Diffusion of Metallic Nanoparticles in Viscous Medium

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Abstract . We analyzed diffusion of metallic nanoparticles in a viscous plastic medium submitted to stochastic, buoyancy and electric forces. Are determined necessary conditions to have only stochastic diffusion process.

Key words: *nanoparticles diffusion; viscous, electric and gravitational forces.***.**

(1)Diffusion equation for particles in viscous medium.

Let us consider metallic nanoparticles in a viscous medium submitted to stochastic and gravitational buoyancy forces and to an uniform static electric field $\mathbf{E_o}$. In these conditions these particles obey the following equation of motion:

$$mdv/dt = F_{stochastic} + F_b + F_E \qquad (1.1),$$

where $F_{stochastic} = - 6\pi\eta Rv + \xi(t)$, is the stochastic force,[1-3]

$F_b = (4\pi R^3/3)\{\rho_p - \rho_M\}g$ is the buoyancy force,[4]

where η is the medium viscosity coefficient, m, R and v are, respectively, the mass, radius and velocity of the particle; ρ_p and ρ_M are, respectively, the densities of the particle and of the medium and g the gravitational acceleration. F_E is the electric force (see **Appendix A)** given by,

F_E = force of $\mathbf{E_o}$ on the dipole moment **d** + interaction force between dipoles,

where $\mathbf{E_o}$ is the applied external electrical field.

(2)Stochastic Diffusion.

As well known[1-3] ***stochastic diffusion*** occurs when,

$$mdv/dt = - 6\pi\eta Rv + \xi(t) \qquad (2.1),$$

that is, only when

$$6\pi\eta Rv >> F_b \quad \text{and} \quad 6\pi\eta Rv >> F_E.$$

Solving **Eq.(2.1),** remembering that v = dx/dt, the *variance* of the particle, $\delta^2 = (< x^2 > - < x >)^2$, is given by[1-3]

$$\delta^2 = 2Dt \qquad \text{where}$$

$$D = k_BT/6\pi\eta R \qquad (2.2)$$

is the *diffusion coefficient*, k_B the Boltzmann constant and T the absolute temperature of the viscous medium.

In the **Appendix A** is shown that for small applied electric field $\mathbf{E_o}$, that is, when we can put $F_\mathbf{E} = 0$, we have only *stochastic diffusion* if the condition

$$6\pi\eta Rv^* >> (4\pi R^3/3)\{\rho_p - \rho_M\}g \qquad (2.3),$$

is satisfied, that is, when

$$\eta >> (2R^2/9v^*)\{\rho_p - \rho_M\}g \qquad (2.4),$$

where $v^* = (8k_BT/\pi m)^{1/2}$ is the average velocity of the particles, k_B the Boltzmann constant, T the temperature of the medium and $m = (4\pi R^3/3)\rho_p$.

(3)Example of stochastic diffusion.

Let us study the particular case of metallic nanoparticles with radius $R \approx 10^{-9}$m and density $\rho_p \approx 10^4$ Kg/m^3 immersed in a dielectric medium at $T \approx 300^o$ K with viscosity $\eta \approx 10^{10}$ MKS and density $\rho_M \approx 10^3$ Kg/m^3. In these conditions $m \approx 10^{-22}$ Kg and $v^* \approx 10^2$ m/s.

Using **Eq.(1.1)** we see that, in the MKS system,

$$F_{viscous} = 6\pi\eta Rv \approx 10^4 \text{ N} \quad \text{and} \quad F_b = (4\pi R^3/3)\{\rho_{np} - \rho_M\}g \approx 10^{-21} \text{ N},$$

that is

$$F_{viscous} >> F_b \qquad (3.1).$$

So, if the composite is submitted to small electric fields, electric forces effects can be neglected (see **Appendix A**). In this way, particle diffusion is **stochastic** and δ^2 will be given by the **Eq.(2.2)**:

$$\delta^2 = 2Dt \quad \text{where} \quad D = k_BT/6\pi\eta R \approx 10^{-19} \text{ cm}^2/\text{s}.$$

In **Appendix B** is seen a particular case of **Eq.(1.7)** when the *viscous force* is very large and the *mass* is very small when Eq.(1.7) would be written as

$$6\pi\eta R\,(dx/dt) \approx F + \xi(t). \qquad (3.2).$$

In this case is possible to have, simultaneously, diffusion and "drift" of the particles.[1-3]

APPENDIX A.

Metallic Sphere submitted to an uniform electric field $\mathbf{E_o}$.

Let us consider a conducting sphere, where a = R, submitted to an uniform electric field $\mathbf{E_o}$ as seen in **Figure 1.**

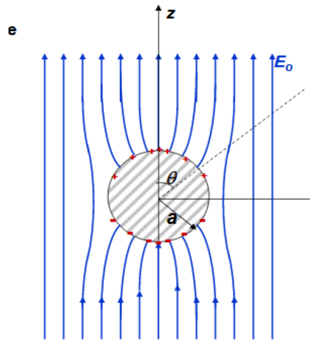

Figure 1. Metallic sphere submitted to an uniform electric field $\mathbf{E_o}$.[5,6]

On the spherical surface is induced a charge density σ(θ) given by[5,6]

$$\sigma(\theta) = 3\varepsilon\, E_o \cos\theta \qquad \text{(A.1)},$$

where ε is the dielectric constant of the medium. The induced charges Q_+ and Q^- on the upper and lower polar surfaces, respectively, are given by,

$$Q \approx 2\pi R^2 < \sigma(\theta) > \approx 12\varepsilon E_o R^2 \qquad \text{(A.2)}.$$

So, each sphere would have an electric dipole $d_p \approx QR$.[7] Of course, the resultant force of the uniform field $\mathbf{E}_o$ on the + and - charges of the molecules will be zero. Remains now to calculate the force between the metallic particles due interactions between their induced dipoles.

So, if ℓ is the average distance between two particles, there is dipole-dipole electric potential between them, given by $U_{dd}(\ell) \approx d_p^2/\ell^3$ [6]. This potential would be responsible to an electric force $F_{dd}(\ell)$ between them given by,

$$F_{dd}(\ell) \approx dU_{dd}(\ell)/d\ell = -\, 3d_p^2/\ell^4 \qquad \text{(A.4)},$$

where $$d_p = QR \approx 12\varepsilon E_o R^3 \qquad \text{(A.5)}.$$

So, for usually small E_o fields, $R \sim 10^{-7}$ cm and $\ell \geq 10^{-7}$ cm the *electrostriction forces* $F_{dd}(\ell) \sim 144(\varepsilon E_o)^2 R^6/\ell^4$ are negligible.

APPENDIX B.

Fokker-Planck equation: diffusion and drift.

When the *viscous force* is very large and the *mass* is very small Eq.(1.7) would be written as

$$dx/dt \approx f(x) + \zeta(t) \quad \text{(B.1)},$$

where $f(x) = F/\alpha$, $\zeta(t) = \xi(t)/\alpha$ and $\alpha = 6\pi\eta R$.

Associated with **Eq.(B.1)** we have the Fokker-Planck equation,[1]

$$\partial P(x,t)/\partial t = -\partial[f(x)P(x,t)]/\partial x + (\Gamma/2)\partial^2 P(x,t)/\partial t^2 \quad \text{(B.2)},$$

that gives the temporal evolution of the probability density P(x,t) that represents the distribution probabilities of the stochastic variable x obtained solving Eq.(B.1). The factor Γ is given by $< \zeta(t)\xi(t') > = \Gamma\ \delta(t-t')$.

When f(x) = constant = c, solving Eq.(B.2), we have[1]

$$P(x,t) = (1/2\pi\Gamma t)^{1/2} \exp\{-(x - x_o - ct)^2/2\Gamma t\} \quad \text{(B.3)}.$$

In reference [1] are shown figures of the distribution probabilities P(x,t) as functions of the time t for the Brownian motion in the cases (a)symmetric (c = 0) and (b) asymmetric with "drift" at right (c > 0).

From these figures we verify that when c = o there is only the diffusive process described by $\delta(t) = (2\Gamma t)^{1/2}$. On the other hand when $c \neq 0$ there is, simultaneously, diffusion and "drift" of particles, with velocity c, induced by the external force F.

Acknowledgements.

The author thanks the librarian Maria de Fatima A. Souza and the administrative technician Tiago B. Alonso for their invaluable assistances in the publication of this paper

REFERENCES

[1]T.Tânia and M.J.de Oliveira. "Stochastic Dynamics and Irreversibility." Springer(2015).
[2]M.Cattani and M.C.Salvadori "Diffusion Process and Brownian Motion"
http://publica-sbi.if.usp.br/PDFs/pd1714.pdf
https://zenodo.org/record/3435003
[3]Brownian Motion. https://en.wikipedia.org/wiki/Brownian_motion
[4]K.R.Symon."Classical Mechanics".Addison-Wesley Publishing Company(1953).
[5]https://courses.cit.cornell.edu/ece303/Lectures/lecture8.pdf
[6]J.D.Jackson."Classical Electrodynamics".John Wiley&Sons(1962).
[7]F.W.Sears. Magnetismo e Eletricidade. LTC (RJ).(1956).