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Particles dispersed in a dilute gas: Limits of validity of the Langevin equation

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Abstract

The problem of the limits of validity of the Langevin equation is considered in detail in the case of (microscopic) test-particles in very dilute gases. It is shown that, in this case, the current Langevin equation follows from the Newton's law in an exact way only in the Maxwell test-particle–gas-particle interaction model, and in an approximate way only in the Rayleigh-gas limit and in the low-velocity limit, while in any other interaction model, or limit, only a Langevin-like equation with speed-dependent friction coefficient and speed-dependent fluctuating force can be written. Such a circumstance, although probably limited to the particular physical situation considered in this paper, suggests that, in general, some preliminary, specific check of the validity of the Langevin equation should be performed before using the said equation to interpret laboratory experiments.
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1. Introduction

As is well known, the motion of a large (Brownian) particle (of mass m and velocity $\vec{v}$) in a fluid is usually described through the Langevin equation [1–5]

$$m\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = -m\lambda\vec{v} + \vec{L}(t). \tag{1}$$

When writing this equation one *assumes* that the particle in the fluid is subject to

(i) a systematic drag force $-m\lambda\vec{v}$ (λ being the friction coefficient), representing the average force exerted by the fluid on the Brownian particle,
(ii) a residual rapidly fluctuating force $\vec{L}(t)$ (whose average $\langle\vec{L}(t)\rangle$ is zero) which is again due to the collisions of the Brownian particle with the (much smaller) particles of the fluid.

The use of Eq. (1) has been successful [1–5] in describing the characteristics of the motion (diffusion) of Brownian particles in liquids (or dense gases) when one also *assumes* that the macroscopic Stokes' law also applies to microscopic Brownian particles in fluids, i.e. when one takes

$$\lambda = \frac{6\pi\eta\mathscr{R}}{m}, \tag{2}$$

where η is the viscosity coefficient of the fluid and $\mathscr{R}$ is the "hydrodynamic radius" of the Brownian particle [i.e. the radius able to make the macroscopic Stokes' law valid on the microscopic (or mesoscopic) scale, in the hydrodynamic regime].

Recently, the Langevin equation has been used [6] to build up a Fokker–Planck kinetic equation which is hoped to successfully interpret the phenomena occurring when large, heavy particles move in a gas in any regime. More in general, the Langevin equation (1) constitutes the starting point from which, by extension or analogy, many other Langevin equations have been (and are currently) written to study a number of phenomena (such as, Brownian motion of a harmonic oscillator, rotational Brownian

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motion with application to the theory of dielectric and magnetic relaxation, inertial effects in orientational relaxation of Brownian particles in liquids, etc.; see Ref. [5]). Thus, the approach based on the Langevin equation (1) has become in the last decades the prototype of a very general method to tackle the study of mechanical systems undergoing fluctuations and, consequently, a useful tool to interpret a number of possible, related experiments.

In spite of this, the problem of the limits of validity of the Langevin equation (1) does not seem to have been, until now, satisfactorily solved. This problem primarily concerns the *actual* possibility of writing the Langevin equation (1), in an exact (or approximate) way, *in ideal or real cases*.

It must be recalled in this regard that papers exist [7,8] where the problem of the derivation of the Langevin equation for a *heavy* particle (of mass m) in a fluid of particles of mass $M \ll m$ is considered. In such papers, equations of motion for the heavy particle are obtained by projection-operator techniques, and their reduction to the Langevin equation is subsequently discussed. These papers are very interesting since they attempt to derive the Langevin equation in the most complicated, general case in which a heavy particle simultaneously interacts with all the (mutually interacting) particles of the fluid. But, in these papers, additional (even if seemingly plausible) assumptions are introduced, and averaging criteria are employed which seem to require an adequate discussion.

It must also be said that the problem of the derivation of the Langevin equation has been also tackled by elementary methods considering very simplified physical situations. So, the unidimensional motion of a heavy particle in a gas of much lighter particles has been investigated [9,10], but the results and the conclusions so achieved strictly refer only to the particular situations considered in such studies (constant collision cross section [9], or constant mean free time between collisions [10]). In fact, in Ref. [9] it is shown that (according to the current belief) the drag force is due to the difference between the numbers of collisions (per unit time) suffered by the heavy particle in front and from behind. But in Ref. [10] such collision frequencies are always equal and nevertheless the drag force exists. Consequently, no general information on the drag force can be deduced from such studies, and the results and conclusions both of Ref. [9] and of Ref. [10] cannot be automatically applied to different situations, even in the simple unidimensional case.

For all the above reasons, the general problem of the derivation of the Langevin equation must be carefully re-examined in order to clarify the questions which can be raised when trying to write the Langevin equation (1).

In effect, the comparison between the most significant articles and books on the Brownian motion and on the Langevin equation, makes particularly evident the fact that some crucial questions relevant to the Langevin equation are still unclear. In fact, one immediately sees that the hypotheses made on the fluctuating force $\vec{L}(t)$ by the different authors are not always the same, and that no well-established, convincing criterion to average such force exists. So, for instance, one can find papers (as Ref. [5]) in which $\vec{L}$ is explicitly assumed to be independent of the Brownian-particle position $\vec{r}$, but no hypothesis is made on the possible dependence (of $\vec{L}$) on $\vec{v}$. Analogously, there are papers (as Ref. [3]) where $\vec{L}$ is assumed independent of $\vec{v}$, but no justification of this assumption is given, and nothing is said about a possible dependence (of $\vec{L}$) on $\vec{r}$. Rather curiously, however, the results derived from the Langevin equation in Ref. [3] imply that, in such paper, $\vec{L}$ is always taken, in practice, function of time t, but independent of both $\vec{r}$ and $\vec{v}$. This choice constitutes in effect the *tacit*, usual assumption of the most part of the papers on the subject, and this justifies the current notation $\vec{L}(t)$ (or any other equivalent notation) in the literature. But, as far as we know, the problem of the possible dependence of $\vec{L}$ on $\vec{r}$ and $\vec{v}$ has been examined only in a particular case [6].

We believe, therefore, that a discussion on the validity of the assumptions involved in the derivation of the Langevin equation, as well as on the correctness of the method followed, would be desirable.

To this end it is necessary, in our opinion, to start from Newton's law and to build up, first of all, in specific cases, the statistical procedure able to yield the drag force exerted by the fluid on the considered particle. Only when this drag force is found to have the linear form $-m\lambda\vec{v}$, and the fluctuating force can actually be deemed to depend only on t, the Langevin equation (1) can really be written, and the statistical averages which have been used to arrive at such a drag force are obviously (and *necessarily*) just the averages which have to be employed for averaging $\vec{L}$. From a study of this type it will also be possible to verify if the hypotheses currently made on $\vec{L}$ are acceptable.

Of course, the greatest success of the proposed method would be the theoretical verification of the validity of the Stokes' law on the microscopic scale so that also the correctness of the current use of Stokes' law for Brownian particles in a dense fluid could be tested. However, the solution of this difficult, still debated problem (see, for instance Ref. [11]) does not constitute the subject of the present paper. To our purposes, we prefer to consider here the case of (microscopic) "test-particles" dilutely dispersed in a very dilute gas. In such case

(i) the test-particles practically collide only with the gas-particles,
(ii) the test-particle–gas-particle collisions (as well as the gas-particle–gas-particle collisions) are binary,
(iii) the gas-particle mean free path and the test-particle mean free path are much larger than the sizes of both types of particles, and
(iv) re-collision processes are practically absent.

In these conditions we are allowed to assume, in accordance with the current kinetic theory of particle swarms in gases [12], that the background gas (even around the test-

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