T = 2\mathbf{D}$, diffusion tensor $\mathbf{D} = k_B T \boldsymbol{\zeta}^{-1}$, and $d\mathbf{W}$ denotes a three-dimensional Gaussian random variable with

$$\langle d\mathbf{W} \rangle = \mathbf{0} \quad \langle d\mathbf{W} d\mathbf{W} \rangle = dt \mathbf{1}. \quad (49)$$

The divergence of \mathbf{D} has to be introduced into Eq. (48) in order to satisfy the FDT, as discussed below. Equations (48) and (49) with (46) and (47) are the basic ingredients for a Brownian dynamics simulation. The FPE for the probability distribution function $\psi(\mathbf{r})$ of the tracer particle, corresponding to the SDE (48), is given by (see, e.g., Ref. 31 or Sec. 11.4 of Ref. 18)

$$\partial_t \psi = -\nabla \cdot \left[(\mathbf{v} + \boldsymbol{\zeta}^{-1} \cdot \mathbf{F}_{\circ}^{\tilde{c}_T}) \psi \right] + \nabla \cdot (\mathbf{D} \cdot \nabla \psi). \quad (50)$$

More specifically, if we disregard terms quadratic in field gradients carried by the solvent, the friction FPE reads, upon inserting the above forces evaluated for spheres into (50),

$$\partial_t \psi = -\nabla \cdot (\mathbf{v}\psi) - \nabla \cdot \left[\mathbf{D} \cdot \left(-\alpha_0 \nabla \ln T - \frac{V_{\circ} \nabla p}{k_B T} - \frac{\nabla \varphi_{(t)}}{k_B T} \right) \psi \right] + \nabla \cdot (\mathbf{D} \cdot \nabla \psi), \quad (51)$$

with $\zeta = \zeta \left\{ \mathbf{1} - \frac{1}{5} [1 + (5\pi/4)a] / (1 + (\pi/8)a) \Gamma \right\}$. In the absence of solvent flow, $\mathbf{v} = \mathbf{0}$, the stationary solution of (51) is given by the Boltzmann distribution function with respect to the potential $\varphi_{(t)} + V_{\circ} p + \alpha_0 k_B T$, irrespective the form of \mathbf{D} , due to insertion of the $(\nabla \cdot \mathbf{D})$ term in (48).

On the bases of Eq. (51), the current of tracer particle in the absence of pressure gradients and external forces is given by $\mathbf{j}_{\psi} = \mathbf{D} \cdot (-\alpha_0 (\nabla \ln T) \psi - \nabla \psi)$ (see Ref. 9), with a thermodiffusion coefficient α_0 given by Eq. (44), in agreement with Ref. 32.

The FPE (51) is the main subject of interest for the remainder of the manuscript, where nonequilibrium thermodynamic techniques will be used to examine its structure in more detail.

IV. GENERIC FORMULATION WITH SINGLE-PARTICLE DISTRIBUTION FUNCTION

Next, the phoretic effects covered by the FPE (51) are embedded into a description of the solvent by using the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC).^{16,33,34} The kinetic derivation of the force of the solvent on the tracer particle has shown that the solvent enters in terms of its hydrodynamic variables only, namely, its temperature, pressure and velocity, and derivatives of these quantities. In that respect, it is sufficient to choose a nonisothermal hydrodynamic description of the solvent. Before proceeding to that embedding, the structure of the full set of equations is given, and notation is introduced.

The solvent is described by the momentum density \mathbf{u} , the mass density ρ , and the internal energy density e . In terms of these variables, the equations describing the nonisothermal hydrodynamics of the solvent and the FPE for the tracer particle take the general form (see, e.g., Ref. 16)

$$\partial_t \mathbf{u} = -\nabla \cdot (\mathbf{v}\mathbf{u}) - \nabla \cdot \boldsymbol{\pi} + \rho \mathbf{F}_{(s)} + \psi m_t \mathbf{F}_{(t)}, \quad (52)$$

$$\partial_t \rho = -\nabla \cdot (\mathbf{v}\rho), \quad (53)$$

$$\partial_t e = -\nabla \cdot (\mathbf{v}e) - (\nabla \mathbf{v})^T : \boldsymbol{\pi} - \nabla \cdot \mathbf{j}_q + m_t \mathbf{F}_{(t)} \cdot \mathbf{j}_{\psi}, \quad (54)$$

$$\partial_t \psi = -\nabla \cdot (\mathbf{v}\psi) - \nabla \cdot \mathbf{j}_{\psi}, \quad (55)$$

with \mathbf{v} the velocity field of the solvent, $\boldsymbol{\pi}$ the total pressure tensor, \mathbf{j}_q the heat flux, and \mathbf{j}_{ψ} the irreversible contribution to the current density of the tracer particle probability. The quantities $\mathbf{F}_{(s)}$ and $\mathbf{F}_{(t)}$ denote external forces (e.g., gravitation) per unit mass of the solvent and tracer particle, respectively, and m_t is the mass of the tracer particle. In the remainder of this section, it is assumed that these external forces can be derived from time-independent potentials.

A. Method

For describing the nonequilibrium system we use the so-called GENERIC (Refs. 33 and 34) formalism which deals with isolated systems, i.e., the total energy is conserved as well as entropy production is non-negative. (A recent extension to open systems can be found in Ref. 35.) The set of independent variables presumably describing the relevant physics in sufficient detail we denote by \mathbf{x} , which may possess discrete as well as continuous indices. Its time evolution,

$$\frac{d\mathbf{x}}{dt} = \mathbf{L}(\mathbf{x}) \cdot \frac{\delta E}{\delta \mathbf{x}} + \mathbf{M}(\mathbf{x}) \cdot \frac{\delta S}{\delta \mathbf{x}}, \quad (56)$$

is fully characterized by two generators E and S , the total energy and entropy functionals, respectively, in terms of the state variables \mathbf{x} , and \mathbf{L} and \mathbf{M} are certain matrices (operators). The symbol \cdot denotes the appropriate inner product. The matrix multiplications imply not only summations over discrete indices but also integration over continuous variables, and $\delta/\delta \mathbf{x}$ typically implies functional rather than partial derivatives.^{16,33,34} The GENERIC framework imposes conditions on the “building blocks” \mathbf{L} and \mathbf{M} . First, Eq. (56) is supplemented by the degeneracy requirements

$$\mathbf{L}(\mathbf{x}) \cdot \frac{\delta S}{\delta \mathbf{x}} = \mathbf{0}, \quad \mathbf{M}(\mathbf{x}) \cdot \frac{\delta E}{\delta \mathbf{x}} = \mathbf{0}. \quad (57)$$

The constraint that the (functional) derivative of the entropy lies in the null space of \mathbf{L} represents the reversible nature of \mathbf{L} . On the other hand, the requirement that the functional derivative of the energy lies in the null space of \mathbf{M} manifests that the total energy is not altered by the \mathbf{M} contribution to the dynamics. Second, \mathbf{L} must be antisymmetric and fulfill the Jacobi identity,³⁶ whereas \mathbf{M} needs to be positive semidefinite and Onsager-Casimir symmetric. The condition (57) implies both the conservation of total energy as well as a non-negative entropy production. The two contributions to the time evolution of \mathbf{x} generated by the total energy E and the entropy S in (56) are called the reversible and irreversible contributions, respectively.

B. Generating functionals

In the choice of variables we are inspired by the similarities between the thermodiffusion model discussed above and two-phase models. Particularly, part of the total volume is occupied by the tracer particle, as manifested in the pressure gradient force on the particle discussed in the previous section. In the following, extensive quantities are referred to as “intrinsic” (denoted by, e.g., $\bar{\rho}$) if they are defined with respect to the volume of the respective phase, and as “extrinsic” (denoted by, e.g., ρ) if defined with respect to the total volume element, i.e., the sum of volumes of both phases. The volume fraction of the solvent is given $\phi_s = 1 - V_{\circ} \psi$, with ψ the distribution function of the tracer particle in space, and $V_{\circ} = (4\pi/3)R^3$ the volume of the tracer particle. The full set of variables chosen here for the GENERIC description of solvent hydrodynamics and tracer particle motion is given by the extrinsic momentum density of the solvent \mathbf{u} , the extrin-

sic mass density of the solvent ρ , the extrinsic energy density of the solvent e , and the distribution function ψ of the tracer particle, i.e., $\mathbf{x}=(\mathbf{u}, \rho, e, \psi)$.

The generating functionals, total energy E and entropy S , are expressed in terms of these variables as follows. The total energy consists of the kinetic energy of the solvent and its internal energy, supplemented by the effects due to external (conservative) interactions with the solvent and the tracer particle. The entropy consists of the entropy of the solvent and configurational entropy due to the distribution function of the tracer particle. In summary, we have

$$E = \int \left(\frac{\mathbf{u}^2}{2\rho} + e + \rho\varphi_{(s)} + \psi\varphi_{(t)} \right) d^3r, \quad (58)$$

$$S = \int \left(\phi_s \hat{s}(\tilde{\rho}_s, \tilde{e}_s) - k_B \psi \ln \frac{\psi}{\psi_0} \right) d^3r, \quad (59)$$

where $\hat{s}()$ is the entropy function of the solvent, and $\tilde{\rho}_s \equiv \rho/\phi_s$ and $\tilde{e}_s \equiv e/\phi_s$ denote the intrinsic mass and energy density of the solvent, respectively. The external potentials $\varphi_{(s)}$ and $\varphi_{(t)}$ acting on the solvent and tracer particle, respectively, are related to the external forces by $\mathbf{F}_{(s)} = -\nabla\varphi_{(s)}$ and $\mathbf{F}_{(t)} = -(1/m_t)\nabla\varphi_{(t)}$. Since the distribution function ψ is dimensional ($[\psi]=\text{m}^{-3}$), a normalization constant ψ_0 needs to be introduced in the logarithmic term of the entropy.

The functional derivatives of the generating functionals are then given by

$$\frac{\delta E}{\delta \mathbf{x}} = \left(\mathbf{v}, -\frac{1}{2}\mathbf{v}^2 + \varphi_{(s)}, 1, \varphi_{(t)} \right)^T, \quad (60)$$

$$\frac{\delta S}{\delta \mathbf{x}} = \left(\mathbf{0}, -\frac{\mu}{T}, \frac{1}{T}, -k_B \left(1 + \ln \frac{\psi}{\psi_0} \right) - \frac{V_{\text{OP}}}{T} \right)^T, \quad (61)$$

where μ and T denote the chemical potential and the temperature, respectively, of the solvent at pressure p , given in terms of partial derivatives of $\hat{s}(\tilde{\rho}_s, \tilde{e}_s)$ as

$$-\frac{\mu}{T} \equiv \frac{\partial \hat{s}}{\partial \tilde{\rho}_s}, \quad (62)$$

$$\frac{1}{T} \equiv \frac{\partial \hat{s}}{\partial \tilde{e}_s}, \quad (63)$$

$$\frac{p}{T} \equiv \hat{s} - \tilde{\rho}_s \frac{\partial \hat{s}}{\partial \tilde{\rho}_s} - \tilde{e}_s \frac{\partial \hat{s}}{\partial \tilde{e}_s}. \quad (64)$$

The velocity of the solvent is defined as $\mathbf{v}=\mathbf{u}/\rho$.

C. Reversible dynamics

In order to determine the reversible dynamics, we now construct the operator \mathbf{L} . It has been discussed and illustrated earlier^{16,34} that this operator is closely related to the generator of space transformations on the field variables. For the evolution equations of momentum density, mass density, and internal energy density, the usual reversible contributions shall be implemented here. The distribution function ψ transforms as a scalar density, in accord with the first term on the

right-hand side of the FPE (51). In view of the functional derivatives (60) and (61), we hence propose the following reversible operator (see also Ref. 16):

$$\mathbf{L} = - \begin{pmatrix} (\nabla \mathbf{u} + \mathbf{u} \nabla)^T & \rho \nabla & e \nabla + \nabla \cdot \boldsymbol{\pi}_{\text{rev}} & \psi \nabla \\ \nabla \rho & 0 & 0 & 0 \\ \nabla e + \boldsymbol{\pi}_{\text{rev}} \cdot \nabla & 0 & 0 & 0 \\ \nabla \psi & 0 & 0 & 0 \end{pmatrix}, \quad (65)$$

with $(\cdot \cdot \cdot)^T$ denoting the transpose with respect to the discrete vector indices. All derivative operators act on everything to their right, also on the functions multiplied to the right of the operator \mathbf{L} . The reversible contribution $\boldsymbol{\pi}_{\text{rev}} = \boldsymbol{\pi}_{\text{rev}}(\rho, e, \psi)$ to the total pressure tensor $\boldsymbol{\pi}$ is determined by way of the degeneracy requirement for the entropy (57), with the result

$$\boldsymbol{\pi}_{\text{rev}} = (p + k_B T \psi) \mathbf{1}, \quad (66)$$

independent of the normalization constant ψ_0 , as expected. Note that this Poisson operator (65) is antisymmetric by construction and satisfies the Jacobi identity.^{16,37,38}

It is straightforward to show that $\mathbf{L} \cdot (\delta E / \delta \mathbf{x})$ results in the reversible contributions to the full set of dynamics equations, i.e., Eqs. (52)–(55) are reproduced with the reversible contribution to the pressure tensor, $\boldsymbol{\pi}_{\text{rev}}$ given by Eq. (66), and with $\mathbf{j}_q = \mathbf{j}_\psi = \mathbf{0}$.

D. Irreversible dynamics

1. Decomposition

The dissipative contributions to the dynamic equations of the variables \mathbf{x} are captured by the metric matrix \mathbf{M} , which can be written in the form³⁹

$$\mathbf{M} = \mathbf{C} \cdot \mathbf{R} \cdot \mathbf{C}^\dagger, \quad (67)$$

where the superscript \dagger denotes not only the transposition of discrete vector indices but implies also calculating the adjoint with respect to the usual scalar product on the space of functions. The idea behind the splitting (67) is to satisfy the degeneracy requirement for the functional derivative of energy in terms of $\mathbf{C}^\dagger \cdot \delta E / \delta \mathbf{x} = \mathbf{0}$, and \mathbf{R} then represents the bare relaxation phenomena. The symmetry and positive semidefiniteness of \mathbf{R} transfer directly to \mathbf{M} by virtue of the decomposition (67).

The dissipative phenomena we concentrate on here shall all originate from spatial inhomogeneities. For the solvent that includes relaxation of the gradients of the velocity field through viscous stresses and heat flow in the internal energy balance, while in the FPE for the tracer particle it is the diffusive motion itself. The driving forces for these effects are gradients of intensive variables. Since the functional derivative of the entropy is free of spatial differentiation, the latter must come into play through the matrix \mathbf{C}^\dagger . Therefore, one needs to satisfy the degeneracy requirement, Eq. (57), for the energy through an operator \mathbf{C}^\dagger that contains spatial derivatives. By inspection of the functional derivative of the energy, a most natural choice for \mathbf{C}^\dagger seems to be

$$\mathbf{C}^\dagger = \begin{pmatrix} \nabla & 0 & -[\nabla \mathbf{v}] & 0 \\ 0 & 0 & \nabla & 0 \\ 0 & 0 & V_{\circ} p \nabla - [\nabla \varphi_{(t)}] & \nabla \end{pmatrix}. \quad (68)$$

The brackets $[\dots]$ indicate that the derivative operator contained therein acts only within the brackets, whereas all other derivative operators in the above equation act also on functions that are multiplied to the right of \mathbf{C}^\dagger . In principle any linear combination of the rows in Eq. (68) could have been chosen. However, with the above definition of \mathbf{C}^\dagger the following expressions are obtained for the thermodynamic driving forces for the relaxation mechanisms:

$$\mathbf{C}^\dagger \cdot \frac{\delta S}{\delta \mathbf{x}} = \begin{pmatrix} -(\nabla \mathbf{v})/T \\ \nabla(1/T) \\ -k_B(\nabla \psi)/\psi - (\nabla \varphi_{(t)})/T - (V_{\circ} \nabla p)/T \end{pmatrix}, \quad (69)$$

which are proportional to “classical” dissipative fluxes of momentum, energy, and tracer particle density. In particular, $V_{\circ} p$ acts as a potential, in accord with the FPE (51).

We point out that since $\delta E/\delta e=1$, we could also have chosen to omit the brackets $[\dots]$ in Eq. (68), and let the derivatives act also on everything multiplied to the right. However, doing so would have resulted in an expression for $\mathbf{C}^\dagger \cdot \delta S/\delta \mathbf{x}$ which is related to Eq. (69) simply through a matrix multiplication. Therefore, the choice to introduce the brackets $[\dots]$ was by no means restrictive, but it simplifies the discussion. For example, the momentum relaxation is comfortably formulated in terms of $(\nabla \mathbf{v})/T$, while using $\nabla(\mathbf{v}/T)$ in conjunction with $\nabla(1/T)$ enforces inconvenient arrangements.

Based on the expression (68) the adjoint operator becomes

$$\mathbf{C} = \begin{pmatrix} -\nabla & 0 & 0 \\ 0 & 0 & 0 \\ -[\nabla \mathbf{v}]^T & -\nabla & -V_{\circ} \nabla p - [\nabla \varphi_{(t)}] \\ 0 & 0 & -\nabla \end{pmatrix}. \quad (70)$$

Since $\mathbf{M} \cdot (\delta S/\delta \mathbf{x})$ must result in the irreversible contributions to the dynamic Eqs. (52)–(55), we can show by virtue of the decomposition (67) and with (70) that

$$\begin{pmatrix} \boldsymbol{\pi}_{\text{visc}} \\ \mathbf{j}_q - V_{\circ} p \mathbf{j}_\psi \\ \mathbf{j}_\psi \end{pmatrix} \equiv \mathbf{R} \cdot \mathbf{C}^\dagger \cdot \frac{\delta S}{\delta \mathbf{x}}, \quad (71)$$

with $\boldsymbol{\pi}_{\text{visc}}$ the viscous contribution to the total pressure tensor $\boldsymbol{\pi} = \boldsymbol{\pi}_{\text{rev}} + \boldsymbol{\pi}_{\text{visc}}$, and \mathbf{j}_q and \mathbf{j}_ψ the total dissipative energy density current and the probability density current of the tracer particle, respectively.

2. Solvent contributions

The pure relaxation processes are specified through the elements of the matrix \mathbf{R} . Since this work focuses on how the solvent couples to the tracer particle, the dissipative effects in the solvent itself are assumed to be given by the standard Newton’s expression for the viscous pressure and Fourier’s law of heat conduction. In view of the physical

interpretation of the thermodynamics fluxes given in Eq. (71) and the thermodynamic driving forces (69), the pure solvent contributions to \mathbf{R} , denoted by $\mathbf{R}_{(s)}$ hereafter, can be given readily (see also Ref. 16),

$$\mathbf{R}_{(s)} = \begin{pmatrix} T\mathbf{D}^{uu} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \lambda T^2 \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} \end{pmatrix}, \quad (72)$$

representing Newton’s expression for the viscous pressure and Fourier’s law of heat conduction. The fourth rank tensor \mathbf{D}^{uu} is described by the elements

$$D_{ijkl}^{uu} = \eta(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \hat{\kappa}\delta_{ij}\delta_{kl}, \quad (73)$$

where the index pairs (i, j) and (k, l) refer to multiplications of \mathbf{D}^{uu} with second rank tensors from the left and right, respectively, and $\hat{\kappa} \equiv \kappa - \frac{2}{3}\eta$. It is tacitly assumed that the material properties are isotropic for simplicity. We note that this fourth rank tensor is symmetric and positive semidefinite if both $\eta \geq 0$ and $\kappa \geq 0$, where η and κ are the shear and the dilational viscosities, respectively. The thermal conductivity of the solvent is denoted as $\lambda \geq 0$. For the case of a rarefied gas, one has $\kappa=0$, and the shear viscosity η and the thermal conductivity λ are given by (4), and the paragraph thereafter.

3. Tracer particle contributions

The irreversible contributions to the FPE for the tracer particle are incorporated into the GENERIC in the following way. First, dynamic contributions to the FPE arise due to entries in the lowest row of \mathbf{R} . Second, in view of (51) and the driving forces (69) one observes that these entries in the lowest row are all proportional to ψ . In this context we note that there is a bound only on the integral of ψ , but not on the local values of ψ itself; so, if the distribution is rather localized, then the values of ψ in that region of space can get relatively large. Hence, in order to achieve positive semidefiniteness of \mathbf{R} for all ψ at all space points \mathbf{r} , all tracer particle contributions to \mathbf{R} must be proportional to ψ . The matrix \mathbf{R} can hence be written as the sum of two terms due to the solvent (s) and the tracer (t), $\mathbf{R} = \mathbf{R}_{(s)} + \mathbf{R}_{(t)}$, where $\mathbf{R}_{(s)}$ is given by (72) and $\mathbf{R}_{(t)}$ is proportional to the distribution function ψ .

Using the driving forces (69), the diffusion term in (51) is reproduced with $\mathbf{R}_{(t), \psi\psi} = \psi \mathbf{D}/k_B$. It is essential to note that by doing so also the term proportional to ∇p is reproduced exactly. For the remaining irreversible terms in the FPE, one gets $\mathbf{R}_{(t), \psi e} = \alpha_0 T \psi \mathbf{D}$, so that the third row of $\mathbf{R}_{(t)}$ takes the form $(\psi/k_B)(\mathbf{0}, \alpha_0 k_B T \mathbf{D}, \mathbf{D})$. Since the matrix $\mathbf{R}_{(t)}$ must be symmetric, the entire third column is also known. The remaining matrix elements are filled in based on the assumption that the effect of the tracer particle on the energy density current is proportional to the particle probability current. This assumption leads to a symmetric and positive semidefinite $\mathbf{R}_{(t)}$ of the form

$$\mathbf{R}_{(t)} = \frac{\psi}{k_B} \begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & (\alpha_0 k_B T)^2 \mathbf{D} & (\alpha_0 k_B T) \mathbf{D} \\ \mathbf{0} & (\alpha_0 k_B T) \mathbf{D} & \mathbf{D} \end{pmatrix} \\ = (0, \alpha_0 k_B T, 1)^T \frac{\psi \mathbf{D}}{k_B} (0, \alpha_0 k_B T, 1). \quad (74)$$

In conjunction with the second component of Eq. (71), one finds that the total dissipative heat flow contains a contribution due to the tracer particles of the form

$$\mathbf{j}_{q,(t)} = (\alpha_0 k_B T + V_{Op}) \mathbf{j}_\psi. \quad (75)$$

The tracer particle transports a thermal energy, $\alpha_0 k_B T$, and a mechanical energy, V_{Op} . The particular form of these terms is connected to the fact that the tracer particle has been assumed both incompressible and athermal, for simplicity.

The above treatment shows also that, on one hand, the (V_{Op}) term in the FPE and the energy density current originates through the degeneracy requirement and physical insight about the meaning of the components of (71). Particularly, the appearance of V_{Op} in the FPE does not depend on choosing some phenomenological coefficients appropriately, but rather originates from proper definitions of the system variables and the entropy function. On the other hand, the terms in the FPE and energy density current proportional to $\alpha_0 k_B T$ enter through the relaxation matrix \mathbf{R} , i.e., through off-diagonal phenomenological coefficients, similar to Refs. 3 and 4. This difference is also of importance in the following.

4. Green-Kubo relation

The elements of the relaxation matrix \mathbf{R} can be interpreted in terms of equilibrium flux-flux correlations,¹⁶ as discussed in the following. The elements of the entire dissipative matrix can be written in the form^{16,40}

$$[1 + \varepsilon(x_j)\varepsilon(x_k)] M_{jk}(\mathbf{r}, \mathbf{r}') = \frac{1}{\tau k_B} \langle \Delta x_j^f(\mathbf{r}) \Delta x_k^{f,*}(\mathbf{r}') \rangle, \quad (76)$$

where $\Delta x_k^{f,*}$ denotes the adjoint of Δx_k^f with respect to the usual scalar product on the space of functions. The quantity $\Delta x_j^f(\mathbf{r})$ is given by the time integral

$$\Delta x_j^f(\mathbf{r}) = \int_0^\tau \dot{x}_j^f(\mathbf{r}, t) dt, \quad (77)$$

with \dot{x}_j^f the rapidly fluctuating part to the evolution of x_j . Here, τ is an intermediate time scale separating the slow degrees of freedom from the fast ones. The symbol $\varepsilon(x_j)$ takes the values +1 and -1 if the variable is even or odd under time reversal, respectively. Writing \mathbf{M} in terms of two space arguments $(\mathbf{r}, \mathbf{r}')$ implies integration over \mathbf{r}' when multiplied with a function from the right. It reduces to the notation in terms of a single variable \mathbf{r} (as used further above) in the case of local-field theories (see Ref. 16 for further details).

In order to satisfy the degeneracy requirement for the energy (57), only energy-conserving fluctuations are considered which satisfy

$$\int \dot{\mathbf{x}}^{f,\dagger}(\mathbf{r}) \cdot \frac{\delta E}{\delta \mathbf{x}(\mathbf{r})} d^3 r = 0, \quad (78)$$

where the superscript \dagger [defined after Eq. (67)] implies both transposition of discrete indices and calculation of the adjoint with respect to the scalar product on function space. In view of the decomposition of \mathbf{M} described above, we make the formal ansatz,

$$\dot{\mathbf{x}}^{f,\dagger} = (\boldsymbol{\pi}^f, \mathbf{j}_q^f, \mathbf{j}_\psi^f) \cdot \mathbf{C}^\dagger. \quad (79)$$

For a microscopic derivation of the occurrence of the operator ∇ in $\dot{\mathbf{x}}^{f,\dagger}$, the reader is referred, e.g., to Ref. 41. The meaning of $\boldsymbol{\pi}^f, \mathbf{j}_q^f$, and \mathbf{j}_ψ^f as the fluctuations in the stress tensor, energy density flux, and particle flux, respectively, becomes evident when calculating the entropy production

$$\int \dot{\mathbf{x}}^{f,\dagger} \cdot \frac{\delta S}{\delta \mathbf{x}} d^3 r = \int (\boldsymbol{\pi}^f, \mathbf{j}_q^f, \mathbf{j}_\psi^f) \cdot \mathbf{C}^\dagger \cdot \frac{\delta S}{\delta \mathbf{x}} d^3 r, \quad (80)$$

with the aid of Eq. (69). The full dissipative matrix for both solvent and tracer particle relaxation can hence be written in the form

$$\mathbf{M}(\mathbf{r}, \mathbf{r}') = \mathbf{C}(\mathbf{r}) \cdot \mathbf{R}_{\text{corr}}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{C}^\dagger(\mathbf{r}'), \quad (81)$$

with the matrix of correlations

$$\mathbf{R}_{\text{corr}} = \frac{1}{2\tau k_B} \left\langle \begin{pmatrix} \Delta_\tau \boldsymbol{\pi}^f(\mathbf{r}) \\ \Delta_\tau \mathbf{j}_q^f(\mathbf{r}) \\ \Delta_\tau \mathbf{j}_\psi^f(\mathbf{r}) \end{pmatrix} \begin{pmatrix} \Delta_\tau \boldsymbol{\pi}^f(\mathbf{r}') \\ \Delta_\tau \mathbf{j}_q^f(\mathbf{r}') \\ \Delta_\tau \mathbf{j}_\psi^f(\mathbf{r}') \end{pmatrix}^T \right\rangle, \quad (82)$$

if one assumes that the stress fluctuations $\boldsymbol{\pi}^f$ are not correlated with \mathbf{j}_q^f and \mathbf{j}_ψ^f . If the correlations are all local, i.e., proportional to the Dirac delta function $\delta(\mathbf{r} - \mathbf{r}')$, the matrix (81) with the $(\mathbf{r}, \mathbf{r}')$ notation can be transformed into the dissipative matrix in the \mathbf{r} notation, corresponding to our discussion in Secs. IV D 1, IV D 2, and IV D 3.

Comparison of the correlation matrix \mathbf{R}_{corr} in Eq. (82) with $\mathbf{R}_{(s)} + \mathbf{R}_{(t)}$ given by Eqs. (72) and (74) nicely illustrates that the thermophoretic effect is directly connected to the cross-correlations of the form $\langle \Delta_\tau \mathbf{j}_q^f(\mathbf{r}) \Delta_\tau \mathbf{j}_\psi^f(\mathbf{r}') \rangle$ (see also Ref. 6 for a similar conclusion). In particular, we know that this correlation gives rise to a term proportional to $\alpha_0 k_B T$ in the FPE of the tracer particle, and to a corresponding contribution to the energy density current. In contrast, the V_{Op} contribution in the FPE and the energy density current is of a different origin, as already discussed.

V. DISCUSSION AND CONCLUSIONS

The phoretic forces on a tracer particle in an inhomogeneous solvent have been examined from two different perspectives. First, in Sec. II, we used a kinetic description of collisions between tracer particles and the particles of a rarefied inhomogeneous gas, i.e., the solvent. We derived the thermo-, baro-, and rheophoretic forces for general convex tracer particles, corresponding to the gradients in temperature, pressure, and velocity of the solvent, respectively. While the appearance of the thermo- and rheophoretic forces goes back to the corresponding terms in the Chapman-Enskog velocity distribution function of the solvent, the barophoretic force originates from the finite spatial extension

of the tracer particle. The results presented in Sec. II C apply to arbitrarily shaped convex tracer particles with or without hydrodynamic approximation and therefore allow, along the lines indicated in this manuscript, and, in particular, with the help of the appendices, to compute results for even more general situations compared with the application to spherical tracers worked out in Sec. III.

In the second part (Sec. IV), we formulated a joint description of the tracer particle diffusion and the nonisothermal hydrodynamics of the solvent. Here, the equation of state of the solvent need not be restricted to rarefied gases. The distinction between thermo- and barophoretic forces again became apparent. On the one hand, the barophoretic force arose naturally due to the finite volume occupied by the tracer particle, in accord to the kinetic description. On the other hand, the thermophoretic effect came into play by way of cross-coupling effects, i.e., off-diagonal elements in the matrix of phenomenological transport coefficients. We have shown how this can be understood, in the setting of the nonequilibrium thermodynamics formalism used here, in terms of correlations between fluctuations in the heat current and the tracer particle current, i.e., in terms of a Green-Kubo expression.

In both the kinetic and the nonequilibrium thermodynamics description of the phoretic effects, the barophoretic force can be traced back to the finite volume of the tracer particle. Also, in both descriptions we found that the barophoretic force is reversible in nature. In contrast, the thermophoretic effect was found to be irreversible in both descriptions.

The nature of the solvent-tracer particle collisions was captured in the accommodation coefficient a , which affects the force exerted on the tracer particles, as discussed in the kinetic description. In the FPE (51) modeled in the nonequilibrium thermodynamics section, the parameter a surfaces only in the diffusion tensor \mathbf{D} of the tracer particle. If we had not neglected terms quadratic in the field gradients carried by the solvent, then also the pressure gradient term in the FPE would depend on a . Including those terms would imply using a more complex expression for the matrix \mathbf{C} when splitting the dissipative matrix \mathbf{M} in the GENERIC treatment. Here, in Sec. IV, we illustrated the dominant effects and their physical background in rather straightforward terms. An extension to include higher-order effects was outside the scope of this manuscript.

The rheophoretic (velocity gradient) force arises in the kinetic description analogously to the thermo- and barophoretic forces. Only in the transition to the FPE in the relaxed momentum approximation the velocity gradient is absorbed into the diffusion tensor \mathbf{D} . In so doing, the gradient in the field variables of the solvent seem to enter asymmetrically into the FPE of the tracer particle. The FPE can be formulated in a more symmetric form if momentum relaxation of the tracer particle is avoided. Then one obtains a FPE for the distribution function $f(\mathbf{r}, \mathbf{p})$, where \mathbf{p} is the momentum of the tracer particle.

This work is currently extended to tracer particles of ellipsoidal, rectangular, cylindrical and other shapes.⁴²

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APPENDIX A: INTEGRATION OVER HALF UNIT SPHERE

Using conventional spherical coordinates and an arbitrary orthogonal system $\{\mathbf{e}_{1,2,3}\}$, a unit vector is usually expressed as

$$\mathbf{n} = n_i \mathbf{e}_i = \cos(\phi) \sin(\theta) \mathbf{e}_1 + \sin(\phi) \sin(\theta) \mathbf{e}_2 + \cos(\theta) \mathbf{e}_3.$$

For any given vector $\mathbf{u} = u\hat{\mathbf{u}}$, $u = |\mathbf{u}| > 0$, we can choose $\mathbf{e}_3 = \hat{\mathbf{u}}$, the condition $\mathbf{u} \cdot \mathbf{n} > 0$ corresponds to $n_3 > 0$, and we have, for an arbitrary function $g(\hat{\mathbf{u}}, \mathbf{n})$

$$\begin{aligned} \int_{\mathbf{u} \cdot \mathbf{n} > 0} g(\hat{\mathbf{u}}, \mathbf{n}) d^2 n &= \int_{n_3 > 0} g(\hat{\mathbf{u}}, \mathbf{n}) d^2 n \\ &= \int_0^{2\pi} \int_0^1 g(\mathbf{e}_3, \mathbf{n}) dn_3 d\phi, \end{aligned} \quad (\text{A1})$$

where the minus sign from $dn_3 = -\sin(\theta)d\theta$ is captured by convenient integration bounds for n_3 . With

$$\begin{aligned} \mathbf{0} &= \int_{S_1} \overline{\otimes^m \mathbf{n}} d^2 n \quad \forall_{m=0,1,2,3} \\ &= \int_{\mathbf{u} \cdot \mathbf{n} < 0} \overline{\otimes^m \mathbf{n}} d^2 n + \int_{\mathbf{u} \cdot \mathbf{n} > 0} \overline{\otimes^m \mathbf{n}} d^2 n, \end{aligned} \quad (\text{A2})$$

where $(\otimes^m \mathbf{n})$ denotes an m -fold dyadic product of \mathbf{n} , all integrals of the type (A1) involving even m 's are immediately evaluated, since the integrand does not change sign under the transformation $\mathbf{n} \rightarrow -\mathbf{n}$, i.e., for arbitrary \mathbf{u} ,

$$\forall_{m=0,2,4,\dots} \int_{\mathbf{u} \cdot \mathbf{n} > 0} \overline{\otimes^m \mathbf{n}} d^2 n = \frac{1}{2} \int_{S_1} \overline{\otimes^m \mathbf{n}} d^2 n = \mathbf{0}, \quad (\text{A3})$$

is independent of \mathbf{u} , specifically, for $m=2$,

$$\begin{aligned} \int_{\mathbf{u} \cdot \mathbf{n} > 0} \mathbf{n} \mathbf{n} d^2 n &= \frac{1}{2} \int_{S_1} \left(\overline{\mathbf{n} \mathbf{n}} + \frac{1}{3} \mathbf{1} \right) d^2 n = \frac{1}{6} \int_{S_1} \mathbf{1} d^2 n \\ &= \frac{2\pi}{3} \mathbf{1}. \end{aligned} \quad (\text{A4})$$

For odd moments, this is different. For the first moment we have, since n_3 is independent of ϕ , and $n_{1,2}$ do change sign under the transformation $\theta \rightarrow -\theta$,

$$\int_{\mathbf{u} \cdot \mathbf{n} > 0} \mathbf{n} d^2 n = - \int_{\mathbf{u} \cdot \mathbf{n} < 0} \mathbf{n} d^2 n = \int_0^{2\pi} \int_0^1 \mathbf{n} dn_3 d\phi = \pi \hat{\mathbf{u}}. \quad (\text{A5})$$

Scalar-valued integrals involving $\hat{\mathbf{u}}$ and \mathbf{n} therefore simplify to

$$\int_{\mathbf{u}\cdot\mathbf{n}>0} (\otimes^m \hat{\mathbf{w}}) \odot^m (\otimes^m \mathbf{n}) d^2n = 2\pi \int_0^1 n_3^m dn_3 = \frac{2\pi}{1+m}, \quad (\text{A6})$$

such that we finally have $\int_{\mathbf{u}\cdot\mathbf{n}>0} \hat{\mathbf{u}} \cdot \mathbf{n} d^2n = \pi$, $\int_{\mathbf{u}\cdot\mathbf{n}>0} \hat{\mathbf{u}} \cdot \mathbf{nn} d^2n = (2\pi/3)\hat{\mathbf{u}}$, $\int_{\mathbf{u}\cdot\mathbf{n}>0} \hat{\mathbf{u}}\hat{\mathbf{u}} \cdot \mathbf{nn} d^2n = 2\pi/3$, $\int_{\mathbf{u}\cdot\mathbf{n}>0} \hat{\mathbf{u}}\mathbf{n} d^2n = \pi\hat{\mathbf{u}}$, etc.

APPENDIX B: INTEGRAL TABLE

The tensors Ω_k , $k=0, 1, 2, \dots$ are defined in (16) as integrals over half a unit sphere, and can be rewritten with the help of Appendix A, where $\hat{\mathbf{u}} = \mathbf{e}_3$ for convenience,

$$\begin{aligned} \Omega_k(\hat{\mathbf{u}}) &\equiv -\frac{1}{\pi} \int_{\mathbf{n}\cdot\hat{\mathbf{u}}<0} (\otimes^k \mathbf{n})(\hat{\mathbf{u}} \cdot \mathbf{n}) d^2n, \\ &= -\frac{1}{\pi} \mathbf{e}_3 \cdot \int_0^{2\pi} \int_{-1}^1 (\otimes^{k+1} \mathbf{n}) dn_3 d\phi. \end{aligned} \quad (\text{B1})$$

The lowest-order tensors read (higher rank tensors can be provided by the second author upon request)

$$\Omega_0 = 1,$$

$$\Omega_1 = -\frac{2}{3} \mathbf{n},$$

$$\Omega_2 = \frac{1}{4} (\mathbf{1} + \mathbf{nn}),$$

$$\Omega_3 = -\frac{2}{3} (\mathbf{nnn} - \hat{\mathbf{n}}\hat{\mathbf{n}}\hat{\mathbf{n}}),$$

$$\Omega_4 = -\frac{7}{24} \hat{\mathbf{n}}\hat{\mathbf{n}}\hat{\mathbf{n}}\hat{\mathbf{n}} + \frac{1}{4} \mathbf{nnnn} + \frac{3}{20} [\mathbf{11}]_{\text{sym}},$$

$$\Omega_5 = -\frac{2}{7} [\mathbf{11n}]_{\text{sym}},$$

$$\begin{aligned} \Omega_6 &= \frac{1}{64} (5[\mathbf{111}]_{\text{sym}} + (\otimes^6 \mathbf{n}) - 5[\mathbf{nnnnn}]_{\text{sym}} \\ &\quad + 15[\mathbf{nn11}]_{\text{sym}}), \end{aligned}$$

$$\Omega_7 = -\frac{2}{9} [\mathbf{n111}]_{\text{sym}}, \quad (\text{B2})$$

where the symbol $\hat{\mathbf{T}}$ denotes the symmetric traceless part¹⁸ of tensor \mathbf{T} , and $[\mathbf{T}]_{\text{sym}}$ the symmetric and normalized part. In particular,

$$[\mathbf{1n}]_{\text{sym}} \equiv \frac{1}{3} (\mathbf{1n} + \mathbf{n1} + \mathbf{n1}),$$

$$[\mathbf{11}]_{\text{sym}} = \frac{1}{3} (\mathbf{11} + \mathbf{111} + \mathbf{111}), \quad (\text{B3})$$

In components, $[\mathbf{11}]_{\text{sym},\mu\nu\kappa\lambda} = \frac{1}{3} (\delta_{\mu\nu}\delta_{\kappa\lambda} + \delta_{\mu\kappa}\delta_{\nu\lambda} + \delta_{\nu\kappa}\delta_{\mu\lambda})$. With the help of Refs. 18 and 43

$$\int_{S_1} \overline{\otimes^k \mathbf{n}} \overline{\otimes^m \mathbf{n}} d^2n = 4\pi \frac{m!}{(2m+1)!!} \delta_{k,m} \Delta^{(m)}, \quad (\text{B4})$$

where $\Delta^{(m)}$ denotes the isotropic tensor of rank m , cf. Refs. 18 and 44, we explicitly calculate nonvanishing integrals to be denoted as Ω_{ij}^k involving Ω_{0-4} over the unit sphere needed to evaluate the force on a tracer in the previous sections

$$\Omega_{ij}^k \equiv \frac{1}{\pi} \int_{S_1} \Omega_i \odot^j (\otimes^k \mathbf{n}) d^2n. \quad (\text{B5})$$

The hereby defined quantity Ω_{ij}^k is a tensor of rank $i+k-2j$ and vanishes for symmetry reasons if $i+k$ is odd. Nonvanishing integrals needed in this manuscript are $\Omega_{00}^0 = \frac{4}{3} \mathbf{1}$, $\Omega_{10}^1 = -\frac{8}{9} \mathbf{1}$, $\Omega_{20}^0 = \frac{4}{3} \mathbf{1}$, $\Omega_{21}^2 = 2[\mathbf{11}]_{\text{sym}}$, $\Omega_{00}^4 = \frac{4}{5} [\mathbf{11}]_{\text{sym}}$, $\Omega_{20}^2 = \frac{1}{5} [\mathbf{11}]_{\text{sym}} + \frac{1}{3} \mathbf{1}$, $\Omega_{30}^1 = -\frac{8}{15} [\mathbf{11}]_{\text{sym}}$, $\Omega_{31}^3 = -\frac{16}{75} [\mathbf{11}]_{\text{sym}} - \frac{8}{45} \mathbf{1}$, $\Omega_{40}^0 = \frac{4}{5} [\mathbf{11}]_{\text{sym}}$, and $\Omega_{41}^2 = \frac{2}{5} [\mathbf{11}]_{\text{sym}}$. Some further use-

ful formulas, if $\Gamma = \hat{\Gamma}$ and \mathbf{u} an arbitrary unit vector,

$$\Gamma \odot^2 \Omega_2 = \frac{1}{3} \Gamma : \mathbf{nn}, \quad (\text{B6})$$

$$\Gamma \odot^2 \Omega_3 = -\frac{4}{15} \Gamma \cdot \mathbf{n}, \quad (\text{B7})$$

$$(\Gamma \mathbf{u}) \odot^3 \Omega_3 = (\mathbf{u} \Gamma) \odot^3 \Omega_3 = -\frac{4}{15} \Gamma : \mathbf{un}. \quad (\text{B8})$$

APPENDIX C: EXPLICIT EXPRESSIONS FOR Z_0, Z_1 , AND FORCE

For the case that $\alpha_{2,i}$ is symmetric traceless, the first terms of the expressions (21) and (22) for Z_0, Z_1 , and $\Pi \cdot \mathbf{n}$ become

$$\begin{aligned} \sqrt{\pi} Z_0 &= \sum_{i=0}^{\infty} \frac{\lambda_1}{2} \alpha_{0,i} - \frac{\lambda_{3/2}}{3} \alpha_{1,i} \cdot \mathbf{n} + \frac{\lambda_2}{8} \alpha_{2,i} : \mathbf{nn} \\ &\quad + \frac{1}{2} \lambda_{5/2} \alpha_{3,i} \odot^3 \Omega_3 + \dots, \end{aligned} \quad (\text{C1})$$

$$\begin{aligned} \sqrt{\pi} Z_1 &= \sum_{i=0}^{\infty} -\frac{\lambda_{3/2}}{3} \alpha_{0,i} \mathbf{n} + \frac{\lambda_2}{8} \alpha_{1,i} \cdot (\mathbf{1} + \mathbf{nn}) - \frac{2}{15} \lambda_{5/2} \alpha_{2,i} \cdot \mathbf{n} \\ &\quad + \frac{1}{2} \lambda_3 \alpha_{3,i} \odot^3 \Omega_4 + \dots, \end{aligned} \quad (\text{C2})$$

by using identities listed in the foregoing section, in particular (B7). Inserting (C1) and (C2) into (12) yields

$$\frac{\mathbf{\Pi}}{p} \cdot \mathbf{n} = \sum_i -\alpha_{0i} \left(\frac{a}{2} \mathbf{l}_1 + \frac{4-2a}{3\sqrt{\pi}} \mathbf{l}_{3/2} \right) \mathbf{n} + \alpha_{1i} \cdot \left\{ \frac{a \mathbf{l}_2}{4\sqrt{\pi}} \mathbf{1} + \left(\frac{4-3a}{4\sqrt{\pi}} \mathbf{l}_2 + \frac{a \mathbf{l}_{3/2}}{3} \right) \mathbf{nn} \right\} + \dots \quad (\text{C3})$$

For example, the first terms of the related force (23) on a spherical tracer, assuming constant pressure p , become

$$\mathbf{F}_\circ = \frac{1}{3} A_\circ p \sum_{i=0}^{\infty} \left\{ \frac{1}{\sqrt{\pi}} \mathbf{l}_2 + \frac{1}{3} a \mathbf{l}_{3/2} \right\} \alpha_{1,i} + \dots \alpha_{3,i} + \dots \\ = \frac{1}{3} A_\circ p \left\{ \frac{8+a\pi}{4\sqrt{\pi}} \alpha_{1,0} + \frac{48+5a\pi}{8\sqrt{\pi}} \alpha_{1,1} \right\} + \dots \quad (\text{C4})$$

¹O. Dupont, F. Dubois, and A. Vedernikov, *Meas. Sci. Technol.* **11**, 331 (2000).

²F. Zheng, *Adv. Colloid Interface Sci.* **97**, 253 (2002).

³A. Pérez-Madrid, J. M. Rubí, and P. Mazur, *Physica A* **212**, 231 (1994).

⁴J. M. Rubí and P. Mazur, *Physica A* **250**, 253 (1998).

⁵J. Fernandez de la Mora and J. M. Mercer, *Phys. Rev. A* **26**, 2178 (1982).

⁶I. Goldhirsch and D. Ronis, *Phys. Rev. A* **27**, 1616 (1983).

⁷Yu. I. Yalamov, V. B. Kutukov, and E. R. Shchukin, *J. Colloid Interface Sci.* **57**, 564 (1976).

⁸L. R. Reed, *J. Aerosol Sci.* **8**, 12 (1977).

⁹L. Waldmann, *Z. Naturforsch. A* **14A**, 589 (1959).

¹⁰G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Clarendon, Oxford, 1994).

¹¹A. L. Garcia and W. Wagner, *Transp. Theory Stat. Phys.* **31**, 579 (2002).

¹²L. Landau and E. Lifshitz, *Physical Kinetics* (Pergamon, Oxford, 1981).

¹³*Thermodynamik der Gase*, Handbuch der Physik Vol. 12, edited by S. Flügge (Springer, Berlin, 1958), p. 373.

¹⁴S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases*, 3rd ed. (Cambridge University Press, Cambridge, 1970).

¹⁵L. E. Reichl, *A Modern Course in Statistical Physics* (Wiley, New York, 1998).

¹⁶H. C. Öttinger, *Beyond Equilibrium Thermodynamics* (Wiley, Hoboken, NJ, 2005).

¹⁷S. Hess in *Vielteilchensysteme*, Bergmann-Schaefer, *Lehrbuch der Experimentalphysik* (W. de Gruyter, Berlin, 1992), Vol. 5, p. 41.

¹⁸M. Kröger, *Models for Polymeric and Anisotropic Liquids*, Lecture Notes in Physics Vol. 675 (Springer, Berlin, 2005).

¹⁹P. S. Epstein, *Proc. Phys. Soc. London* **47**, 259 (1945).

²⁰L. Waldmann, in *Rarefied Gas Dynamics, Proceedings of the Second International Symposium on Rarefied Gas Dynamics*, edited by L. Talbot (Academic, New York, 1961), pp. 323–344.

²¹W. F. Phillips, *Phys. Fluids* **15**, 999 (1972).

²²E. A. Mason and S. Chapman, *J. Chem. Phys.* **36**, 627 (1962).

²³L. Monchick, K. S. Yun, and E. A. Mason, *J. Chem. Phys.* **39**, 654 (1963).

²⁴A. Toda, Y. Ohi, and R. Dobashi, *J. Chem. Phys.* **105**, 7083 (1996).

²⁵P. S. Epstein, *Phys. Rev.* **23**, 710 (1924).

²⁶W. H. Schwarz and T. S. Margulies, *J. Acoust. Soc. Am.* **90**, 3209 (1991).

²⁷M. E. Schimpf and S. N. Semenov, *Phys. Rev. E* **70**, 031202 (2004).

²⁸A. Einstein, *Z. Phys.* **27**, 1 (1924).

²⁹K. H. Schmitt, *Z. Naturforsch. A* **14A**, 870 (1959).

³⁰L. Waldmann and K. H. Schmitt, *Z. Naturforsch. A* **16A**, 1343 (1961).

³¹H. C. Öttinger, *Stochastic Processes in Polymeric Fluids* (Springer, Berlin, 1996).

³²E. A. Mason, *J. Chem. Phys.* **27**, 732 (1957).

³³M. Grmela and H. C. Öttinger, *Phys. Rev. E* **56**, 6620 (1997).

³⁴H. C. Öttinger and M. Grmela, *Phys. Rev. E* **56**, 6633 (1997).

³⁵H. C. Öttinger, *Phys. Rev. E* (accepted).

³⁶M. Kröger and M. Hütter, *H. C. Öttinger, Comput. Phys. Commun.* **137**, 325 (2003).

³⁷Since the Jacobi identity is invariant with respect to a transformation of variables, a useful procedure to prove the Jacobi identity consists in performing a transformation of variables (see also Ref. 16) from the set of variables $\{\mathbf{u}, \rho, e, \psi\}$ to $\{\mathbf{u}, \rho, s, \psi\}$, where s is the total entropy density. In the latter set of variables, the Jacobi identity can be shown by a direct, straightforward calculation.

³⁸M. Hütter, *J. Non-Equilib. Thermodyn.* **27**, 349 (2002).

³⁹B. J. Edwards, *J. Non-Equilib. Thermodyn.* **23**, 301 (1998).

⁴⁰M. Kröger, and H. C. Öttinger, *J. Non-Newtonian Fluid Mech.* **120**, 175 (2004).

⁴¹H. C. Öttinger (submitted).

⁴²M. Kröger and M. Hütter, *J. Chem. Phys.* (submitted).

⁴³M. Kröger, *Phys. Rep.* **390**, 453 (2004).

⁴⁴S. Hess and W. Köhler, *Formeln zur Tensor-Rechnung* (Palm & Enke, Erlangen, 1980).