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Quantum corrections to drift-diffusion equations in graphene with smoothed energy-band

Abstract. Quantum corrections to the semiclassical drift-diffusion equation are obtained for electrons in graphene with a regularized energy-band. The derivation starts from the single-particle, single-band Wigner equation and exploits the quantum maximum entropy principle together with the classical Chapman-Enskog method. The functional calculus in phase-phase space is then used to expand the model to second order in the scaled Planck's constant. The model is shown to be singular in the limit where the regularization parameter goes to zero.

Keywords. Graphene, quantum diffusion, subleading corrections.

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To the dearest memory of Giampiero Spiga, with deep gratitude.

1 - Introduction

The many possible applications to microelectronics have led to a considerable research activity concerning hydrodynamic and diffusive models for electrons in graphene (see Refs. [17, 20] and the references therein). In the vast majority of cases, these models are "semiclassical", which means that electrons are treated as classical particles with a peculiar form of the kinetic energy, namely

$$\mathcal{E}(\boldsymbol{p}) = \pm c|\boldsymbol{p}|,$$

hence linear in the modulus of the momentum, where c is the so-called Fermi velocity. Finding "quantum corrections" to such models means that the coherent

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nature of electrons, as quantum particles, is taken into account to some degree. Such quantum corrections are already well known for standard (parabolic energy bands) particles but are still not well understood for particles with conical energy bands. The reasons are many. First, in the limit $p \rightarrow 0$ the energy looses the smoothness which is necessary for the semiclassical expansion of the model (typically involving higher derivatives of the energy); second, the presence of the negative energy cone requires a description in terms of electrons and holes, where the concept of hole is typically semiclassical; third, the absence of an energy gap implies that the transport is always in the Fermi-Dirac regime, for which the theory necessary to calculate the corrections is not as well developed as in the Maxwell case.

Quantum hydrodynamic or diffusive equations for graphene have been obtained for pure states [6] and in the opposite regime of "well mixed" states [24]. Without such assumptions, troubles quickly arise, mainly due to the conical singularity. In Ref. [16], Luca and Romano consider a single-band quantum hydrodynamic model where the maximum entropy principle [14] is applied only to the leading order of the semiclassical expansion of the local equilibrium state. They show that the model is singular (the transport coefficients diverge) unless a band-gap parameter (γ , in our notations) is introduced, so that the energy band takes the smoothed form

$$\mathcal{E}(\boldsymbol{p}) = \sqrt{c^2 |\boldsymbol{p}|^2 + \gamma^2}$$

(it should be noted that the presence of a small band gap can be justified also from a physical point of view [8,16]). In Ref. [5], a single-band hydrodynamic model is still considered where the maximum entropy principle is applied up to the second-order, according to the "quantum maximum entropy principle" theory by Degond, Ringhofer and Méhats [11,12]. The result is that the quantum corrections to the Euler equations are non-singular, while singularities are still present in the "viscous" corrections, requiring again the regularization of the energy band.

In the present work we still consider a regularized single-band and compute the quantum corrections to the diffusion equations. We start from the Wigner equation and apply the quantum maximum entropy principle to describe the relaxation of the system, in a typical time τ , towards a local equilibrium state. Then, the classical Chapman-Enskog method is used to derive fully quantum drift-diffusion equations. Such equations are then semiclassical expanded to second-order in the scaled Planck constant ε , yielding the sought quantum corrections. It turns out that the corrections are singular in the conical band limit $\gamma \to 0$. This was somehow expected, since the diffusion is given by the first-order (in τ) Chapman-Enskog term, analogously to the above-mentioned viscous corrections.

This paper is organized as follows. In Section 2 we introduce the microscopic description, based on the single-particle, single-band quantum Hamiltonian and the corresponding Wigner equation. The Wigner equation is endowed with a "collisional" term describing the relaxation of the system towards a local-equilibrium Wigner function g. In Section 3, after rewriting the equation in diffusive scaling, we perform the Chapman-Enskog analysis and obtain a fully-quantum diffusive equation. In Section 4 the diffusive equation is closed by means of the quantum maximum entropy principle, which provides a selfconsistent, although very implicit, quantum model. In Section 5, using Moyal calculus, the equilibrium Wigner function and the related Lagrange multipliers are expanded to order ε^2 . Finally, in Section 6, the results of the previous sections are used to obtain a semiclassical drift-diffusion equation and its second-order quantum corrections.

2 - Microscopic description

We assume that the microscopic dynamics of a single electron is described by (the quantization of) the following Hamiltonian [8]:

(2.1)
$$h(\boldsymbol{x}, \boldsymbol{p}) = \mathcal{E}(\boldsymbol{p}) + V(\boldsymbol{x})$$

where $\boldsymbol{x} = (x_1, x_2)$ and $\boldsymbol{p} = (p_1, p_2)$ are the two-dimensional space and momentum coordinates of the electron, $V(\boldsymbol{x})$ is the electrostatic potential and $\mathcal{E}(\boldsymbol{p})$ is the energy band of the positive-energy electrons:

(2.2)
$$\mathcal{E}(\boldsymbol{p}) = \sqrt{c^2 |\boldsymbol{p}|^2 + \gamma^2}.$$

Here, c > 0 is the Fermi velocity and $\gamma > 0$ is a regularization parameter, which can be physically related to higher-order terms of the tight-binding approximation of the band [8, 16]. In the semiclassical theory [20],

(2.3)
$$\boldsymbol{v}(\boldsymbol{p}) = \nabla_{\boldsymbol{p}} \mathcal{E} = \frac{c^2 \boldsymbol{p}}{\sqrt{c^2 |\boldsymbol{p}|^2 + \gamma^2}}$$

is the group velocity of the electron and

(2.4)
$$\pi_{ij}(\boldsymbol{p}) = \frac{\partial^2 \mathcal{E}}{\partial p_i \partial p_j} = \frac{\partial v_i}{\partial p_j} = \frac{1}{\mathcal{E}} \left(c^2 \delta_{ij} - v_i v_j \right)$$

is the inverse effective-mass tensor [3]. The above description is valid for conduction electrons, which are the only carriers that will be considered in this

[4]

work. A specular description could be applied to holes in the valence band, which are positively charged and whose group velocity is -v.

In the Wigner (phase-space) formalism, a mixed (statistical) state of a population of electrons is described by means of the Wigner function

(2.5)
$$w(\boldsymbol{x},\boldsymbol{p}) = \frac{1}{(2\pi\varepsilon)^2} \int_{\mathbb{R}^2} \varrho\left(\boldsymbol{x} + \frac{\boldsymbol{\xi}}{2}, \boldsymbol{x} - \frac{\boldsymbol{\xi}}{2}\right) \mathrm{e}^{-i\boldsymbol{p}\cdot\boldsymbol{\xi}/\varepsilon} d\boldsymbol{\xi}$$

where $\rho(\boldsymbol{x}, \boldsymbol{y})$ denotes the density matrix of the system and ε denotes the scaled Planck's constant.¹ The inverse transformation is

(2.6)
$$\rho(\boldsymbol{x},\boldsymbol{y}) = \int_{\mathbb{R}^2} w\left(\frac{\boldsymbol{x}+\boldsymbol{y}}{2},\boldsymbol{p}\right) e^{i(\boldsymbol{x}-\boldsymbol{y})\cdot\boldsymbol{p}/\varepsilon} d\boldsymbol{p}$$

which corresponds to the Weyl quantization Op(w), up to the identification of the operator Op(w) with its integral kernel ρ [13,23].

In order to write down an evolution equation for the time-dependent Wigner function $w(\boldsymbol{x}, \boldsymbol{p}, t)$, we recall that the Moyal product is the operator product translated into phase-space functions by inverse Weyl quantization [13,23]:

(2.7)
$$a\#b = \operatorname{Op}^{-1}(\operatorname{Op}(a) \operatorname{Op}(b)) = \sum_{k=0}^{\infty} \varepsilon^k a \#_k b,$$

where

(2.8)
$$a\#_k b = \frac{1}{(2i)^k} \sum_{|\alpha|+|\beta|=k} \frac{(-1)^{|\alpha|}}{\alpha!\,\beta!} \left(\nabla^{\alpha}_{\boldsymbol{x}} \nabla^{\beta}_{\boldsymbol{p}} a \right) \left(\nabla^{\alpha}_{\boldsymbol{p}} \nabla^{\beta}_{\boldsymbol{x}} b \right).$$

In the last equation we use the standard multi-index notation applied to the x- and p-gradients (denoted ∇_x and ∇_p , respectively): in 2D a multi-index α is a couple (α_1, α_2) of non-negative integers indicating the order of derivation with respect to the two variables. Moreover, $|\alpha| = \alpha_1 + \alpha_2$ is the total order of derivation and $\alpha! := \alpha_1!\alpha_2!$. The evolution of the Wigner function comes directly from the von Neumann equation for ρ (Schrödinger equation for mixed states) and reads as follows [5, 16]:

(2.9)
$$\partial_t w + \Lambda w + \Theta_V w = 0,$$

¹We use ε instead of \hbar both for readability and to emphasize the small-parameter character of the Planck constant in the semclassical expansion (one can think of ε as a suitably scaled version of \hbar).

where

(2.10)
$$\Lambda w = \frac{i}{\varepsilon} [\mathcal{E}, w]_{\#} = \sum_{k=0}^{\infty} \varepsilon^{2k} \Lambda^{(2k)} w, \quad \Lambda^{(2k)} = \sum_{|\alpha|=2k+1} \frac{(-1)^k}{4\alpha!} \nabla^{\alpha}_{p} \mathcal{E} \nabla^{\alpha}_{x}, \\ \Theta_{V} w = \frac{i}{\varepsilon} [V, w]_{\#} = \sum_{k=0}^{\infty} \varepsilon^{2k} \Theta^{(2k)}_{V} w, \quad \Theta^{(2k)}_{V} = -\sum_{|\alpha|=2k+1} \frac{(-1)^k}{4\alpha!} \nabla^{\alpha}_{x} V \nabla^{\alpha}_{p} V \nabla^{\alpha}_$$

and $[a,b]_{\#} = a \# b - b \# a$ is the Moyal commutator. Note that, for $\varepsilon \to 0$, Λ and Θ_V converge to the corresponding classical operators, namely

(2.11)
$$\Lambda^{(0)} = \boldsymbol{v} \cdot \nabla_{\boldsymbol{x}}, \qquad \Theta_V^{(0)} = -\nabla_{\boldsymbol{x}} V \nabla_{\boldsymbol{p}},$$

and the Wigner equation (2.9) reduces to the Liouville equation for the Hamiltonian (2.1).

In the classical kinetic theory, the macroscopic, fluid-dynamical equations are derived from Boltzmann equation, which is a one-particle Liouville equation endowed with the celebrated Boltzmann's collisional operator [9]. In the fully quantum theory, however, the equivalent of such operator is nonlocal in both space and time, and is too involved to be useful in analytical or numerical investigations (see Ref. [7]). In intermediate regimes, namely regimes that can be considered as a perturbation of the classical one, a Boltzmann-like semiclassical collision operator, possibly augmented with a $\mathcal{O}(\varepsilon^2)$ quantum correction, can be used [16,21,22]. Here, we decided to adopt a fully quantum perspective, while maintaining a relatively simple description of collisions. So, following Degond-Ringhofer-Méhats' theory [11, 12], we prescribe that collisions will drive the system, in a typical time τ , towards a quantum state of local equilibrium that maximises a suitable entropy functional. Then, the collisional Wigner equation takes the form

(2.12)
$$\partial_t w + \Lambda w + \Theta_V w = \frac{1}{\tau} (g - w),$$

where g is the Wigner function corresponding to the local equilibrium state and is chosen so that it maximises the quantum (von Neumann) entropy among all the Wigner functions that share some given moments [11, 12, 15]. This is the quantum version of the classical entropy principle [14]. Since, in this work, we are interested in the diffusive regime, then we assume that inelastic collisions with a thermal bath of phonons are the dominant interaction mechanism. Such collisions conserve the number of electrons but not their momentum nor their energy and, therefore, we only have to prescribe the conservation of the local electron density n:

(2.13)
$$\langle g \rangle(\boldsymbol{x},t) = \langle w \rangle(\boldsymbol{x},t) := n(\boldsymbol{x},t).$$

where $\langle \cdot \rangle$ is a shorthand for $\int \cdot d\mathbf{p}$. For the moment, we do not need more details about the local equilibrium g and we will resume its description in the dedicated Section 4.

We remark that, in general, the typical collision time τ depends on the momentum but here, for the sake of simplicity, it is assumed to be constant. Moreover, we can always think that we are working in non-dimensional variables and parameters, so that τ is to be considered as a scaled collisional time (the rescaling procedure is standard and we can refer, e.g., to Ref. [15] for it). Note therefore that Eq. (2.12) contains two non-dimensional parameters: the scaled Planck constant ε and the scaled collision time τ , which will be considered as small parameters in the following.

3 - Diffusion limit

Let us now study the diffusion limit of the Wigner equation (2.12). First of all we need to rewrite the equation in the "diffusive scaling" form. Since we are already working with non-dimensional variable, we just have to rescale time as follows:

$$t \to \frac{t}{\tau}$$

which means that we are zooming out in time in order to observe the dynamics over a longer time scale. The Wigner equation takes therefore the form

(3.1)
$$\tau^2 \partial_t w + \tau T w = Q(w),$$

where

(3.2)
$$T = \Lambda + \Theta_V$$
 and $Q(w) = g - w$.

We remark that g depends nonlinearly on w through the constraint (2.13), which guarantees

$$(3.3)\qquad \qquad \langle Q(w)\rangle = 0$$

The diffusion limit of (3.1) is obtained by means of the classical Chapman-Enskog ansatz [9, 10], which consists in the expansion

(3.4)
$$w = w^{(0)} + \tau w^{(1)} + \tau^2 w^{(2)} + \cdots,$$

where each $w^{(k)}$ depends on τ (in some complex way) but has a finite limit for $\tau \to 0$ (that we still denote $w^{(k)}$, for the sake of simplicity). Plugging (3.4) into (3.1) and taking the limit $\tau \to 0$ yields

(3.5)
$$w^{(0)} = g$$

At next order, dividing by τ and taking the limit $\tau \to 0$, we obtain

(3.6)
$$w^{(1)} = -Tw^{(0)} = -Tg.$$

Similarly, at second order, we obtain

(3.7)
$$w^{(2)} = -Tw^{(1)} - \partial_t w^{(0)} = TTg - \partial_t g.$$

Now, from our assumptions and from the constraint (2.13) we have that

$$\langle w^{(0)} \rangle = \langle g \rangle = n$$
 and $\langle w^{(k)} \rangle = 0, \quad k \ge 1.$

Hence, integrating with respect to $p \in \mathbb{R}^2$ both sides of Eq. (3.7), finally yields the macroscopic diffusive equation

$$(3.8) \qquad \qquad \partial_t n = \langle TTg \rangle$$

which is the equation we were looking for. Of course, (6.3) is still written in an implicit form, since the right-hand side depends on ρ through the specific form of g and through the constraint (2.13). In the next sections we will work on these aspects.

4 - Quantum drift-diffusion equations

As already mentioned in Sec. 2, the microscopic equilibrium state g is chosen to maximize a quantum entropy functional [11, 12, 15]. In addition, the equilibrium state must reflect some general properties of collisions, such as the conservation of particle number, momentum, energy. In the present work, we are assuming that the main collisional mechanism for our system is represented by collisions with a phonon bath at given temperature. Such collisions are inelastic and do not conserve momentum, so we just impose the conservation of the number of particles.

The suitable entropy functional for a fermionic diffusion problem is a freeenergy functional (to be minimised) [4], given by

(4.1)
$$\mathcal{F}(w) = \int_{\mathbb{R}^2} \int_{\mathbb{R}^2} \left\{ hw + \operatorname{Op}^{-1}[s(\operatorname{Op}(w)] \right\} d\boldsymbol{p} \, d\boldsymbol{x},$$

where Op is the Weyl quantization, already introduced in Sec. 2, and s is (minus) the entropy function

$$s(z) = z \log(z) + (1 - z) \log(1 - z).$$

We remark that this particular entropy function leads to Fermi-Dirac statistics (see below), which is necessary to describe a zero-gap material such as graphene. Note also that we assume here to work in non-dimensional variables such that no temperature-dependent constants appear in (4.1) (otherwise the constant k_BT_0 should be multiplying s, where k_B is the Boltzmann constant and T_0 is the temperature of the thermal bath). Then, we choose the local-equilibrium state g according to the above-described quantum maximum entropy principle, which, in our specific case, reads as follows: for any given function n(x, t), find g such that

(4.2)
$$g = \arg\min\left\{\mathcal{F}(w) \mid \langle w \rangle = n\right\}.$$

It can be proven [11, 12, 15, 18, 19] that a Lagrange multiplier A(x, t) exists such that g is given by

(4.3)
$$g = \operatorname{Op}^{-1}\left(\frac{1}{\mathrm{e}^{\operatorname{Op}(h-A)}+1}\right), \quad \text{with} \quad \langle g \rangle = n.$$

Equation (4.3) completely identifies the local-equilibrium Wigner function g that appears in the quantum drift-diffusion equation (3.8). Now,

$$Tg = \frac{i}{\varepsilon} [h,g]_{\#} = \frac{i}{\varepsilon} [h-A,g]_{\#} + \frac{i}{\varepsilon} [A,g]_{\#} = \Theta_A g,$$

where we used the fact that the commutator between h - A and g (which is function of h - A through functional calculus) is zero. Hence,

$$TTg = \Lambda \Theta_A g + \Theta_V \Theta_A g$$

and, from the property

(4.4)
$$\langle \Theta_V w \rangle = 0$$

(which can be immediately obtained from (2.10)), Eq. (3.8) becomes

(4.5)
$$\partial_t n = \langle TTg \rangle = \langle \Lambda \Theta_A g \rangle.$$

Equation (4.5), together with (4.3), yields a self-consistent (albeit very implicit) quantum drift-diffusion model for the density n. In the next section we shall perform the semiclassical expansion of g and A, and therefore of the quantum drift-diffusion model, up to order ε^2 .

5 - Semiclassical expansion

5.1 - Expansion of the equilibrium state

We can compute the semiclassical expansion of the maximum entropy state,

$$g = g^{(0)} + \varepsilon g^{(0)} + \varepsilon^2 g^{(2)} + \cdots,$$

as follows. Let

$$F(z) = \frac{1}{\mathrm{e}^z + 1},$$

then, according to (4.3),

$$g = \operatorname{Op}^{-1} \left[F \left(\operatorname{Op}(h - A) \right) \right].$$

By using the holomorphic functional calculus, we can express the operator $F(\operatorname{Op}(h-A))$ as

(5.1)
$$F(\operatorname{Op}(h-A)) = \frac{1}{2\pi i} \int_{\Gamma} F(z)(z - \operatorname{Op}(h-A))^{-1} dz,$$

where Γ is a positively oriented path in the complex plane encompassing the real line. Applying to both sides the inverse Weyl quantization,

(5.2)
$$g = \frac{1}{2\pi i} \int_{\Gamma} F(z) \operatorname{Op}^{-1} \left[(z - \operatorname{Op}(h - A))^{-1} \right] dz,$$

shows that computing the semiclassical expansion of g reduces to computing the semiclassical expansion $R_{\varepsilon} = R^{(0)} + \varepsilon R^{(1)} + \varepsilon^2 R^{(2)} + \cdots$ of the transformed resolvent

$$R(z) = \operatorname{Op}^{-1} \left[(z - \operatorname{Op}(h - A))^{-1} \right],$$

so that [2]

(5.3)
$$g^{(k)} = \frac{1}{2\pi i} \int_{\Gamma} F(z) R^{(k)}(z) \, dz$$

The semiclassical expansion of R(z) can be obtained from the identities

$$(z - h + A) \# R(z) = R(z) \# (z - h + A) = 1,$$

that combine to yield

(5.4)
$$\frac{1}{2}\left[(z-h+A)\#R(z)+R(z)\#(z-h+A)\right]=1.$$

[10]

Since the odd-order Moyal product is anti-commutative (see (2.7)), Eq. (5.4) immediately gives us that $R^{(k)} = 0$ for odd k and therefore,

(5.5)
$$R(z) = R^{(0)}(z) + \varepsilon^2 R^{(2)}(z) + \varepsilon^4 R^{(4)}(z) + \cdots$$

where the even-order terms $R^{(2k)}$ are given by the recursive relation

(5.6)
$$\begin{cases} R^{(0)}(z) = (z - h + A)^{-1}, \\ R^{(2k)}(z) = \sum_{j=1}^{n} h \#_{2j} R^{2(k-j)}(z), \quad k \ge 1. \end{cases}$$

The leading-order equilibrium is therefore given by (5.3) with k = 0

(5.7)
$$g^{(0)} = \frac{1}{2\pi i} \int_{\Gamma} \frac{F(z)}{z - h + A} \, dz = F(h - A) = \frac{1}{\mathrm{e}^{\mathcal{E} - \mu} + 1},$$

which is the classical Fermi-Dirac distribution, where, for shortness, we put

$$\mu = A - V.$$

The first subleading correction is of order ε^2 and is given by (5.3) with k = 2, where, from (5.6),

$$R^{(2)}(z) = R^{(0)}(z) \left((h-A) \#_2 R^{(0)}(z) \right).$$

We are not giving here all the details of calculations, which are lengthy but straightforward, and we shall limit ourselves to write down the result: (5.8)

$$g^{(2)} = \frac{1}{8}F''(\mathcal{E}-\mu)\frac{\partial^2\mu}{\partial x_i\partial x_j}\pi_{ij} + \frac{1}{24}F'''(\mathcal{E}-\mu)\left(\frac{\partial^2\mu}{\partial x_i\partial x_j}v_iv_j - \frac{\partial\mu}{\partial x_i}\frac{\partial\mu}{\partial x_j}\pi_{ij}\right),$$

where v_i and π_{ij} are defined in (2.3) and (2.4), and summation over i = 1, 2 and j = 1, 2 is understood. A similar result was obtained (with different techniques) in Ref. [4] for a parabolic energy band.

5.2 - Expansion of the Lagrange multiplier

We now expand the reciprocal dependence between the Lagrange multiplier A (or, equivalently, $\mu = A - V$) and the density n, as it results from the constraint $\langle g \rangle = n$ in (4.3). Hence, we write

$$\mu(n) = \mu^{(0)} + \varepsilon \mu^{(1)} + \varepsilon^2 \mu^{(2)} + \cdots$$

From (5.7), at leading order the constraint reads as follows:

(5.9)
$$\langle F(\mathcal{E}-\mu)\rangle = n_{\rm f}$$

where

[11]

$$\langle F(\mathcal{E} - \mu) \rangle = \int_{\mathbb{R}^2} \frac{d\mathbf{p}}{e^{\sqrt{c^2 |\mathbf{p}|^2 + \gamma^2} - \mu} + 1} = 2\pi \int_0^\infty \frac{\rho \, d\rho}{e^{\sqrt{c^2 \rho^2 + \gamma^2} - \mu} + 1}$$
$$= \frac{2\pi}{c^2} \int_{\gamma}^\infty \frac{t \, dt}{e^{t - \mu} + 1} = \frac{2\pi}{c^2} \, \phi_2^{\gamma}(\mu).$$

Here, $\phi_s^{\gamma}(\mu)$ denotes the incomplete Fermi integral of order s, namely:

(5.10)
$$\phi_s^{\gamma}(\mu) = \frac{1}{\Gamma(s)} \int_{\gamma}^{+\infty} \frac{t^{s-1} dt}{e^{t-\mu} + 1}.$$

Since $\phi_2^{\gamma}(\mu)$ is a strictly increasing function of μ from \mathbb{R} to $(0, +\infty)$, then, Eq. (5.9) has a unique solution

(5.11)
$$\mu^{(0)}(n) = (\phi_2^{\gamma})^{-1} \left(\frac{c^2 n}{2\pi}\right)$$

for any given n > 0.

Since $g^{(1)} = 0$, and, consequently, $\mu^{(1)} = 0$, the next step is to find the correspondence between μ and n at second order, according to

(5.12)
$$\langle g^{(0)} \rangle + \varepsilon^2 \langle g^{(2)} \rangle = n.$$

Integrating (5.8) with respect to $\boldsymbol{p} \in \mathbb{R}^2$, for evident symmetry reasons, we obtain

$$(5.13) \quad \langle g^{(2)} \rangle = \left\langle \frac{1}{8} F''(\mathcal{E} - \mu) \pi_{ii} \frac{\partial^2 \mu}{\partial x_i^2} + \frac{1}{24} F'''(\mathcal{E} - \mu) \left[v_i^2 \frac{\partial^2 \mu}{\partial x_i^2} - \pi_{ii} \left(\frac{\partial \mu}{\partial x_i} \right)^2 \right] \right\rangle$$
$$= \frac{c^2}{16} \left\langle F''(\mathcal{E} - \mu) \frac{\mathcal{E}^2 + \gamma^2}{\mathcal{E}^3} \Delta \mu + \frac{1}{3} F'''(\mathcal{E} - \mu) \left[\frac{\mathcal{E}^2 - \gamma^2}{\mathcal{E}^2} \Delta \mu - \frac{\mathcal{E}^2 + \gamma^2}{\mathcal{E}^3} |\nabla \mu|^2 \right] \right\rangle,$$

where we used the fact that, for any function f depending on p only through its modulus |p| and for fixed i = 1, 2,

$$\langle v_i^2 f \rangle = \frac{1}{2} \langle |\boldsymbol{v}|^2 f \rangle = \frac{c^2}{2} \left\langle \frac{\mathcal{E}^2 - \gamma^2}{\mathcal{E}^2} f \right\rangle,$$
$$\langle \pi_{ii} f \rangle = \left\langle \frac{c^2 - v_i^2}{\mathcal{E}} f \right\rangle = \frac{c^2}{2} \left\langle \frac{\mathcal{E}^2 + \gamma^2}{\mathcal{E}^3} f \right\rangle.$$

[12]

A simple calculation with Taylor's formula (see also Ref. [4]) shows that the inversion of the second-order relation (5.12) (for the unknown μ) reads as follows:

(5.14)
$$\mu^{(2)}(n) = \frac{c^4}{32\pi} \frac{1}{\phi_1^{\gamma}(\mu^{(0)}(n))} \left[\frac{1}{3} |\nabla \mu^{(0)}(n)|^2 \left\langle F'''(\mathcal{E} - \mu^{(0)}(n)) \frac{\mathcal{E}^2 + \gamma^2}{\mathcal{E}^3} \right\rangle -\Delta \mu^{(0)}(n) \left\langle F''(\mathcal{E} - \mu^{(0)}(n)) \frac{\mathcal{E}^2 + \gamma^2}{\mathcal{E}^3} + \frac{1}{3} F'''(\mathcal{E} - \mu^{(0)}(n)) \frac{\mathcal{E}^2 - \gamma^2}{\mathcal{E}^2} \right\rangle \right],$$

where $\mu^{(0)}(n)$ is the solution to the leading-order equation (5.9), given by (5.11), and the property $(\phi_s^{\gamma})' = \phi_{s-1}^{\gamma}$ has been used.

6 - Quantum corrections to drift-diffusion equations

Let us come back to the quantum drift-diffusion equation (4.5). The expansion (2.10) of the operators Λ and Θ and the results of Section 5 can now be used to write down the approximation of Eq. (4.5) at order ε^2 , according to

$$\partial_t n = \langle \Lambda^{(0)} \Theta^{(0)}_{A^{(0)}} g^{(0)} \rangle + \sum_{i+j+k+l=1} \varepsilon^2 \langle \Lambda^{(2i)} \Theta^{(2j)}_{A^{(2k)}} g^{(2l)} \rangle + \mathcal{O}(\varepsilon^4),$$

where

$$A^{(0)} = V + \mu^{(0)}, \qquad A^{(2)} = \mu^{(2)}$$

(here and in the following $\mu^{(k)} = \mu^{(k)}(n)$ will be understood). From (2.11), at leading order we obtain

$$\langle \Lambda^{(0)} \Theta_{A^{(0)}}^{(0)} g^{(0)} \rangle = -\frac{\partial}{\partial x_i} \left\langle v_i \frac{\partial (\mu^{(0)} + V)}{\partial x_j} \frac{\partial g^{(0)}}{\partial p_j} \right\rangle$$

$$= \frac{\partial}{\partial x_i} \left(\frac{\partial (\mu^{(0)} + V)}{\partial x_j} \left\langle \frac{\partial v_i^{(0)}}{\partial p_j} g^{(0)} \right\rangle \right) = \frac{\partial}{\partial x_i} \left[\left(\frac{d\mu^{(0)}}{dn} \frac{\partial n}{\partial x_j} + \frac{\partial V}{\partial x_j} \right) \left\langle \pi_{ij} g^{(0)} \right\rangle \right]$$

Similarly, we have

$$\langle \Lambda^{(0)} \Theta^{(0)}_{A^{(0)}} g^{(2)} \rangle + \langle \Lambda^{(0)} \Theta^{(0)}_{A^{(2)}} g^{(0)} \rangle$$

$$= \frac{\partial}{\partial x_i} \left[\left(\frac{d\mu^{(0)}}{dn} \frac{\partial n}{\partial x_j} + \frac{\partial V}{\partial x_j} \right) \langle \pi_{ij} g^{(2)} \rangle + \left(\frac{d\mu^{(2)}}{dn} \frac{\partial n}{\partial x_j} \right) \langle \pi_{ij} g^{(0)} \rangle \right].$$

Moreover, from (2.10),

$$S := \langle \Lambda^{(2)} \Theta_{A^{(0)}}^{(0)} g^{(0)} \rangle + \langle \Lambda^{(0)} \Theta_{A^{(0)}}^{(2)} g^{(0)} \rangle$$
$$= \sum_{|\alpha|=3} \frac{1}{4\alpha!} \left[\nabla^{\alpha} \left(H_{\alpha,j} \frac{\partial}{\partial x_j} (\mu^{(0)} + V) \right) + \frac{\partial}{\partial x_j} \left(H_{\alpha,j} \nabla^{\alpha} (\mu^{(0)} + V) \right) \right],$$

where (recalling that $\alpha = (\alpha_1, \alpha_2)$)

$$H_{\alpha,j} = \langle F(\mathcal{E} - \mu^{(0)}) \nabla^{\alpha}_{\boldsymbol{p}} v_j \rangle = \Big\langle F(\mathcal{E} - \mu^{(0)}) \frac{\partial^4 \mathcal{E}}{\partial p_1^{\alpha_1} \partial p_2^{\alpha_2} \partial p_j} \Big\rangle.$$

Hence, by symmetry considerations,

(6.1)
$$S = \frac{\partial^3}{\partial x_i^2 \partial x_j} \Big(H_{ij} \frac{\partial}{\partial x_j} (\mu^{(0)} + V) \Big) + \frac{\partial}{\partial x_j} \Big(H_{ij} \frac{\partial^3}{\partial x_i^2 \partial x_j} (\mu^{(0)} + V) \Big),$$

where

(6.2)
$$H_{ij} = \begin{cases} \frac{1}{8} \left\langle F(\mathcal{E} - \mu^{(0)}) \frac{\partial^4 \mathcal{E}}{\partial p_1^2 \partial p_2^2} \right\rangle, & \text{if } i \neq j \\ \frac{1}{24} \left\langle F(\mathcal{E} - \mu^{(0)}) \frac{\partial^4 \mathcal{E}}{\partial p_1^4} \right\rangle, & \text{if } i = j. \end{cases}$$

Hence, the $\mathcal{O}(\varepsilon^2)$ drift-diffusion equation reads as follows

(6.3)
$$\partial_t n = \operatorname{div}\left[\left(D^{(0)} + \varepsilon^2 D^{(2)}\right)\nabla n + \left(M^{(0)} + \varepsilon^2 M^{(2)}\right)\nabla V\right] + \varepsilon^2 S,$$

where,

(6.4)

$$M^{(0)} = \langle \pi_{ij} g^{(0)} \rangle = \left\langle \frac{\mathcal{E}^2 + \gamma^2}{\mathcal{E}^3} F(\mathcal{E} - \mu^{(0)}) \right\rangle,$$

$$D^{(0)} = \frac{d\mu^{(0)}}{dn} M^{(0)} = \frac{c^2}{2\pi \phi_1^\gamma(\mu^{(0)})} M^{(0)}$$

$$M^{(2)} = \langle \pi_{ij} g^{(2)} \rangle \quad (\text{independent on } i \text{ and } j)$$

$$M^{(2)} = \langle \pi_{ij} g^{(2)} \rangle \quad \text{(independent on } i \text{ and} \\ D^{(2)} = \frac{d\mu^{(0)}}{dn} M^{(2)} + \frac{d\mu^{(2)}}{dn} M^{(0)}$$

and S is given by (6.1). We can make some remarks about equation (6.3).

1. The leading order diffusion and mobility coefficients, $D^{(0)}$ and $M^{(0)}$, depend on n, while the second-order ones, $D^{(2)}$ and $M^{(2)}$ depend on n and its derivatives up to second order (see (5.8)).

- 2. The term S contains derivatives of n and V up to third-order. This term does not appear in standard quantum drift-diffusion equations with parabolic energy bands [11, 15] because, in that case, the third-order derivatives of \boldsymbol{v} (fourth-order derivatives of \mathcal{E}) vanish and, consequently, $H_{ij} = 0$.
- 3. The quantum corrections become singular in the conical-band limit $\gamma \to 0$. In fact, when $\gamma = 0$, we have that $\pi_{ij}g^{(2)} \sim |\boldsymbol{p}|^{-1}$ and $\nabla_{\boldsymbol{p}}^{\alpha} \mathcal{E} \sim |\boldsymbol{p}|^{1-|\alpha|}$, for $|\boldsymbol{p}| \to 0$. Since in \mathbb{R}^2 a singularity of the form $|\boldsymbol{p}|^{-k}$ is non-integrable when $k \geq 2$, then the coefficients $M^{(2)}$ and H_{ij} become infinite. As already remarked in the Introduction, this phenomenon is known also for hydrodynamic-type equations in graphene [5, 16].

One might suspect that the singularities are due to our choice to use a singleband microscopic description, and that they can disappear when considering the complete two-band Hamiltonian [8]. However, our first calculations (not reported here) show that this is not the case and singularities still pop up. These results indicate that the semiclassical expansion of quantum diffusion or quantum hydrodynamic equations is problematic in the presence of a conical band intersection. The two-band model, moreover, brings an additional difficulty due to the fact that the Hamiltonian is unbounded from below. Indeed, the unboundedness of the negative-energy band means that more and more convenient energy states are always available, which implies that, at thermodynamic equilibrium, the lower band is "filled" and the electron density is infinite. The semiclassical way to overcome this difficulty is to describe negative-energy electrons in terms of holes in the "Fermi sea". However, it is unclear how to fit the concept of hole in the framework of quantum maximum entropy principle, at least in the standard form that we used here. A more accurate discussion on the two-band case is deferred to a future work.

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