## New stochastic models of thermodiffusion : entropic validation through kinetic theory

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A new entropic criterium is proposed to assess the validity of the diffusion approximation. This criterium is applied to particle diffusion in a dilute gaz. It is found that the diffusion approximation is, at least in this case, quite robust and valid even if the mass of the Brownian particle is not much larger than the mass of the solvent particles. This result is then used to validate new stochastic models of thermodiffusion.

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## 1 Introduction

Diffusions are ubiquitous in scientific modelling, with applications ranging from Physics and Chemistry[1] to Economics[2], through Biology[3, 4, 5, 6] and population dynamics[7]. In Physics, diffusion is only an approximate description of transport, valid when the mass of the transported object is much larger than the mass of the solvent particles[8]. Though very well-known, this qualitative statement still lacks a quantitative counterpart. Indeed, such a counterpart would presuppose the existence of a method to measure or ascertain quantitatively the validity of the diffusion approximation, and no such method has been yet proposed in the literature.

The aim of this article is (i) to propose a new, quantitative method to measure the validity of the diffusion approximation, (ii) to apply this method to the problem of Brownian particle transport, in order to assess how the validity of the approximation varies with the mass ratio r between the transported particle and the solvent particles (iii) to use this analysis to ascertain the physical relevance of new, recently derived contributions[9, 10] to the noise experienced by a particle diffusing in a temperature gradient.

Here is a brief summary of how these goals are implemented and of the conclusions that are reached. We start from a simple kinetic model of Brownian particles diffusing in a solvent and derive from this model friction force and a white Gaussian noise *i.e.* a Markov process which describe the net, global effect of the collisions undergone by the Brownian particle. We also compute the equilibrium distribution  $\Phi_{\rm E}$  of this process in velocity space; this function is different from the Maxwell-Boltzmann distribution  $\Phi_{M}$  predicted by the *a priori* more precise, kinetic description. We then propose to measure the validity of the diffusion approximation by the conditional entropy  $S_c$  of  $\Phi_{\rm M}$  with respect to  $\Phi_{\rm E}$ . Roughly speaking, this entropy represents the difference of information content between  $\Phi_{\rm M}$  and  $\Phi_{\rm E}[11, 12]$ . Note that  $S_{\rm c}$  vanishes if  $\Phi_{\rm E} = \Phi_{\rm M}$ . We compute this conditional entropy as a function of the mass ratio r between the transported particle and the solvent particles and conclude that the diffusion approximation is actually quite robust. For example, with a mass ratio  $r = 10^{-2}$  (Brownian particle only 100 times heavier than solvent particles), the conditional entropy  $S_c$  is as low as  $2.210^{-4}$ . As an application, we finally use the above material to prove that the diffusion approximation is valid in the mass ratio range for which the new, recently published [9, 10] corrections to the noise experienced by a particle diffusing in a temperature gradient are comparable to say, the thermophoresis force. This definitely confirms the physical relevance of these noise corrections and their importance in building realistic stochastic models of thermodiffusion.

## 2 The diffusion approximation: from kinetics to stochastics

Consider a solvent S made of particles of mass  $m_s$ , conveniently called Sparticles, in which particles of mass  $m_B$ , conveniently called Brownian or Bparticles, are transported by short-range interactions with the S-particles. We suppose that there are sufficiently few B-particles in S to neglect interactions between B-particles and between more than one B- and one S-particle at a time. All the properties of transport can then be recovered by studying the motion of a single, arbitrary *B*-particle and the statistical properties of this motion are entirely characterized by the solvent one-particle distribution and the law fixing the short-range interaction between a *B* and an *S*-particle. We neglect the internal structure of *B*-particles and assume that the short-range interaction between a *B*- and an *S*-particle can be modelled as an elastic collision between hard spheres and that the associated sphere radii are  $R_s$  and  $R_B$ .

In the above model, the trajectory of a *B*-particle is a succession of line segments started and ended by collisions with *S*-particles. At a fixed initial momentum  $\mathbf{p}$  of the *B*-particle before such a collision, the momentum loss  $\mathbf{q}$  of the *B*-particle during the collision is a random variable whose distribution depends on the collision cross-section and on the distribution of *S*-particles. Diffusions are by definition governed by Langevin-like equations (Ito processes [13]) and these are driven by Gaussian noises. Approximating the motion of a *B*-particle by a diffusion thus comes down to approximating, for each  $\mathbf{p}$ , the distribution of the momentum loss  $\mathbf{q}_B$  by a Gaussian. The law of a stochastic process defined by such a Langevin equation is described by a distribution function  $\Phi$  of the time t and of the position  $\mathbf{r}$  and velocity  $\mathbf{v}$  of a *B*-particle; this function obeys the Fokker-Planck equation [13, 1]:

$$\frac{\partial \Phi}{\partial t} + v^i \frac{\partial \Phi}{\partial r^i} = \frac{1}{m_{\scriptscriptstyle B}} \frac{\partial}{\partial v^i} \left( -F^i \Phi + \frac{1}{m_{\scriptscriptstyle B}} \frac{\partial}{\partial v^j} \left( D^{ij} \Phi \right) \right) \tag{1}$$

where **F** is the deterministic part of the force experienced by the *B*-particle, and D is the noise tensor. This force **F** and the noise tensor D can be computed from the expectation (mean value) of **q** and  $\mathbf{q} \otimes \mathbf{q}$  respectively[10]. This delivers:

$$\mathbf{F} = -\alpha_0(v) \mathbf{v}, \quad \text{and} \quad D = \sigma_0(v) \mathcal{E} + \sigma_2(v) \mathbf{v} \otimes \mathbf{v}$$
(2)

where  $\mathcal{E}$  is the (inverse) Euclidean metric tensor ( $\mathcal{E}^{ij} = 1$  if i = j and 0 otherwise). Naturally, all coefficients introduced above also depend on the temperature of the solvent, on the masses  $m_B$  and  $m_S$ , and on the characteristic radii  $R_B$  and  $R_S$ .

## 3 Expressions for the friction and noise coefficients

In what follows, the velocities and the momenta of both solvent particles (*S*-particles) and Brownian particles (*B*-particles) need to be considered. Thus, to avoid confusion, the subscript "*B*" is appended to all symbols related to Brownian particles. For example, the notation  $\mathbf{v}_B$  is used for the velocity of *B*-particles, instead of  $\mathbf{v}$  as in (2). Of course  $\mathbf{v}_S$  denotes the velocity of *S*-particles. The same convention applies to all kinetic variables introduced hereafter.

#### 3.1 Kinetic model for the solvent

If S is sufficiently dilute, all statistical properties of S-particles are encoded in the one-particle distribution function f. If one neglects the internal structure of S-particles, f is a time-dependent function of six real degrees of freedom (for example, three position coordinates and three velocity components) and this function obeys the standard Boltzmann equation:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f = 
\int d^3 v_1 \int |\mathbf{v} - \mathbf{v}_1| \Big( f(\mathbf{v}') f(\mathbf{v}'_1) - f(\mathbf{v}) f(\mathbf{v}_1) \Big) d\sigma_S$$
(3)

where usual notations have been used [8, 14]; in particular,  $\mathbf{v}'$  and  $\mathbf{v}'_1$  are the velocities of the particles which result from the collision of two particles with initial velocities  $\mathbf{v}$  and  $\mathbf{v}_1$ , and  $d\sigma_S$  is the differential cross-section characterizing the collisions between two *S*-particles.

The equilibrium solution of (3) is the standard Maxwell distribution :

$$f_e(\mathbf{v}_s) = \left(\frac{2\pi k_B T}{m_s}\right)^{-\frac{3}{2}} \exp\left(-\frac{m_s {v_s}^2}{2k_B T}\right),\tag{4}$$

where  $k_B T$  is the Boltzmann factor. We will suppose that (4) correctly describes the state of the solvent particles. This comes down to assuming that the presence of *B*-particles does not noticeably modify the the statistics of the incoming *S*particles.

#### **3.2** Collisions between Brownian and solvent particles

Exact analytical expressions for these coefficients can be derived by supposing that (i) the onteraction potential between B- and S particle has spherical symmetry (ii) the diffusion angle  $\alpha(b)$  depends only on the impact parameter b. Let  $\mu = (m_B^{-1} + m_S^{-1})^{-1}, u = \sqrt{\frac{m_S}{k_B T}}v$ , and  $\zeta(u)$  and  $\xi(u)$  be defined by (??). One finds :

• Friction coefficient :

$$\alpha_{0}(v) \equiv \tilde{\alpha}_{0}(u) =$$

$$\sqrt{\frac{2}{\pi}} K_{1} n_{s} \mu \sqrt{\frac{k_{B}T}{m_{s}}} \times$$

$$\left(\frac{-1+2u^{2}+u^{4}}{u^{2}} \zeta(u) + \frac{1+u^{2}}{u^{2}} \xi(u)\right),$$
(5)

• Noise coefficient:

$$\sigma_{0}(v) \equiv \tilde{\sigma}_{0}(u) = \sqrt{\frac{2}{\pi}} K_{1} n_{s} \mu^{2} \sqrt{\frac{k_{B}T}{m_{s}}^{3}} \frac{1}{3+\rho} \times \left( \frac{-\rho + (3+2\rho) u^{2} + (6+\rho) u^{4} + u^{6}}{u^{2}} \zeta(u) + \frac{\rho + (5+\rho) u^{2} + u^{4}}{u^{2}} \xi(u) \right),$$
(6)

• Second order noise coefficient :

$$\sigma_{2}(v) \equiv \tilde{\sigma}_{2}(u) = \sqrt{\frac{2}{\pi}} K_{1} n_{s} \mu^{2} \sqrt{\frac{k_{B}T}{m_{s}}} \frac{\rho}{3+\rho} \times \left(\frac{3-3u^{2}+3u^{4}+u^{6}}{u^{4}} \zeta(u) + \frac{-3+2u^{2}+u^{4}}{u^{4}} \xi(u)\right),$$
(7)

where the collision-dependent coefficients  $K_1$  and  $\rho$  are:

$$K_1 \equiv 2\pi \int_0^{+\infty} \left(1 + \cos \alpha(b)\right) b \,\mathrm{d}b \tag{8}$$

and:

$$\rho \equiv \frac{\int_{0}^{+\infty} \left(1 + 4\cos\alpha(b) + 3\cos^{2}\alpha(b)\right) b \,\mathrm{d}b}{\int_{0}^{+\infty} \sin^{2}\alpha(b) \,b \,\mathrm{d}b}.$$
(9)

For hard spheres,  $K_1 = \pi (R_B + R_S)^2$  and  $\rho = 3$ . Note that, for conciseness, the *B* subscripts have been omitted for the variables *u* and *v* in the above expressions.

# 4 Invariant measure of the diffusion process in velocity space

The density  $\Phi_{\rm E}$  of this invariant measure with respect to the Lebesgue measure  $d^3v$  obeys:

$$\frac{\partial}{\partial v^{i}} \left( -F^{i} \Phi_{\rm E} + \frac{1}{m_{\scriptscriptstyle B}} \frac{\partial}{\partial v^{j}} \left( D^{ij} \Phi_{\rm E} \right) \right) = 0.$$
 (10)



Figure 1: Invariant measure of the diffusion process for a mass ratio r = 0.01, as a function of the dimensionless velocity  $v/v_0$  with  $v_0 = \sqrt{k_B T/m_B}$  (solid curve). The corresponding Maxwellian distribution is plotted in dashed line. The scale of the vertical axis is arbitrary.

By isotropy, the solution of (10) can be expressed as a function the modulus v of the velocity:  $\Phi_{\rm E}(\mathbf{v}) = \phi(v)$ . Inserting this form into the above equation leads to:

$$A(v)\phi'(v) + B(v)\phi(v) = 0$$
(11)

where  $\phi'(v)$  stands for the derivative of  $\phi$  with respect to v. In (11), the coefficients A(v) and B(v) are:

$$A(v) = \alpha_0(v) + \frac{1}{m_B} \left( \frac{\sigma'_0(v)}{v} + v \sigma'_2(v) + 4\sigma_2(v) \right),$$
(12)

and

$$B(v) = \frac{1}{m_{\scriptscriptstyle B}} \left( \frac{\sigma_0(v)}{v} + v \sigma_2(v) \right). \tag{13}$$

The solution of (11) is:

$$\phi(v) = \phi_0 \exp\left[-\int_0^v \frac{A(\nu)}{B(\nu)} d\nu\right],\tag{14}$$

the constant  $\phi_0$  being determined by the normalization condition  $\int_0^{\infty} \phi(v) 4\pi v^2 dv = 1$ . The function  $\phi(v)$  can be determined numerically for all values of the mass ratio r; it is plotted in Figure 1 for hard-sphere collisions and r = 0.01 (Brownian particle 100 times heavier than solvent particles), together with the corresponding Maxwellian distribution.

#### 5 Conditional Entropy

The real, physically relevant equilibrium distribution of a *B*-particle in velocity space is not  $\Phi_{\rm E}$  but the standard Maxwell-Boltzmann distribution:

$$\Phi_{\rm M}(\mathbf{v}) = \left(\frac{2\pi k_B T}{m_B}\right)^{-\frac{3}{2}} \exp\left(-\frac{m_B v^2}{2k_B T}\right). \tag{15}$$

The conditional or Kullback entropy  $S_c [\Phi_{\rm M}/\Phi_{\rm E}]$  of  $\Phi_{\rm M}$  with respect to  $\Phi_{\rm E}$  is defined by the following relation[11, 12]:

$$S_{c}\left[\Phi_{\rm M}/\Phi_{\rm E}\right] \equiv \int_{\mathbb{R}^{3}} \Phi_{\rm M}(\mathbf{v}) \ln\left(\frac{\Phi_{\rm M}(\mathbf{v})}{\Phi_{\rm E}(\mathbf{v})}\right) d^{3}v.$$
(16)

Roughly speaking, this entropy measures the difference of information content between  $\Phi_{\rm M}$  and  $\Phi_{\rm E}$  and it can serve as a quantitative estimate of the error made in approximating the real transport by a diffusion process. Indeed, if both distributions are close to each other, say symbolically  $\Phi_{\rm E}(\mathbf{v}) = \Phi_{\rm M}(\mathbf{v})(1 + \epsilon(\mathbf{v}))$ with  $\epsilon \ll 1$ , then

$$S_c \left[ \Phi_{\rm M} / \Phi_{\rm E} \right] \simeq \int_{\mathbb{R}^3} \Phi_{\rm M}(\mathbf{v}) \ \frac{(\epsilon(\mathbf{v}))^2}{2} d^3 v \tag{17}$$

and the conditional entropy then measures the mean value or average of the squared discrepancy between the  $\Phi_{\rm E}$  and  $\Phi_{\rm M}^{-1}$ . Thus, the smaller the conditional entropy, the better the diffusion approximation. Note that the definition of the conditional entropy  $S_c [\Phi_{\rm M}/\Phi_{\rm E}]$  is asymmetrical between  $\Phi_{\rm E}$  and  $\Phi_{\rm M}$  and that  $S_c [\Phi_{\rm M}/\Phi_{\rm E}]$  makes more physical sense than  $S_c [\Phi_{\rm M}/\Phi_{\rm E}]$  because it makes more sense to compute the above average by using the true equilibrium measure  $\Phi_{\rm M} d^3 v$  rather than the approximation  $\Phi_{\rm E} d^3 v$ .

The conditional entropy  $S_c [\Phi_{\rm M}/\Phi_{\rm E}]$  is a function of the mass ratio r only (no dependence on the temperature) and is plotted in Figure 2 for hard-sphere collisions. Moreover, using Equations (14) to (16), it is possible to show that for small mass ratios,  $S_c [\Phi_{\rm M}/\Phi_{\rm E}]$  scales as the square of the mass ratio, and to derive the following asymptotic expression for the conditional entropy:

$$S_c \left[ \Phi_{\rm M} / \Phi_{\rm E} \right] \simeq \frac{27(1+\rho)^2}{5(3+\rho)^2} r^2, \qquad \text{when } r << 1.$$
 (18)

In the hard sphere case,  $\rho = 3$  and thus,  $S_c \left[\Phi_M / \Phi_E\right] \simeq \frac{12}{5}r^2$ . On Figure 2, this asymptotic behavior is plotted as a dashed line.

Historically, the Langevin approach has been introduced to model the random motion of small but macroscopic particles. The resulting mass ratios were thus extremely small (lower than  $10^{-8}$ ). However, the scaling law (??) shows that this stochastic approach seems to be robust, and that its application range spreads over a much wider domain of mass ratios. For example, with a mass

 $<sup>^1 {\</sup>rm The}$  first order tem in  $\epsilon$  vanishes because both because  $\Phi_{\rm E}$  and  $\Phi_{\rm M}$  are normed to unity.



**Figure 2**: Conditional entropy  $S_c [\Phi_M/\Phi_E]$  of  $\Phi_M$  with respect to  $\Phi_E$ , as a function of the mass ratio  $r = m_s/m_B$ . The dashed line is the asymptotic behavior for small values of the mass ratio:  $S_c [\Phi_M/\Phi_E] \simeq \frac{12}{5} r^2$ 

ratio as high as r = 0.01 (Brownian particles only 100 times heavier than solvent particles), the conditional entropy  $S_c \left[\Phi_{\rm M}/\Phi_{\rm E}\right]$  is as low as  $2.2 \, 10^{-4}$ .

But Figure 2 also displays the breakdown of the diffusion approximation. Indeed, a mass ratio of r = 1 leads to a conditional entropy of order 0.3, which means that, for this mass ratio,  $\Phi_{\rm M}/\Phi_{\rm E}$  is of order 1.3 when v stays inside the central peak of the Gaussian  $\Phi_{\rm M}$ ; the corresponding mean relative difference between  $\Phi_{\rm M}$  and  $\Phi_{\rm E}$  is thus around 30%.

#### 6 New stochastic models for thermodiffusion

Thermodiffusion [17, 18] is diffusion induced by temperature gradients. Earlier stochastic models [19, 20] take these gradients into account by adding a single, deterministic term to the Langevin equation of motion; this term is called the thermophoresis force and is proportional to the temperature gradient. It has been argued recently [9, 10] that such models are incomplete, and that a temperature gradient not only introduces a thermophoresis term, but also modifies the friction term and the noise tensor. These modifications can be computed explicitly if the, as already assumed, the collisions between B- and S-particles exhibit shperical symmetry and if the diffusion angle depends only on the impact parameter. The deterministic force  $\mathbf{F}$  and the noise tensor D then take the form :

$$\mathbf{F} = \kappa(v)\nabla T - \left(\alpha_0(v) + \alpha_1(v)\,\mathbf{v}\cdot\nabla T\right)\mathbf{v},\tag{19}$$

and

$$D = \left(\sigma_0(v) + \sigma_1(v) \mathbf{v} \cdot \nabla T\right) \mathcal{E} + \left(\sigma_2(v) + \sigma_3(v) \mathbf{v}_B \cdot \nabla T\right) \mathbf{v} \otimes \mathbf{v} + \sigma_4(v) \frac{\mathbf{v} \otimes \nabla T + \nabla T \otimes \mathbf{v}}{2}$$
(20)

In addition to the usual thermophoresis coefficient  $\kappa(v)$ , these expressions for **F** and *D* involve four new coefficients:  $\alpha_1(v)$ ,  $\sigma_1(v)$ ,  $\sigma_3(v)$ , and  $\sigma_4(v)$  to account for the modifications of the friction term and of the noise term induced by a temperature gradient. Analytical expressions for these new coefficients in the hard-sphere collision case can be found in [10].

An important question is: are these new terms comparable to the well known thermophoresis term? In the limit of very low mass ratios (Brownian particles much heavier than solvent particles), all these new effects become negligible. However, for intermediate mass ratios, the new terms have noticeable contributions, especially the  $\sigma_4$  term (see [10]). For example, when the mass ratio r ranges from  $10^{-2}$  to  $10^{-1}$ , the relative effect of the  $\sigma_4$  term, compared to the usual thermophoresis term, ranges from 0.29 to 2.8, which is far from being negligible. In this range of mass ratios, the conditional entropy  $S_c [\Phi_M/\Phi_E]$  varies from  $2.2 \, 10^{-4}$  to  $1.3 \, 10^{-2}$ . Thus, modelling thermodiffusion with stochastic processes definitely makes sense in this range of mass ratios, and it does require the introduction of the new terms introduced in [9, 10].

#### 7 Conclusion

#### 7.1 Summary

In this article, we have suggested that the validity of the diffusion approximation can be measured quantitatively by the conditional entropy of the physically correct equilibrium distribution  $\Phi_{\rm M}$  with respect to the spurious distribution  $\Phi_{\rm E}$ predicted by the approximation. The smaller this entropy, the better the approximation. This entropy has been computed for spherically symetric collisions models (including hard sphere collisions) as a function of the mass ratio between the transported particle and the solvent particles. The main conclusion is that the diffusion approximation is actually quite robust; for example, assuming hard sphere collisions, a mass ratio of 0.01 corresponds to a conditional entropy of  $2.2 \, 10^{-4}$ . FInally, this entropic measure has also been used to validate the physical relevance of new correction terms recently derived in stochastic models of the Soret effect[9, 10].

#### 7.2 Discussion

Let us now discuss the various approaches to the diffusion approximation that can be found in the physics literature on particle transport and how these articulate with each other and with the material presented in this article. Particle transport is usually modelled, either by differential or integro-differential kinetic equations [27, 26], or by stochastic processes [11, 1]. The Boltzmann integro-differential equation [14] is considered to be the most precise transport model. The diffusion approximation replaces this equation, for particle transport, by a substantially simpler, differential equation called a Kolmogorov or Fokker-Planck equation [13]. This is done [8] by expanding the collision kernel in the Boltzmann model, assuming that, statistically, the momentum of the diffusion particle does not change substantially during one collision. This is true only if the mass of the diffusing particle (*B*-particle) is much larger than the mass of the particles with (*S*-particles). This is the validity condition of the diffusion approximation.

Consider now [25] a *B*-particle and follow its motion over a time interval  $\Delta t$ during which it undergoes  $N_c$  collisions. Let **p** be the initial momentum of this *B*-particle in the rest frame of the solvent and let  $\Delta \mathbf{p}_1, ..., \Delta \mathbf{p}_{N_c}$  be the momentum changes of the diffusing particle during the  $N_c$  collisions. By Boltzmann 'Stosszahl Ansatz' [14], all these collisions are statistically independent. The law of collision k depends on the momentum  $\mathbf{p} + \sum_{i=1}^{k-1} \Delta \mathbf{p}_i$  of the diffusing particle just before this collision. However, if  $\mathbf{p} \neq 0$ , all relative momentum changes  $\Delta \mathbf{p}_i \mid / \mid \mathbf{p} \mid$  tend to zero as the mass ratio between the diffusing particles and the fluid particles tends to infinity. Since the total number of collisions  $N_c$ remains bounded in this limit, all individual collisions then have the same law, which is fixed by  $\Delta t$  and **p**; note that the total number  $N_c$  of collisions then depends only on  $\Delta t$  and **p**. If  $N_c(\Delta t, \mathbf{p})$  is large enough, the *total* momentum change  $\Delta \mathbf{p} = \sum_{i=1}^{N_c} \Delta \mathbf{p}_i$  during  $\Delta t$  is then the sum of a large number of identically distributed independent random variables; by the central limit theorem [28], the law of  $\Delta \mathbf{p}$  is then approximately Gaussian. Of course, this approach is only consistent if the mean value of  $\Delta \mathbf{p}^2$  is much smaller than the mean value of  $\mathbf{p}^2$  for most statistically relevant values of  $\mathbf{p}$ . The motion of the diffusing particle can then be approximated, over time intervals much larger than  $\Delta t$ , by a stochastic process driven by a Gaussian white noise [25] *i.e.* an Itô process.

Note that the above reasoning clearly shows that the noise coefficient then generally depends on the momentum  $\mathbf{p}$ . By the fluctuation-dissipation theorem [8, 25], so does the friction coefficient. If the mass ratio between the *B*-particle and the *S*-particles is not much greater than unity the relative momentum change during one collision cannot be *a priori* neglected and the whole above argument collapses. Modelling the stochastic force acting on the diffusing particle by a Gaussian white noise then becomes an assumption.

#### 7.3 Future developments

Let us conclude by listing a few natural extensions to this work. One should first extend all computations to collision models more general than those investigated in this first publication; this can only be carried out numerically. One should also investigate if the validity of the diffusion approximation can be quantitatively assessed by other measures than equilibrium conditional entropies and, if that is the case, how these measures compare with each other. The material presented in this article should also be extended to deal with situations where the basic kinetic model is more general than the Boltzmann one. Finally, assessing the validity of the diffusion approximation is also important in the relativistic regime, to deal for example with runaway electrons[21, 22] and transport in both astrophysical and non astrophysical plasmas[23, 24].

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