The thermohydrodynamical picture of a charged Brownian particle.

L. A. Barreiro, J. R. Campanha and R. E. Lagos
Departamento de Física, IGCE UNESP
CP 178, 13500-970 Rio Claro, SP, Brazil

Abstract

We study a charged Brownian gas with a non uniform bath temperature, and present a thermohydrodynamical picture. Expansion on the collision time probes the validity of the local equilibrium approach and the relevant thermodynamical variables. For the linear regime we present several applications (including some novel results). For the lowest nonlinear expansion and uniform bath temperature we compute the gradient corrections to the local equilibrium approach and the fundamental (Smoluchowsky) equation for the nonequilibrium particle density.

PACS codes: 05.40.Jc, 05.70.Ln, 82.20.Mj
Keywords: Kramers & Smoluchowsky equation, Brownian motion, Nonequilibrium thermodynamics, hydrodynamical equations

Corresponding author: R. E. Lagos
Departamento de Física- IGCE, Universidade Estadual Paulista (UNESP)
C.P. 178, Rio Claro 13500-970, SP, Brazil
Fax: (55)-19-534-8250, email:monaco@rc.unesp.br
We generalize previous work [1], considering a magnetic field [2] and a non-uniform bath temperature $T(x,t)$. Following [1] we write down Kramers equation for the probability distribution $P(x,v,t)$ in phase space for the Brownian particle (mass $m$ charge $e$) under an external force $F$.

\[
\left( \frac{\partial}{\partial t} + v \frac{\partial}{\partial x} + \frac{1}{m} F \frac{\partial}{\partial v} \right) P = J \tag{1}
\]

\[
J = \frac{1}{\tau} \frac{\partial}{\partial v} \left( v + v_T^2 \frac{\partial}{\partial v} \right) P - \frac{1}{\tau_0} (P - n_0 f_0(v)) \tag{2}
\]

The Fokker-Planck collision time $\tau$ is the inverse of the friction coefficient and the thermal velocity $v_T$ is given by $mv_T^2 = T$ (hereinafter $k_B = 1$). The diffusion coefficient $D$ and the mobility $\xi = \tau/m$ are related via the celebrated Einstein relation $D = \xi T = \tau v_T^2$. In the collision term $J$ we include a generalized BGK collision mechanism [3]. The latter is characterized by a relaxation time $\tau_0$ and a prescribed referential particle density $n_0(x,t)$ (for example, as in [3] $n_0$ is the actual Brownian particle density $n(x,t)$) and $f_0$ is the normalized equilibrium distribution function

\[
f_0(v) = \left( \frac{1}{2\pi v_T^2} \right)^{\frac{3}{2}} \exp \left( -\frac{v^2}{2v_T^2} \right)
\]

The external force (not necessarily uniform) includes a mechanical part $-\nabla V_{\text{mech}}$, an electric field $E = -\nabla \phi$ and a magnetic field $B$. Let us define a potential function $V = V_{\text{mech}} + e\phi$ and a covariant derivative $\nabla_{\text{cov}} = \nabla + \Gamma$, where $\nabla = \frac{\partial}{\partial x}$ and $\Gamma = T^{-1} \nabla V$. Also define the vector $\omega$ (notice the cyclotron frequency is $|\omega| = \omega_c$) by $mc \omega = eB$. Thus the external force $F$ is given by $F(x,v) = -\nabla V - m\omega \times v$. Generalizing our previous ansatz [1] as

\[
E = f_0(v) \sum_{n_i = -\infty}^{\infty} \Psi_n(x,t) \prod_{k=1}^{3} \left( \frac{\Phi_{n_k}(w_k)}{\Phi_0(w_k)} \right), \quad w_k = \frac{v_k}{\sqrt{2v_T}} \tag{3}
\]

where $\Phi_{n_k}(w_k)$ are the orthonormal Hermite functions and with $n = (n_1, n_2, n_3)$. As before, we require the density of Brownian particles to be $n(x,t) = \int d\mathbf{v} P(x,\mathbf{v},t)$. By direct substitution of the ansatz into equation (1), and as in [1] a set of differential recursive (difference) equations for the $\Psi_n$’s are readily obtained (in [1], the one dimensional case, a continued
fraction expansion was obtained, the general case is amenable to a multibranched continued fraction scheme as in \cite{4}). After a partial integration we obtain

\[ \frac{\tau}{\tau_0} n_0 \delta_{n,0} + \tau \omega \cdot A^* \times A Z_n = (A^* A + \tau R) Z_n \]  

\[ R = \partial + \nabla A^* + v_T^2 \left( \nabla_{\text{cov}} A + A \left( \frac{\partial g}{\partial t} + Q \nabla g \right) \right) \]

where

\[ Z_n = \frac{v_T^{n_1+n_2+n_3} \Psi_n}{\sqrt{n_1!n_2!n_3!}} \]

\[ \partial = \frac{\partial}{\partial t} + \frac{1}{\tau_0}, \quad g = \frac{1}{2} \ln T \]

The asymmetric lowering and raising operators \( A, A^* \) and the displacement operator \( Q \) are defined respectively by

\[ A_1 Z_n = Z_{n-1,n_2,n_3} \]

\[ A_1^* Z_n = (1+n_1)Z_{n+1,n_2,n_3} \]

\[ Q = v_T^2 A + A^*. \]

(similarly for the remaining components \( A_2 \) and \( A_3 \)). The particle number balance equation (equation (4) with \( |n| = 0 \)) defined here as the generalized Smoluchowsky equation, is given by:

\[ \frac{\partial n}{\partial t} + \nabla J = -\frac{1}{\tau_0} (n - n_0) \]

with \( J = (Z_{100}, Z_{010}, Z_{001}) \). The passage to hydrodynamics is performed as before \cite{1} defining the particle flux, the charge flux, the pressure tensor and the energy flux, respectively by:

\[ J = \int d\mathbf{v} v P(\mathbf{x}, v, t), \quad J_e = eJ \]

\[ \Pi(\mathbf{x}, t) = m \int d\mathbf{v} v P(\mathbf{x}, v, t) \]

\[ J_E(\mathbf{x}, t) = \frac{1}{2} m \int d\mathbf{v} v^2 P(\mathbf{x}, v, t). \]
We also define the energy density $E$ and the nonequilibrium temperature $\Theta$ as before \cite{1}:

$$E(x,t) = \frac{1}{2} Tr \Pi = \frac{3}{2} \rho = \frac{3}{2} n \Theta$$

Again from equation (4), this time with $|n| = 1$, we derive the balance equation for the charge flux (generalized Ohm law \cite{2}):

$$\tau^* \frac{\partial J_e}{\partial t} + J_e = \sigma^* \left( E + R_H J_e \times B - \frac{1}{e} \nabla \text{V}_{me} - \frac{1}{en} \nabla \Pi \right)$$

where

$$\frac{1}{\tau^*} = \frac{1}{\tau} + \frac{1}{\tau_0}, \quad \sigma^* = \frac{e^2 \tau^* n}{m}, \quad R_H = \frac{1}{n\epsilon}$$

With the additional definitions $\varepsilon = mnv_T^2$ and $\varepsilon_0 = mn_0v_T^2$ we obtain for the energy flux balance equation (equation (3), with $1 < |n| \leq 3$):

$$\frac{\partial E}{\partial t} + \nabla J_E = -J e \nabla V = -\frac{2}{\tau} (E - \varepsilon) - \frac{1}{\tau_0} (E - \varepsilon_0)$$

We perform the passage to thermodynamics \cite{1} with the definition for the entropy density

$$S = \int d\mathbf{v} S^*(x, \mathbf{v}, t) = -\int d\mathbf{v} P(x, \mathbf{v}, t) \ln \lambda P(x, \mathbf{v}, t), \quad \lambda = \frac{1}{e_n} \left( \frac{h}{m} \right)^3$$

(where $\ln e_n = 1$, so in the appropriate limit we retrieve the usual thermodynamical entropy \cite{1}). The entropy flux is defined as $J_S = \int d\mathbf{v} \mathbf{v} S^*(x, \mathbf{v}, t)$, then the entropy density balance equation is given by

$$\frac{\partial S}{\partial t} + \nabla J_S = -\int d\mathbf{v} J (1 + \ln \lambda P) = \sigma_S$$

(7)

where $\sigma_S$ is the entropy production Also as in \cite{1} we define the generalized free energy densities $F$ and $G$, and the intrinsic and total chemical potentials respectively as

$$F = E - \Theta S, \quad G = F + p = n\mu_{int}, \quad \mu = \mu_{int} + V$$

Here we introduce no a priori assumptions on the functional dependence of the entropy (as in the local equilibrium approach, LEQ) nor do we assume relevant variables as is extended irreversible thermodynamics (EIT, \cite{6}). As in \cite{1}, all fluxes (including the ones not computed
here), Θ, µ, S, in fact all thermodynamic potentials can be expanded in powers of τ (adequate at least in the overdamped limit and with τ₀ ≫ τ), formally rendering all variables universal functions of the set \{∇, D, n, T, B\}. Thus, at any given τ expansion stage, the only relevant variables are n and T. For Brownian motion, the universal equation for the particle density is the generalized Smoluchowsky equation plus a set of boundary conditions (BC). This picture is distinct but not inconsistent with EIT [6], where incorporating the BC to the fluxes, the latter may be interpreted as relevant variables. LEQ is satisfied only to first order in τ, where

\[ \Theta = T \left( 1 - \tau \frac{\partial \ln q}{\partial t} \right) = T - \frac{\tau \partial T}{2 \partial t} \]

For the linear (first order in τ) case and a stationary (time independent) temperature \( T = \Theta \), the particle and heat fluxes are cast as (with \( B = B \hat{z} \))

\[ J = -K_1 (\xi n \nabla V + \nabla (Dn)) \]  

(8)

\[ J_E = \frac{5}{2} T \left( J - \xi n K_{1\xi} \nabla T \right) \]  

(9)

\[ K_q = \begin{pmatrix} \alpha_q & q \alpha_q \theta & 0 \\ -q \alpha_q \theta & \alpha_q & 0 \\ 0 & 0 & q \end{pmatrix}, \quad \alpha_q = \frac{q}{1 + (q \theta)^2} \]  

(10)

with \( \theta = DD_B^{-1} \) and where Bohm’s diffusion coefficient is \( D_B = cT(eB)^{-1} \). Notice that \( \theta = \sigma_0 B R_H = \tau \omega_c \) where \( \sigma_0 = m^{-1} e^2 \tau n \).

The scope of the Brownian motion scheme is highlighted with some direct applications of equation (8):

a) If diffusion is disregarded (\( \nabla n = 0 \), say electrons in a metal) and with \( \nabla T = 0 \) we retrieve the classical magnetoresistance and Hall effect models [7];

b) If we consider two Brownian gases, say electrons and holes (inhomogeneous semiconductors), with the \( n_0 \)'s the equilibrium carriers’ densities and the \( \tau_0 \)'s generation-recombination times, then (6) together with (8) constitute generalized transport equations [7];

c) The diffusive part has the ‘correct Fick law’ for nonuniform temperature [8];

d) Equation (8) can also be cast as
\[ \mathbf{J} = -\xi K_1 (n \nabla \mu + S \nabla T) \quad (11) \]

in agreement with [9] for the $\nabla T = 0$ case, suggesting that diffusive mass transport is solely convective transport of both mass and entropy; and finally

e) In the high magnetic field regime and with $\nabla T = 0$ the cross diffusion current is driven by $D_B \sim B^{-1}$ the anomalous Bohm coefficient, never derived but proposed to explain the observed $B^{-1}$ behavior instead of the expected $B^{-2}$ term [10].

f) Onsager's reciprocal relations are retrieved from equations (8) and (9) only in the small magnetic field regime, with $\alpha_q \approx q$ (see equation (10)).

Results up to $\tau^2$ (lowest non-linear regime) are presented only for the uniform case $\nabla T \equiv \frac{\partial T}{\partial T} \equiv 0$. Define the magneto-covariant derivative $\vartheta = K_1 \nabla_\text{cov}$. Then the particle and energy fluxes are given respectively by

\[
\mathbf{J} = -D \vartheta n - \frac{\tau D}{\tau_0} K_1 \vartheta n_0 \\
\mathbf{J}_E = \frac{5}{2} T \mathbf{J},
\]

The nonequilibrium temperature is cast as

\[ \Theta = T \left( 1 + \frac{\tau D}{3n} \vartheta^2 n \right) \]

the nonequilibrium entropy, chemical potential and entropy production are given respectively by

\[ S = S_{eq}(n, \Theta) - \frac{1}{2n v_T^2} \mathbf{J}^2 = S_{eq}(n, \Theta) - \frac{\tau D}{2n} |\vartheta n|^2 \]

\[ \mu = \mu_{eq}(n, \Theta) + \frac{m D^2}{2n} |\vartheta n|^2 \]

\[ \sigma_S = \frac{D}{n} \left( |\vartheta n|^2 - n \vartheta^2 n \right) \]

(the latter for the case $\tau_0 = \infty$). The universal (Smoluchowsky) equation for the nonequilibrium density is
\[
\frac{\partial n}{\partial t} = D \nabla \left( \partial n + \frac{\tau}{\tau_0} K_1 \partial n_0 \right) - \frac{1}{\tau_0} (n - n_0)
\]

Work in progress includes illuminated systems [11], chemical reactions [12], the non linear regime in earnest, transport and entropy production general properties, and the validity of any Onsager-like scheme.

Acknowledgments This work was supported by FAPESP, SP Brazil.

References

[1] L. A. Barreiro, J. R. Campanha and R. E. Lagos, arXiv: cond-mat/9910405; Physica A 283 (2000) 160.

[2] R. Czopnik and P. Garbaczewsky, arXiv: cond-mat/0005353 & 0011105.

[3] P. L. Bathnagar, E. P. Gross and M. Krook, Phys. Rev. 94 (1954) 511.

[4] R. E. Lagos and R. A. Friesner, J. Chem. Phys. 81 5899 (1984) 5899

[5] D. R. Nicholson, Introduction to Plasma Theory (John Wiley & Sons, 1983)

[6] D. Jou, J. Casas-Vásquez and G. Lebon, Rep. Prog. Phys. 62 (1999) 1035.

[7] N. W. Ashcroft and N. D. Mermin, Solid State Physics (Holt, Rinehart and Winston, 1976).

[8] N. G. van Kampen, Z. Phys. B 68 (1987) 135.

[9] R. Landauer, Helvetica Physica Acta 56 (1983) 847.

[10] F. C. Chen, Introduction to Plasma Physics (Plenum Press, NY & London, 1974).

[11] R. E. Lagos, H. Suhl and T. Tiedje, J. Appl. Phys. 54 (1983) 3951.

[12] R. E. Lagos, T. P. Simões and A. L. Godoy; Physica A 257 (1998) 401.