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Charged Brownian particles: Kramers and Smoluchowski equations and the hydrothermodynamical picture

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ABSTRACT

We consider a charged Brownian gas under the influence of external and non-uniform electric, magnetic and mechanical fields, immersed in a non-uniform bath temperature. With the collision time as an expansion parameter, we study the solution to the associated Kramers equation, including a linear reactive term. To the first order we obtain the asymptotic (overdamped) regime, governed by transport equations, namely: for the particle density, a Smoluchowski-reactive like equation; for the particle's momentum density, a generalized Ohm's-like equation; and for the particle's energy density, a Maxwell–Cattaneo-like equation. Defining a nonequilibrium temperature as the mean kinetic energy density, and introducing Boltzmann's entropy density via the one particle distribution function, we present a complete thermohydrodynamical picture for a charged Brownian gas. We probe the validity of the local equilibrium approximation, Onsager relations, variational principles associated to the entropy production, and apply our results to: carrier transport in semiconductors, hot carriers and Brownian motors. Finally, we outline a method to incorporate non-linear reactive kinetics and a mean field approach to interacting Brownian particles.

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1. Introduction

The ubiquitous Brownian motion [1–8] remains an outstanding paradigm in modern physics [9]. The theoretical framework [10,11] consisting of Kramers equation (a Fokker–Planck equation in phase space), Smoluchowski equation (asymptotic or overdamped contraction of the latter) and the associated stochastic Langevin equation, have been widely applied to diverse problems, such as: Brownian motion in potential wells, chemical reactions rate theory, nuclear dynamics, stochastic resonance, surface diffusion, general stochastic processes and evolution of nonequilibrium systems, in both classical and quantum contexts. More recent applications include thermodynamics of small systems, molecular motors, chemical and biological nanostructures, mesoscopic motors power output and efficiency, and the fractional Kramers equation applied to anomalous diffusion. Concerning reviews and applications, we mention some representative but by no means an exhaustive list of Refs. [10–60], some monographs [61–70] in addition to the “founding papers” [3–8]. In his celebrated 1943 Brownian motion paper [11], Chandrasekhar outlined the method for solving a Brownian particle in a general field of force. It took approximately sixty years to report exact solutions for the Brownian motion of a charged particle in uniform and static electric and/or magnetic fields [71–85] (see also some previous related works [86,87]).

In Section 2 we generalize and extend previous work [75,77] and consider a charged Brownian particle in a general field of force (including magnetic fields), in an inhomogeneous medium (a non-uniform/non-isothermal bath temperature

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profile [88–113]). Furthermore we include a reactive linear term (BGK-like [114–117]) and obtain a general associated Kramers equation. In Section 3 we expand the solution generalizing a previous result [75] yielding recursive relations (for other expansions in the literature see for example Refs. [64,73,118–120]). In Section 4 we use these recursive relations to obtain the hydrothermodynamical picture of Brownian motion. In Section 5 we present some straightforward applications namely, the linear Onsager-like expansions for the entropy production for Brownian motion, generalized Shockley carrier transport equations, hot carrier transport and chemically reacting Brownian gases. Finally in Section 6 our concluding remarks include further applications of our results.

2. Generalized Kramers equation for a Brownian charged particle

Consider a charged Brownian gas composed of N particles (mass m , charge q) in an inhomogeneous bath temperature profile, under the influence of external fields (not necessarily uniform in space, nor time independent). Our starting point is *Kramers* equation for the one particle distribution function $P(\mathbf{x}, \mathbf{v}, t)$, at position \mathbf{x} , with \mathbf{v} and at time t , being in contact with an inhomogeneous bath temperature $T(\mathbf{x})$ (natural units $k_B = 1$) and under a general field of force: a mechanical contribution $\mathbf{F}_{\text{mec}} = -\nabla W$, with $W = -\mathbf{x}\mathbf{F}_{\text{ext}}(t) + U_{\text{mec}}$ (allowing for potential derived forces and non potential homogeneous external forces); an electric contribution $\mathbf{F}_{\text{elec}} = q\mathbf{E} = -q\nabla\phi$ and a magnetic contribution (Lorentz's velocity dependent force) $\mathbf{F}_{\text{mag}} = \frac{1}{c}q\mathbf{v} \times \mathbf{B}$. The total external force can be cast as a potential derived force plus a velocity contribution

$$\mathbf{F}(\mathbf{x}, \mathbf{v}, t) = \mathbf{F}_{\text{mec}}(\mathbf{x}, t) + \mathbf{F}_{\text{elec}}(\mathbf{x}, t) + \mathbf{F}_{\text{mag}}(\mathbf{x}, t) = \mathbf{F}_{\text{pot}} - m\boldsymbol{\omega} \times \mathbf{v} \quad (1)$$

where

$$\begin{aligned} \mathbf{F}_{\text{pot}} &= -\nabla U \\ U &= -\mathbf{x}\mathbf{F}_{\text{ext}}(t) + U_{\text{mec}} + q\phi \\ \boldsymbol{\omega} &= \frac{q}{mc}\mathbf{B}. \end{aligned} \quad (2)$$

For a charged Brownian particle, Kramers equation for the distribution $P(\mathbf{x}, \mathbf{v}, t)$ reads (see for example Refs. [73,75,77])

$$\frac{\partial P}{\partial t} + \mathbf{v} \frac{\partial P}{\partial \mathbf{x}} + \frac{1}{m}\mathbf{F}(\mathbf{x}, \mathbf{v}, t) \frac{\partial P}{\partial \mathbf{v}} = \frac{1}{\tau} \frac{\partial}{\partial \mathbf{v}} \left(\mathbf{v}P + \frac{T(\mathbf{x})}{m} \frac{\partial P}{\partial \mathbf{v}} \right) = \frac{\partial}{\partial \mathbf{v}} \left(\tau^{-1}\mathbf{v}P + \Gamma \frac{\partial P}{\partial \mathbf{v}} \right) \quad (3)$$

where the Brownian collision time is denoted by τ , the mobility by λ , defined by the relation $m\lambda = \tau$ ($\gamma = \lambda^{-1}$ is Stokes friction coefficient). The mobility and the diffusion coefficient D , are both related to the bath temperature via the celebrated fluctuation dissipation theorem $D = \lambda k_B T$ (Sutherland–Einstein relation [4,5]). Notice that in our scheme the mobility (or τ) may also have a position dependent profile; and Γ is related to fluctuations, as given by $D = \tau^2 \Gamma$. The left hand side of the previous equation may be denoted as the streaming operator \mathbb{L} , operating on P along the (Newtonian) trajectory $\mathbf{v} = \dot{\mathbf{x}}$, $m\dot{\mathbf{v}} = \mathbf{F}$. The right hand side is denoted as the Fokker Planck collision kernel operator \mathbb{K}_{FP} where the first term is the contribution of the (dissipative) Stokes force $\mathbf{F}_S = -\gamma\mathbf{v}$ and the second term the fluctuating contribution, so in explicit form we have

$$\mathbb{L}(\mathbf{F}) = \frac{\partial}{\partial t} + \mathbf{v} \frac{\partial}{\partial \mathbf{x}} + \frac{1}{m}\mathbf{F}(\mathbf{x}, \mathbf{v}, t) \frac{\partial}{\partial \mathbf{v}} \quad (4)$$

$$\mathbb{K}_{\text{FP}}(\lambda, \Gamma) = \frac{\partial}{\partial \mathbf{v}} \left(\tau^{-1}\mathbf{v} + \Gamma \frac{\partial}{\partial \mathbf{v}} \right) \quad (5)$$

and we may cast Eq. (3) in the compact form

$$\mathbb{L}(\mathbf{F})P(\mathbf{x}, \mathbf{v}, t) = \mathbb{K}_{\text{FP}}(\tau, \Gamma)P(\mathbf{x}, \mathbf{v}, t). \quad (6)$$

Let us define a tensorial Stokes force [75,77] as

$$\mathbf{F}_{\text{TS}} = -\lambda^{-1}\mathbf{v} - m\boldsymbol{\omega} \times \mathbf{v} = -\mathbf{M}^{-1}\mathbf{v} \quad (7)$$

where the magneto mobility tensor \mathbf{M} is defined (when operating over an arbitrary vector \mathbf{V}) as

$$\mathbf{M}(\tau, \boldsymbol{\omega})\mathbf{V} = \lambda \frac{\mathbf{V} + \tau\mathbf{V} \times \boldsymbol{\omega} + \tau^2\boldsymbol{\omega}(\boldsymbol{\omega} \cdot \mathbf{V})}{1 + \tau^2\boldsymbol{\omega}^2}. \quad (8)$$

In particular we notice the familiar form [77] for the case $\mathbf{B} = B\hat{z}$

$$\mathbf{M}(\tau, \boldsymbol{\omega}) = \frac{\lambda}{1 + \tau^2\omega^2} \begin{pmatrix} 1 & \tau\omega & 0 \\ -\tau\omega & 1 & 0 \\ 0 & 0 & 1 + \tau^2\omega^2 \end{pmatrix}. \quad (9)$$

It was shown [74,77] that by defining such a tensorial Stokes force Eq. (6) is equivalent to

$$\mathbb{L}(U)P(\mathbf{x}, \mathbf{v}, t) = \mathbb{K}_{FP}(\mathbf{M}, \Gamma)P(\mathbf{x}, \mathbf{v}, t) \quad (10)$$

thus, the streaming operator includes only de (scalar) potential derived force and the magnetic contribution enters as a dissipative non diagonal contribution in the collision kernel (for convenience we have denoted $\mathbb{L}(U) = \mathbb{L}(\mathbf{F}_{\text{pot}} = -\nabla U)$). Now as in Refs. [75,115] we add a BGK contribution to the collision kernel denoted by \mathbb{K}_{BGK} . This collision operator is single relaxation time approximation [114–117] where the distribution P relaxes (collision time τ_0) to a prescribed distribution P_0 , the latter instantly equilibrated in the velocity coordinates, to the bath temperature, thus

$$P_0(\mathbf{x}, \mathbf{v}, t) = n_0(\mathbf{x}, t)f_0(\mathbf{v}, T(\mathbf{x})) \quad f_0(\mathbf{v}, m, T(\mathbf{x})) = \left(\frac{m}{2\pi T(\mathbf{x})}\right)^{\frac{3}{2}} \exp\left(-\frac{m\mathbf{v}^2}{2T(\mathbf{x})}\right) \quad (11)$$

where f_0 is a (normalized) Maxwellian distribution, n_0 is a prescribed density profile. For the Brownian gas we define particle density as $n(\mathbf{x}, t) = \int d\mathbf{v}P(\mathbf{x}, \mathbf{v}, t)$ where $N = \int d\mathbf{x}n(\mathbf{x}, t)$. In general $n_0(\mathbf{x}, t)$ need not satisfy $N = \int d\mathbf{x}n_0(\mathbf{x}, t)$ (BGK is not a particle conserving approximation). The BGK kernel is given by

$$\mathbb{K}_{BGK}(n_0(\mathbf{x}, t), \tau_0, k)P(\mathbf{x}, \mathbf{v}, t) = -\frac{1}{\tau_0} (P(\mathbf{x}, \mathbf{v}, t) - P_0(\mathbf{x}, \mathbf{v}, t)) \quad (12)$$

and represents the simple chemical reaction $A \longleftrightarrow A_0$, both compounds with particle density $n(\mathbf{x}, t)$ and $n_0(\mathbf{x}, t)$, respectively, and with forward (backward) rate k_+ (k_-), we have

$$\left(\frac{\partial n(\mathbf{x}, t)}{\partial t}\right)_r = \int d\mathbf{v}\mathbb{K}_{BGK}P(\mathbf{x}, \mathbf{v}, t) = -k_+n(\mathbf{x}, t) + k_-n_0(\mathbf{x}, t) = -\left(\frac{\partial n_0(\mathbf{x}, t)}{\partial t}\right)_r \quad (13)$$

where we have defined the rates as $k_+ = k_- = \tau_0^{-1}$. Then, Kramers equation for a charged Brownian particles under a general field of force in an inhomogeneous medium, including a linear reactive term, is compacted as

$$\mathbb{L}(U)P(\mathbf{x}, \mathbf{v}, t) = \mathbb{K}_{FP}(\mathbf{M}, \Gamma)P(\mathbf{x}, \mathbf{v}, t) + \mathbb{K}_{BGK}(n_0(\mathbf{x}, t), \tau_0)P(\mathbf{x}, \mathbf{v}, t) = \mathbb{K}P(\mathbf{x}, \mathbf{v}, t). \quad (14)$$

This is a generalized kinetic equation in the Fokker–Planck (FP) context for a charged Brownian particle. The *novel aspect in our approach* is to include *on an equal footing* the following aspects: An external magnetic field (a velocity dependent force) rarely considered in the Brownian context; an inhomogeneous bath temperature profile $T(\mathbf{x})$ and, in addition to the particle conserving FP collision kernel, we add a non conserving particle collision contribution (a generalized BGK mechanism), enabling our approach to incorporate chemical reactions and/or generation–recombination processes (for the latter we may consider an inhomogeneous collision time profile $\tau_0(\mathbf{x})$).

3. Recursive expansion of Kramers equation

We expand Kramers equation (14) in order to obtain a recursive solution. Some expansion methods include [118–120], and we review a method outlined in Ref. [75]. The expansion is cast as

$$P(\mathbf{x}, \mathbf{v}, t) = \sum_{n,m,l=0}^{\infty} \psi_{nml}(\mathbf{x}, t)\Phi_{nml}(\mathbf{w}) \quad \mathbf{w} = \sqrt{\frac{1}{2}}\frac{\mathbf{v}}{v_T}, \quad v_T^2 = \frac{T(\mathbf{x})}{m} \quad (15)$$

where $\Phi_{nml}(\mathbf{w}) = \phi_n(w_x)\phi_m(w_y)\phi_l(w_z)$ is the product of (normalized) Hermite functions [121]. Following Ref. [75] and using appropriate recursion relations [121], Eq. (14) reduces to a difference–differential recursive system of equations for the ψ 's (\mathbf{v} has been integrated out). These recursion relations are better displayed in the compact form, and as before [75] we allow for a slowly time varying (compared with τ) external temperature field $T(\mathbf{x}, t)$.

$$k\frac{\tau}{\tau_0}n_0\delta_{\mathbf{n},\mathbf{0}} = \tau\boldsymbol{\omega} \cdot \mathbf{A}^* \times \mathbf{A}Z_{\mathbf{n}} + (\mathbf{A}^*\mathbf{A} + \tau R)Z_{\mathbf{n}} \quad \mathbf{n} = (n_1, n_2, n_3) \quad (16)$$

where

$$R = \frac{\partial}{\partial t} + \frac{1}{\tau_0} + \nabla\mathbf{A}^* + v_T^2\left(\nabla\mathbf{A} + \mathbf{A}\frac{\nabla U}{T} + \mathbf{A}^2\left\{(v_T^2\mathbf{A} + \mathbf{A}^*)\frac{\nabla T}{2T} + \frac{1}{2T}\frac{\partial T}{\partial t}\right\}\right) \quad (17)$$

with $\nabla = \frac{\partial}{\partial \mathbf{x}}$ and

$$Z_{\mathbf{n}} = \frac{v_T^{n_1+n_2+n_3}\psi_{n_1n_2n_3}}{\sqrt{n_1!n_2!n_3!}}. \quad (18)$$

The asymmetric lowering and raising operators \mathbf{A}, \mathbf{A}^* are defined respectively by

$$\begin{aligned} A_1Z_{\mathbf{n}} &= Z_{n_1-1, n_2, n_3} & A_1^*Z_{\mathbf{n}} &= (1+n_1)Z_{n_1+1, n_2, n_3} \\ A_2Z_{\mathbf{n}} &= Z_{n_1, n_2-1, n_3} & A_2^*Z_{\mathbf{n}} &= (1+n_2)Z_{n_1, n_2+1, n_3} \\ A_3Z_{\mathbf{n}} &= Z_{n_1, n_2, n_3-1} & A_3^*Z_{\mathbf{n}} &= (1+n_3)Z_{n_1, n_2, n_3+1}. \end{aligned} \quad (19)$$

4. Hydrothermodynamics of Brownian motion

We now proceed in a standard fashion [122–125] and define some relevant moments of the distribution $P(\mathbf{x}, \mathbf{v}, t)$. The usual (lower) moments are: particle density $n(\mathbf{x}, t)$, particle flux vector density $\mathbf{J}_M(\mathbf{x}, t)$, pressure tensor density $\mathbf{\Pi}(\mathbf{x}, t)$, kinetic energy density $E(\mathbf{x}, t)$, energy flux vector density $\mathbf{J}_E(\mathbf{x}, t)$ and the total energy flux vector density $\mathbf{J}_Q(\mathbf{x}, t)$. Some useful auxiliary quantities are also defined, namely: mass density $\rho(\mathbf{x}, t)$, mass flux density $\mathbf{J}_\rho(\mathbf{x}, t)$, charge flux density $\mathbf{J}_q(\mathbf{x}, t)$, scalar pressure $p(\mathbf{x}, t)$ and the stream velocity $\mathbf{u}(\mathbf{x}, t)$. All of the above are defined by:

$$n(\mathbf{x}, t) = \int d\mathbf{v} P(\mathbf{x}, \mathbf{v}, t), \quad \rho(\mathbf{x}, t) = mn(\mathbf{x}, t) \quad (20)$$

$$\mathbf{J}_M(\mathbf{x}, t) = \int d\mathbf{v} \mathbf{v} P(\mathbf{x}, \mathbf{v}, t) = n(\mathbf{x}, t) \mathbf{u}(\mathbf{x}, t) \quad (21)$$

$$\mathbf{J}_\rho(\mathbf{x}, t) = m\mathbf{J}_M(\mathbf{x}, t), \quad \mathbf{J}_q(\mathbf{x}, t) = q\mathbf{J}_M(\mathbf{x}, t) \quad (22)$$

$$\mathbf{\Pi}(\mathbf{x}, t) = m \int d\mathbf{v} \mathbf{v} \mathbf{v} P(\mathbf{x}, \mathbf{v}, t), \quad p(\mathbf{x}, t) = \frac{1}{3} \sum_{i=1}^3 \Pi_{ii}(\mathbf{x}, t) \quad (23)$$

$$\mathbf{\Pi}_u(\mathbf{x}, t) = m \int d\mathbf{v} (\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u}) P(\mathbf{x}, \mathbf{v}, t) = \mathbf{\Pi}(\mathbf{x}, t) - \rho \mathbf{u}(\mathbf{x}, t) \mathbf{u}(\mathbf{x}, t)$$

$$E(\mathbf{x}, t) = \frac{1}{2} m \int d\mathbf{v} |\mathbf{v}|^2 P(\mathbf{x}, \mathbf{v}, t) = \frac{3}{2} p(\mathbf{x}, t) \quad (24)$$

$$\mathbf{J}_E(\mathbf{x}, t) = \frac{1}{2} m \int d\mathbf{v} |\mathbf{v}|^2 \mathbf{v} P(\mathbf{x}, \mathbf{v}, t) \quad (25)$$

$$\mathbf{J}_Q(\mathbf{x}, t) = \int d\mathbf{v} \left(\frac{1}{2} m |\mathbf{v}|^2 + U(\mathbf{x}, t) \right) \mathbf{v} P(\mathbf{x}, \mathbf{v}, t) = \mathbf{J}_E(\mathbf{x}, t) + U(\mathbf{x}, t) \mathbf{J}_M(\mathbf{x}, t). \quad (26)$$

These relevant moments can be readily associated with the expansion coefficients Z_n , see Eq. (18)

$$n(\mathbf{x}, t) = Z_{000}, \quad \Phi_{000}(\mathbf{w}) = f_0(\mathbf{v}, m, T(\mathbf{x})) \quad (27)$$

$$\mathbf{J}_M(\mathbf{x}, t) = \begin{pmatrix} Z_{100} \\ Z_{010} \\ Z_{001} \end{pmatrix} \quad (28)$$

$$\mathbf{\Pi}(\mathbf{x}, t) = n(\mathbf{x}, t) T(\mathbf{x}) + m \begin{pmatrix} 2Z_{200} & Z_{110} & Z_{101} \\ Z_{110} & 2Z_{020} & Z_{011} \\ Z_{101} & Z_{011} & Z_{002} \end{pmatrix} \quad (29)$$

$$\mathbf{J}_E(\mathbf{x}, t) = \frac{5}{2} T(\mathbf{x}) \mathbf{J}_M(\mathbf{x}, t) + m \begin{pmatrix} 3Z_{300} + Z_{120} + Z_{102} \\ Z_{210} + 3Z_{030} + Z_{012} \\ Z_{201} + Z_{021} + 3Z_{003} \end{pmatrix}. \quad (30)$$

Then, the recursive relations, Eq. (16), as outlined in Ref. [75] can be compacted into a set of balance equations (conservation of mass, momentum and energy, respectively) yielding the hydrodynamical picture. For the particle density the recursive relations yield

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{J}_M = -k_+ n + k_- n_0 = \left(\frac{\partial n}{\partial t} \right)_{\text{reac}}, \quad (31)$$

a generalized Smoluchowski equation with a dissipative (reactive) term; for the particle flux we obtain

$$\frac{\partial \mathbf{J}_M}{\partial t} + \left(\frac{1}{\tau} + \frac{1}{\tau_0} \right) \mathbf{J}_M = \mathbf{J}_M \times \boldsymbol{\omega} - \frac{n}{m} \nabla U - \frac{1}{m} \nabla \cdot \mathbf{\Pi}, \quad (32)$$

if cast in terms of the stream velocity, and using Eq. (31) we obtain the Navier–Stokes equation for Brownian flow

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \frac{1}{\rho} \nabla \cdot \mathbf{\Pi}_u = \frac{1}{m} (-\nabla U + \mathbf{F}_{\text{diss}}), \quad \mathbf{F}_{\text{diss}} = - \left(\Lambda^{-1} + \frac{mn_0}{\tau_0 n} \right) \mathbf{u}. \quad (33)$$

Other equivalent versions of Eq. (32) in terms of the charge flux density and with $\mathbf{F}_{\text{ext}} = 0$ in Eq. (2) are

$$\tau^* \frac{\partial \mathbf{J}_q}{\partial t} + \mathbf{J}_q = \sigma^* (\mathbf{E} + R_H \mathbf{J}_q \times \mathbf{B}) - \frac{q\tau^* n}{m} \nabla U_{\text{mec}} - \frac{q\tau^*}{m} \nabla \cdot \mathbf{\Pi} \quad (34)$$

$$\mathbf{J}_q = \sigma^* \Lambda^\times (\tau^*, \boldsymbol{\omega}) \left(\mathbf{E} - \frac{1}{q} \nabla U_{\text{mec}} - \frac{1}{qn} \nabla \cdot \mathbf{\Pi} \right) - m \Lambda (\tau^*, \boldsymbol{\omega}) \frac{\partial \mathbf{J}_q}{\partial t}. \quad (35)$$

A generalized Ohm's law [124] where the effective relaxation time τ^* , the effective conductivity σ^* and Hall's coefficient are respectively given by

$$\frac{1}{\tau^*} = \frac{1}{\tau} + \frac{1}{\tau_0}, \quad \sigma^*(\mathbf{x}, t) = \frac{q^2 \tau^* n}{m}, \quad R_H(\mathbf{x}, t) = \frac{1}{nqc}. \quad (36)$$

Finally we obtain the energy balance equation

$$\frac{\partial E}{\partial t} + \nabla \mathbf{J}_E = -\mathbf{J}_M \nabla U - \frac{1}{\tau_0} (E - E_0) \quad E_0 = \frac{3}{2} n_0 T. \quad (37)$$

Thermodynamics is introduced by defining the kinetic temperature Θ [75,77,126] (a generalization of the equipartition theorem, assuming the Brownian particle to have only translational degrees of freedom) defined as

$$E(\mathbf{x}, t) \equiv \frac{3}{2} n(\mathbf{x}, t) \Theta(\mathbf{x}, t) \quad (38)$$

when substituted into (37) yields

$$\frac{3}{2} n \frac{\partial \Theta}{\partial t} + \nabla \mathbf{J}_Q = \left(\frac{3}{2} \Theta + U \right) \nabla \mathbf{J}_M - \frac{3}{2} \frac{1}{\tau_0} n_0 (\Theta - T). \quad (39)$$

We define entropy density S and the entropy flux density \mathbf{J}_S respectively as Refs. [73,75,77]

$$S(\mathbf{x}, t) = - \int d\mathbf{v} P(\mathbf{x}, \mathbf{v}, t) \ln \kappa P(\mathbf{x}, \mathbf{v}, t) \quad (40)$$

$$\mathbf{J}_S(\mathbf{x}, t) = - \int d\mathbf{v} \mathbf{v} P(\mathbf{x}, \mathbf{v}, t) \ln \kappa P(\mathbf{x}, \mathbf{v}, t)$$

where the constant κ ($\ln \kappa = -1 + 3 \ln \frac{h}{m}$) is chosen such that under equilibrium conditions $S \rightarrow S_{\text{eq}}$ [75,127] (for a simple ideal gas, where h is Planck's constant).

$$S_{\text{eq}}(n_{\text{eq}}, T_{\text{eq}}) = n_{\text{eq}} \left(\frac{5}{2} + \ln \frac{n_Q(T_{\text{eq}})}{n_{\text{eq}}} \right), \quad n_Q(T_{\text{eq}}) = \left(\frac{2\pi m}{h^2} T_{\text{eq}} \right)^{\frac{3}{2}}. \quad (41)$$

An entropy balance equation is readily obtained [123], yielding an expression for the entropy production Σ_S solely in terms of the particle distribution

$$\frac{\partial S(\mathbf{x}, t)}{\partial t} + \frac{\partial \mathbf{J}_S(\mathbf{x}, t)}{\partial \mathbf{x}} = \Sigma_S = \int d\mathbf{v} (1 + \ln \kappa P(\mathbf{x}, \mathbf{v}, t)) \mathbb{K}(P). \quad (42)$$

Finally [73,75] we define the various thermodynamical *potential densities*, namely: F (Helmholtz), G (Gibbs), μ^I (intrinsic chemical potential), and μ (total chemical potential), respectively given by Ref. [127]

$$F(\mathbf{x}, t) = E(\mathbf{x}, t) - \Theta(\mathbf{x}, t) S(\mathbf{x}, t)$$

$$G(\mathbf{x}, t) = F(\mathbf{x}, t) + p(\mathbf{x}, t) = n(\mathbf{x}, t) \mu^I(\mathbf{x}, t) \quad (43)$$

$$\mu(\mathbf{x}, t) = \mu^I(\mathbf{x}, t) + U(\mathbf{x}, t)$$

the equilibrium expression for the chemical potential is [127]

$$\mu_{\text{eq}}(n_{\text{eq}}, T_{\text{eq}}) = -T_{\text{eq}} \ln \frac{n_Q(T_{\text{eq}})}{n_{\text{eq}}}. \quad (44)$$

All moments, or equivalently, the expansion coefficients $Z_{\mathbf{n}}$, $\mathbf{n} \neq \mathbf{0}$, see Eq. (18), are expandable in powers of τ , when solving the recurrence relation (16), and considering $\tau\omega$ as an independent parameter. Hereafter, when referring to the expansion order, we mean in powers of τ , for example, the magneto mobility tensor \mathbf{M} in Eq. (8), is a first order quantity. We further expand the expansion coefficients as

$$Z_{\mathbf{n}} = \sum_{k=1}^{\infty} \tau^k Z_{\mathbf{n}}^{(k)}. \quad (45)$$

For $|\nabla T| \neq 0$ we have $Z_{\mathbf{n}}^{(k)} \equiv 0$ for $k < \text{integer} \left[\frac{N+2}{3} \right]$. For the isothermal case $|\nabla T| = \frac{\partial T}{\partial t} \equiv 0$ we have $Z_{\mathbf{n}}^{(k)} \equiv 0$ for $k < N$.

Now, we discuss several relevant cases concerning the heat bath interaction with the Brownian gas (a gas of real particles or some collective property of a given macroscopic system). In order to simplify the discussion we denote the Brownian gas as the solute and the heat bath as the solvent (the fluid in which the Brownian particle is immersed). As the solute fluctuates

and dissipates in the solvent, towards an equilibrium (or non-equilibrium steady) state, the solute temperature $\Theta(\mathbf{x}, t)$ evolves according to the Brownian dynamics (given by Eq. (3)) adjusting itself to the solvent temperature $T(\mathbf{x}, t)$ and the external fields acting on the solute. On the other hand the solvent temperature is perturbed by the solute temperature, a very weak interaction indeed, since as a heat bath, $T(\mathbf{x}, t)$ relaxes instantly (or very fast compared with τ) to a prescribed heat bath temperature profile $T_{\text{in}}(\mathbf{x})$, the latter a stationary function to be considered as both an initial and a boundary condition. We realize that ∇T is not controlled at all in the interior of the system but only on its surfaces. In the bulk, the solute performs its Brownian evolution, while the solvent temperature relaxes (very fast) to the prescribed profile. This is an unsatisfactory state of affairs since in the bulk, the control parameter $T_{\text{in}}(\mathbf{x})$ evolves as $T(\mathbf{x}, t)$ perturbed by the solute, at temperature $\Theta(\mathbf{x}, t)$, which in turn evolves following $T(\mathbf{x}, t)$, thus a clear cut distinction between controlled external (thermal) fields and the resulting (thermal) fluxes cease to exist [125].

We analyze three simple cases, with no attempt to model the heat bath at this point (see for example Refs. [65,128]).

- Strictly isothermal bath, with $T(\mathbf{x}, t) = T_{\text{in}}(\mathbf{x}) = T_R$
- Strictly stationary inhomogeneous bath with $T(\mathbf{x}, t) = T_{\text{in}}(\mathbf{x})$, $|\nabla T| \neq 0$, and
- Weakly interacting bath, first order in τ , where $T(\mathbf{x}, t) = T_{\text{in}}(\mathbf{x})$ only at the boundaries.

From the recursion relations (16), for the strictly isothermal case, the solute temperature has a second order correction (in τ), already obtained by us, as an asymptotic solution to a particular isothermal exact solution [77]. We present our result, as in Ref. [77], in terms of the stream velocity $\mathbf{u}(\mathbf{x}, t)$, in turn expressed as a magnetocovariant derivative

$$\Theta(\mathbf{x}, t) = T_R + \frac{1}{3} m \mathbf{u}^2(\mathbf{x}, t) \quad (46)$$

where

$$\mathbf{u}(\mathbf{x}, t) = -\frac{T_R}{n(\mathbf{x}, t)} \mathbf{M} \exp\left(-\frac{U(\mathbf{x}, t)}{T_R}\right) \nabla \left[n(\mathbf{x}, t) \exp\left(\frac{U(\mathbf{x}, t)}{T_R}\right) \right]. \quad (47)$$

This is a generalization of Shockley's expression for hot carriers effective temperature [129,130]. Shockley's result coincides with our result at zero magnetic field and homogeneous carrier concentration (provided we identify the hot carrier with the solute, at temperature Θ , and the solvent with the lattice, at temperature T_R).

For the weakly interacting bath, to the first order in τ , we obtain

$$\Theta(\mathbf{x}, t) = T(\mathbf{x}, t) + \frac{\tau}{2} \frac{\partial T(\mathbf{x}, t)}{\partial t} = T\left(\mathbf{x}, t + \frac{\tau}{2}\right) \quad (48)$$

identical to Eq. (7.2) obtained by Ref. [126], provided we identify the solute with electrons, at temperature Θ and the solvent with the lattice, at temperature T .

5. Applications

(A) For the strictly isothermal bath case, we present the second order results, from the recursion relations (16) and by expanding (40). Our results are equivalent to the asymptotic regime for an exact solution [77]: the local equilibrium approximation [131–135] is not fulfilled [136]; in particular the entropy density and the chemical potential are given, respectively by the expressions

$$\begin{aligned} S(n(\mathbf{x}, t), \Theta(\mathbf{x}, t)) &= S_{\text{eq}}(n(\mathbf{x}, t), \Theta(\mathbf{x}, t)) - \frac{m}{2T_R} n(\mathbf{x}, t) \mathbf{u}^2(\mathbf{x}, t) \\ \mu(n(\mathbf{x}, t), \Theta(\mathbf{x}, t)) &= \mu_{\text{eq}}(n(\mathbf{x}, t), \Theta(\mathbf{x}, t)) + U(\mathbf{x}, t) + \frac{1}{2} m \mathbf{u}^2(\mathbf{x}, t) \end{aligned} \quad (49)$$

where the temperature Θ and the stream velocity \mathbf{u} are given respectively by Eqs. (46) and (47).

(B) For the strictly stationary inhomogeneous bath case, the local equilibrium approximation holds, in particular the entropy density and the chemical potential are given, respectively by the expressions

$$\begin{aligned} S(\mathbf{x}, t) &= S_{\text{eq}}(n(\mathbf{x}, t), T_{\text{in}}(\mathbf{x})) \\ \mu(\mathbf{x}, t) &= \mu_{\text{eq}}(n(\mathbf{x}, t), T_{\text{in}}(\mathbf{x})) + U(\mathbf{x}, t). \end{aligned} \quad (50)$$

(C) For the weakly interacting bath, again as in case (A) the local equilibrium approximation does not hold, to first order (in τ). The particle flux density is given by the (equivalent) expressions

$$\begin{aligned} \mathbf{J}_M(\mathbf{x}, t) &= -n(\mathbf{x}, t) \mathbf{M} \nabla U(\mathbf{x}, t) - \mathbf{M} \nabla (\Theta(\mathbf{x}, t) n(\mathbf{x}, t)) \\ &= -n(\mathbf{x}, t) \mathbf{M} \nabla (U(\mathbf{x}, t) + \Theta(\mathbf{x}, t)) - \mathbf{D}(\mathbf{x}, t) \nabla n(\mathbf{x}, t), \end{aligned} \quad (51)$$

where $\mathbf{D} = \Theta(\mathbf{x}, t) \mathbf{M}$ is the magneto-diffusion tensor. The total energy flux density is given by

$$\mathbf{J}_Q(\mathbf{x}, t) = \left(\frac{5}{2} \Theta(\mathbf{x}, t) + U(\mathbf{x}, t) \right) \mathbf{J}_M(\mathbf{x}, t) - \frac{5}{6} n(\mathbf{x}, t) \Theta(\mathbf{x}, t) \mathbf{M}_3 \nabla \Theta(\mathbf{x}, t) \quad (52)$$

and where we have incorporated, at no cost, an inhomogeneous collision time profile $\tau(\mathbf{x})$ as well as a space varying magnetic field, with the compact definitions

$$\begin{aligned}\mathbf{M}_k \mathbf{V} &= \theta(\mathbf{x}) \left(\mathbf{V} + \tau_k(\mathbf{x}) \mathbf{V} \times \boldsymbol{\omega}(\mathbf{x}) + \tau_k^2(\mathbf{x}) \boldsymbol{\omega}(\mathbf{x}) (\boldsymbol{\omega}(\mathbf{x}) \cdot \mathbf{V}) \right) \\ \theta(\mathbf{x}) &= \frac{\lambda(\mathbf{x})}{1 + (\tau_k(\mathbf{x}) \boldsymbol{\omega}(\mathbf{x}))^2} \quad \tau_k(\mathbf{x}) = \frac{1}{k} \tau(\mathbf{x}) \\ \mathbf{M}_k(\tau, \boldsymbol{\omega}) &= \mathbf{M}\left(\frac{\tau}{k}, \boldsymbol{\omega}\right) \quad \mathbf{M}_1 = \mathbf{M} \quad k = 1, 2, \dots\end{aligned}\quad (53)$$

Notice that in Eqs. (51) and (52) according to Eq. (48) $\Theta(\mathbf{x}, t)$ can be substituted by $T(\mathbf{x}, t)$ since the magnetic mobility tensor \mathbf{M} , Eq. (8), is already a first order quantity. With the last observation in mind, we rewrite the “fluxes” in terms of the “forces”, following Refs. [125,133]. Thus, we define the matter and heat “forces” as

$$\mathbf{X}_M(\mathbf{x}, t) = -\nabla\left(\frac{\mu}{T}\right) \quad \mathbf{X}_Q(\mathbf{x}, t) = \nabla\left(\frac{1}{T}\right) \quad (54)$$

where

$$\mu(\mathbf{x}, t) = \mu_{\text{eq}}(n(\mathbf{x}, t), T(\mathbf{x}, t)) + U(\mathbf{x}, t) \quad (55)$$

so to the first order in τ we have the linear flux-force relations

$$\begin{aligned}\mathbf{J}_M(\mathbf{x}, t) &= \mathbf{L}_{MM}(\mathbf{x}, t) \mathbf{X}_M(\mathbf{x}, t) + \mathbf{L}_{MQ}(\mathbf{x}, t) \mathbf{X}_Q(\mathbf{x}, t) \\ \mathbf{J}_Q(\mathbf{x}, t) &= \mathbf{L}_{QM}(\mathbf{x}, t) \mathbf{X}_M(\mathbf{x}, t) + \mathbf{L}_{QQ}(\mathbf{x}, t) \mathbf{X}_Q(\mathbf{x}, t)\end{aligned}\quad (56)$$

where the coefficients are given by

$$\begin{aligned}\mathbf{L}_{MM}(\mathbf{x}, t) &= n(\mathbf{x}, t) T(\mathbf{x}, t) \mathbf{M} \\ \mathbf{L}_{MQ}(\mathbf{x}, t) &= \mathbf{L}_{QM}(\mathbf{x}, t) = n(\mathbf{x}, t) T(\mathbf{x}, t) \left(\frac{5}{2} T(\mathbf{x}, t) + U(\mathbf{x}, t) \right) \mathbf{M}\end{aligned}\quad (57)$$

$$\begin{aligned}\mathbf{L}_{QQ}(\mathbf{x}, t) &= n(\mathbf{x}, t) T(\mathbf{x}, t) \left(\frac{5}{2} T(\mathbf{x}, t) + U(\mathbf{x}, t) \right)^2 \mathbf{M} + \frac{5}{2} n(\mathbf{x}, t) T^3(\mathbf{x}, t) \mathbf{M} \\ \mathbf{L}_{QM}^\dagger(\mathbf{B}) &= \mathbf{L}_{MQ}(-\mathbf{B}),\end{aligned}\quad (58)$$

the last equation indicating that Onsager relations are satisfied [125,131–135]. Nevertheless, the Onsager-like coefficients do not depend solely on the equilibrium values of the state variables (mass density, temperature). Instead they are functions of the external potentials and nonequilibrium state variables, namely $n(\mathbf{x}, t)$ and $\Theta(\mathbf{x}, t)$, which in turn evolve according to Eqs. (31) and (39) respectively (for simplicity of presentation we omit the spatial and temporal dependence)

$$\begin{aligned}\frac{\partial n}{\partial t} &= -\nabla \mathbf{J}_M - k_+ n + k_- n_0 \\ \frac{3}{2} n \frac{\partial \Theta}{\partial t} &= -\left(\frac{5}{2} \nabla \Theta + \nabla U \right) \mathbf{J}_M - \Theta \nabla \mathbf{J}_M + \frac{5}{6} \nabla (n \Theta \mathbf{M}_3 \nabla T) - \frac{3}{2} \frac{1}{\tau_0} n_0 (\Theta - T)\end{aligned}\quad (59)$$

and substituting from Eq. (48), within the linear approximation (first order in τ) we obtain the coupled equations for the evolution of the state variables $n(\mathbf{x}, t)$ and $T(\mathbf{x}, t)$ (or Θ)

$$\frac{\partial n}{\partial t} + \frac{1}{\tau_0} (n - n_0) = \nabla \mathbf{M}_1 \mathbf{Y} \quad \mathbf{Y} = n \nabla U + n \nabla T + T \nabla n \quad (60)$$

$$\frac{3}{2} \left(n + \frac{\tau n_0}{2 \tau_0} \right) \frac{\partial T}{\partial t} + \frac{3 \tau n}{4} \frac{\partial^2 T}{\partial t^2} = \left(\frac{5}{2} \nabla T + \nabla U \right) \mathbf{M}_1 \mathbf{Y} + T \nabla (\mathbf{M}_1 \mathbf{Y}) + \frac{5}{6} \nabla (\mathbf{M}_3 n T \nabla T). \quad (61)$$

Eq. (60) is a generalized Smoluchowski-like advection diffusion reactive equation, and Eq. (61) is a Maxwell–Cattaneo like equation, generalizing Fourier’s heat equation, incorporates inertial effects [70,126,137–139], as noticed from the time delay character of Eq. (48), where the time needed for the acceleration of the heat flow is considered.

Thus, even though Onsager relations are satisfied, the coefficient’s dependence on nonequilibrium state variables and external fields, indicates that any variational principle associated with the entropy production [132,134,135,140,141], is not applicable to the present case [69,142]

In the absence of the BGK reactive term, null magnetic field, and for the strictly stationary inhomogeneous bath case, we recover the inhomogeneous media advection–diffusion equation, presented by Ref. [96] and given by

$$\frac{\partial n(\mathbf{x}, t)}{\partial t} = \nabla (\lambda(\mathbf{x}) [n(\mathbf{x}, t) \nabla U(\mathbf{x}) + n(\mathbf{x}, t) \nabla T(\mathbf{x}) + T(\mathbf{x}) \nabla n(\mathbf{x}, t)]) \quad (62)$$

and for the rigid conductor (constant particle density n), no reactive term and null external fields, we retrieve the inertial corrections to Fourier's law, known as the Maxwell–Cattaneo equation [137–139] (of the hyperbolic type, known also as the telegrapher's equation)

$$\frac{\partial T(\mathbf{x}, t)}{\partial t} + \frac{\tau}{2} \frac{\partial^2 T(\mathbf{x}, t)}{\partial t^2} = K \left(T(\mathbf{x}, t) \nabla^2 T(\mathbf{x}, t) + (\nabla T(\mathbf{x}, t))^2 \right) = -\nabla \mathbf{J}_F(T(\mathbf{x}, t)) \quad (63)$$

$$\mathbf{J}_F(T) = KT^3(\mathbf{x}, t) \nabla \left(\frac{1}{T(\mathbf{x}, t)} \right) = -KT(\mathbf{x}, t) \nabla T(\mathbf{x}, t) = -\kappa(\mathbf{x}, t) \nabla T(\mathbf{x}, t), \quad (64)$$

with $K = \frac{20}{9} \lambda$. The right hand side of the last equation is known as the fundamental form of Fourier's law [63].

(D) Carrier transport in semiconductors, in the Brownian scheme, for the strictly stationary inhomogeneous bath case [143,144]. Consider two Brownian gases, say electrons (density n_c , collision time τ_c , mobility $\mathbf{M}_c = \mathbf{M}(\tau_c, \omega_c)$, effective mass m_c and charge $-e$) and holes (density p_v , collision time τ_v , mobility $\mathbf{M}_v = \mathbf{M}(\tau_v, \omega_v)$, effective mass m_v and charge e , and with $m_{c,v}c = \omega_{c,v}|e\mathbf{B}|$). The BGK mechanism is associated in this case to carrier generation–recombination with the respective generation–recombination times $\tau_{c,v}^0$ and with the n^0 's the respective equilibrium carrier concentrations. Then, by applying Eq. (60) we obtain

$$\begin{aligned} \frac{\partial n_c}{\partial t} &= \nabla \mathbf{M}_c (-en_c \mathbf{E} + n_c \nabla T + T \nabla n_c) - \frac{1}{\tau_c^0} (n_c - n_c^0) \\ \frac{\partial p_v}{\partial t} &= \nabla \mathbf{M}_v (+ep_v \mathbf{E} + p_v \nabla T + T \nabla p_v) - \frac{1}{\tau_v^0} (p_v - p_v^0). \end{aligned} \quad (65)$$

Shockley's equations (unidimensional, isothermal, null magnetic field case) are readily recovered [143,144]. Inhomogeneous generalizations of Shockley's equations are of current interest [145–152].

(E) Our scheme can readily be generalized for several Brownian gases ($\alpha = 1, \dots, l$) interacting via non reactive potential $U_{\alpha\beta}$ and with the usual BGK reactive term associated to each gas. By applying a mean field approximation scheme to a many component Brownian gas [153,154], as worked out in several contexts in Refs. [155–161], Kramers system of equations can readily be generalized to

$$\mathbb{L}_\alpha(U_\alpha^{\text{eff}})P_\alpha(\mathbf{x}, \mathbf{v}, t) = (\mathbb{K}_{FP}(\mathbf{M}_\alpha, \mathbf{\Gamma}_\alpha) + \mathbb{K}_{BGK}^\alpha) P_\alpha(\mathbf{x}, \mathbf{v}, t) \quad (66)$$

where

$$U_\alpha^{\text{eff}}(\mathbf{x}, t) = U_\alpha(\mathbf{x}, t) + \sum_\beta \int d\mathbf{y} U_{\alpha\beta}(\mathbf{x} - \mathbf{y}) n_\beta(\mathbf{y}, t) \quad n_\beta(\mathbf{y}, t) = \int d\mathbf{v} P_\beta(\mathbf{y}, \mathbf{v}, t). \quad (67)$$

(F) We briefly sketch how to incorporate several chemical reactions schemes, beyond the BGK scheme (deterministic, stochastic, photoreactions, etc., see for example Refs. [162–175]) in order to model molecular motors. We present two chemical reactions that can be approximated at the Kramers equation level, yielding the correct Smoluchowski–reactive equation.

For the nonlinear reaction



the kinetic equations are retrieved if we start consider the BGK like scheme

$$\begin{aligned} \mathbb{K}_{BGK}^A P_A(\mathbf{x}, \mathbf{v}, t) &= -k_+ n_B P_A + k_- n_C n_D f_0(\mathbf{v}, m_A, T) \\ \mathbb{K}_{BGK}^B P_B(\mathbf{x}, \mathbf{v}, t) &= -k_+ n_A P_B + k_- n_C n_D f_0(\mathbf{v}, m_B, T) \\ \mathbb{K}_{BGK}^C P_C(\mathbf{x}, \mathbf{v}, t) &= -k_- n_D P_C + k_+ n_A n_B f_0(\mathbf{v}, m_C, T) \\ \mathbb{K}_{BGK}^D P_D(\mathbf{x}, \mathbf{v}, t) &= -k_- n_C P_D + k_+ n_A n_B f_0(\mathbf{v}, m_D, T). \end{aligned} \quad (69)$$

Finally, for the reaction cycle



we reproduce the correct kinetics with the approximation

$$\mathbb{K}_{BGK}^\alpha P_\alpha(\mathbf{x}, \mathbf{v}, t) = -k_\alpha P_\alpha + k_{\alpha-1} f_0^{(\alpha)}(\mathbf{v}, m_\alpha, T) n_{\alpha-1} \quad n_0 = n_l \quad \alpha = 1, \dots, l. \quad (71)$$

6. Concluding remarks

We have extended our previous work on charged Brownian particles [73,75,77], in order to obtain a consistent expansion scheme in powers of the collision time. We presented the complete hydrothermodynamical picture for charged Brownian particles in the Kramers equation scheme, considering the action of external magnetic, electric and mechanical fields, chemical transformations within the BGK scheme, and furthermore space dependent thermal fields (inhomogeneous media).

We developed a recursive method, in order to expand in powers of the collision time τ , the several moments of the solution of Kramers equation, enabling us to compute the governing equations for mass (charge), momentum (stream velocity) and energy (heat) flow. In the appropriate limits we retrieve previous results, and present novel formulations and results with immediate physical consequences.

Applications A, B and C (previous section) clearly indicate that the Brownian scheme cannot be modelled, in general and in earnest, by the local equilibrium approximation, no variational principle associated with entropy production is applicable, and hyperbolic extensions of the Fourier heat conduction law must be considered even in the lowest order. Therefore, variational principles relevant to the Brownian scheme, must go beyond entropy production considerations, and include among others, free energies, efficiency factors and power output as well [69,70] and connected to nonequilibrium fluctuation and work relations [176–185].

In the following applications items we briefly outline, from the formalism developed in this work, some novel schemes: (D) the incorporation of magnetic field effects on the nonequilibrium state variables (including an application for carrier transport in inhomogeneous semiconductors); (E) inclusion of interacting Brownian fluids via mean field approximation schemes, and (F) inclusion of chemical reactions to Kramers approach to Brownian motion.

Our future work concentrates in variational principles associated to the Brownian motion, inclusion of chemical reactions and the magnetic field effects in hot carrier transport in semiconductors [186].

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