Thermo-kinetic approach of single-particles and clusters involving anomalous diffusion under viscoelastic response

I. Santamaría-Holek*, J. M. Rubí†, A. Gadomski‡

*Facultad de Ciencias, Universidad Nacional Autónoma de México.

Circuito exterior de Ciudad Universitaria. 04510, México D. F., México

†Facultat de Física, Universitat de Barcelona.

Av. Diagonal 647, 08028, Barcelona, Spain and

‡Institute of Mathematics and Physics,

University of Technology and Natural Sciences,

Kaliskiego 7, 85-796 Bydgoszcz, Poland

ABSTRACT

We present a thermo-kinetic description of anomalous diffusion of single-particles and clusters in a viscoelastic medium in terms of a non-Markovian diffusion equation involving memory functions. The scaling behaviour of these functions is analyzed by considering hydrodynamics and cluster-size space random walk arguments. We explain experimental results on diffusion of Brownian particles in the cytoskeleton, in cluster-cluster aggregation and in a suspension of micelles.

Keywords: Microrheology,Cytoskeleton,Brownian motion,Non-Markovian,Memory functions.

I. INTRODUCTION

Diffusion is an irreversible phenomenon which arises in systems of different natures. The understanding of the mechanisms intrinsic to this process remains an open question in cases where the host liquid displays a variety of time and length scales. Such cases include diffusion in slow relaxation systems [1, 2, 3, 4], in viscoelastic media [5, 6, 7, 8] or in the presence of soft matter aggregations [2, 3, 9, 10, 11, 12]. To find out the peculiar behaviour of the mean square displacement (MSD) of the particles observed in these situations is a theme of vital importance in areas such as soft condensed matter, biophysics and material science.

The properties of viscoelastic fluids can be characterized through microrheological experiments in which the MSD of passively diffusing particles is measured [4, 5, 7]. For example, it has been shown both experimentally [4] and theoretically [8] that the MSD of a probe particle moving through a medium made up of a solution of F-actin networks obeys a power law, with an exponent depending on the aspect ratio between the particle radius and the characteristic length of the polymer network. Similar results for the MSD have also been obtained in the case of living cells [6] and then used to explain the viscoelastic properties of the intracellular medium. This explanation is usually given in terms of the single-point generalized Stokes-Einstein relation in the frequency domain [6, 13, 14, 15]. The viscoelastic and non-Newtonian properties are modified when the system is subjected to shear stresses or temperature gradients [16], and to geometrical confinement [2, 17] in which the finite size of the particles may also play an important role in the dynamics of the system [8, 18].

Matter aggregation phenomena in viscoelastic environments show up many other interesting features both at molecular as well as supramolecular or mesoscopic levels of organization [10, 19, 20]. Although the molecular level is by now thoroughly accessible through modern

experimental techniques and computer simulations, its mesoscopic counterpart lends itself readily amenable to theoretical modeling, regardless of whether the process under study reflects subdiffusive or superdiffusive dynamic properties [8, 15]. As for the former, one could mention formations of networks and gels [10, 21], viscoelastic phase separation [12, 22] as well as formations of biomembranes and/or soft biomaterials [9]. As for the latter, one could point out colloidal and protein systems in which nucleation-growth phase transformations often lead to a global superdiffusive behavior, especially when formation of non-Kossel protein crystals or colloidal crystals comes into play [18, 23]. In such systems, finiteness [8, 18] and mass flucutations [24] of the basic constituent (a large Brownian-type particle, or a cluster of smaller particles) as well as some detected viscoelastic response of the system upon aggregation are of prior significance and point undoubtedly to more realistic descriptions.

In this paper, we propose a thermo-kinetic framework based on mesoscopic nonequilibrium thermodynamics [19] giving a coarse-grained description of the anomalous transport of particles and their clusters in a viscoelastic medium through a non-Markovian diffusion equation, engaging thoroughly the slowest dynamic variable termed the reaction coordinate [20]. This equation is derived under the assumption of a non-instantaneous response of the system in which transport coefficients become memory functions [25, 26, 27]. These coefficients are introduced into the description through the expression of the probability current obtained from the entropy production equation [19, 20].

The paper is organized as follows. In section **II** we will derive the non-Markovian diffusion equation accounting for the dynamics of the particles in a viscoelastic medium. In Sec. **III** we will analyze the scaling of the memory function in a polymer solution and in Sec. **IV** we will analyze the scaling of the MSD in cluster-cluster aggregation. Section **V** will be devoted to comparing theory with experiments and Sec. **VI** to discussion and summary of

our main results.

II. THE NON-MARKOVIAN DIFFUSION EQUATION

Let us consider the Brownian motion of a particle through a viscoelastic medium such as a polymer melt in which the macromolecules are distributed as to form a network which exerts elastic forces on the particle [5, 6, 7]. In general, the medium may also involve dynamical processes associated with changes in the conformation and the growth of its costitutents as is the case of the polymerization of microtubules or the aggregation and crystallization of lipids and proteins [6, 9, 10, 23]. For simplicity we will obtain the properties of this viscoelastic heat bath under an effective medium approximation [5, 8].

The dynamics of the particle can be described [19, 20, 28] by means of the probability density $\rho(\mathbf{r},t)$ depending on its position $\mathbf{r}$ and time t. Since ρ is normalized to the unity it obeys the continuity equation

$$\frac{\partial}{\partial t}\rho = -\nabla\cdot\mathbf{J}, \tag{1}$$

where $\nabla = \frac{\partial}{\partial \mathbf{r}}$. The explicit form of the diffusion current $\mathbf{J}$ can be inferred from the entropy production of the diffusion process. This quantity can be obtained from the nonequilibrium entropy [19, 20, 28]

$$s(t) = -k_B \int \rho(\mathbf{r},t)\ln\frac{\rho}{\rho_{le}}d\mathbf{r} + s_{le}, \tag{2}$$

where k_B is Boltzmann's constant and s_{le} its value at the reference local equilibrium state characterized by the probability density

$$\rho_{le}(\mathbf{r}) = e^{\frac{1}{k_B T}[\mu_{le}-\phi_T]}. \tag{3}$$

Here μ_{le} is the corresponding chemical potential and $\phi_T(\mathbf{r})$ the interaction potential which contains two contributions: ϕ_e related to the potential energy of the external forces and

$\phi_B(\mathbf{r})$ resulting from the interactions between the particle and the viscoelastic medium.

By taking the time derivative of Eq. (2), using (1) and integrating by parts we obtain the entropy production

$$\sigma = -\frac{1}{T}\int \mathbf{J}\cdot\nabla\mu\, d\mathbf{r}, \tag{4}$$

where we have defined the nonequilibrium chemical potential: $\mu(\mathbf{r},t) = k_BT\ln\rho/\rho_{le} + \mu_{le}$. A similar type of chemical potential was obtained during a structural transition of mono-olein bicontinuous cubic phase induced by inclusion of protein lysozyme solutions, cf. Ref. [29]. In this case, the ratio of nonequilibrium and equilibrium densities ρ/ρ_{le} is interpreted as a confinement factor which corresponds to the ratio of the volume of water channels, v_w, and the volume available for the center of lysozyme molecules v_a, namely v_w/v_a, cf. Table II and Eq. (9) therein. The structural frustration is caused by a moderate attraction of the lysozyme molecules mediated by the lipid system [9], and can be attributed to a (viscoelastic) phase separation [12].

Following now the scheme of nonequilibrium thermodynamics [28], we may establish a relationship between the probability current $\mathbf{J}$ and its conjugated force $\nabla\mu$. Taking into account that in a viscoelastic medium the response of the system is, in general, not instantaneous [25] we obtain

$$\mathbf{J}(\mathbf{r},t) = -\int_0^t \zeta(t-t')\rho(\mathbf{r},t')\left(\nabla\phi_T + k_BT\nabla\ln\rho(\mathbf{r},t')\right)dt', \tag{5}$$

where we have used the explicit expression of ρ_{leq} and introduced the memory function $\zeta(t-t')$. Notice that in the case of non-isotropic systems $\zeta(t-t')$ becomes a tensor.

After substituting Eq. (5) into (1), one obtains the non-Markovian diffusion equation

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} = \int_0^t \zeta(t-t')\nabla\cdot\left[\rho(\mathbf{r},t')\nabla\phi_T\right]dt' + \int_0^t D(t-t')\nabla^2\rho(\mathbf{r},t')dt', \tag{6}$$

where we have defined the memory function $D(t) = k_B T \zeta(t)$. The first term on the right-hand side of Eq. (6) contains the force exerted by the viscoelastic medium on the particle. In the case of diffusion in an intracellular medium, there may be elastic forces arising from the polymer network and the forces due to the activity of molecular motors [4, 18, 30]. In the case of diffusion-limited growth processes [9], these forces could also be of an elastic nature or be related to the presence of electrostatic fields [18, 23]. The diffusion coefficient obeys the Stokes-Einstein law

$$D(\omega) = k_B T \beta^{-1}(\omega), \tag{7}$$

where $\beta(\omega) = 6\pi a \eta(\omega)$ is the friction coefficient containing the radius a of the particle and the frequency-dependent viscosity $\eta(\omega)$, [15, 31]. The memory function $\zeta(t)$ and $\beta(\omega)$ are related through the inverse Laplace transform: $\zeta(t) = \pounds^{-1}\left[\beta^{-1}(\omega)\right]$. Equation (6) is similar to the ones previously derived in the context of the continuous-time random walk formalism and of projector operator techniques [25, 27].

Explicit expressions for the memory functions $\zeta(t)$ and $D(t)$ can be obtained from hydrodynamics. It has been shown [32, 33] that the frequency-dependent corrections to the friction coefficient are given by a power expansion of the inverse penetration length: $\alpha_0 = (\omega/\nu_0)^{1/2}$, with ν_0 the kinematic viscosity of the heat bath [32]. In the case when the heat bath is a viscoelastic fluid, the inverse penetration length incorporates the frequency dependent kinematic viscosity $\nu(\omega)$: $\alpha(\omega) = [\omega/\nu(\omega)]^{1/2}$, leading to the expression [14, 32, 33]

$$\beta(\omega) \simeq \beta_0 \left[1 + a\alpha(\omega)\right]. \tag{8}$$

This length behaves as: $\alpha(\omega) \sim (a\Delta_\omega)^{-1}(\tau_D\omega)^{\left(\frac{1-\delta}{2}\right)}$, where τ_D is a characteristic relaxation time. We have assumed that, within a given range of frequencies, the kinematic viscosity of the viscoelastic medium obeys the scaling: $\nu(\omega) \simeq \nu_0 \left(\tau_D\omega\right)^{\delta}$ [14]. The quanti-

ties δ and Δ_ω may, in general, depend on the free space around the particle [34] and on the temperature [14, 35]. The scaling factor Δ_ω has its origin in the fact that the relaxation time of the system may depend on the concentration of, for instance, polymers or micelles making up the viscoeastic medium [14, 35, 36].

The exponent δ also admits different interpretations. An important one of these is the one related to the Brownian motion of clusters or small crystals which are still in their late growing stage, e.g. when forming semi-orderly amorphous mesostructures [34]. In this case, the exponent may reflect the specific dynamics obeyed by the radius of these objects as has been analyzed in Ref. [10].

III. SCALING OF THE MEMORY FUNCTION

The scaling of the memory function and, consequently, the microrheological properties of the viscoelastic medium can be inferred from the MSD of a test particle. The MSD can be obtained experimentally by using diffusing-wave spectrometry techniques or video-based methods [4, 6, 13]. It has been found that, in a certain range of frequencies, the complex shear modulus obeys the scaling behavior: $G''_{msd}(\omega) \sim \omega^\gamma$ with $\gamma < 1$, [4, 13].

These experimental results can be described by using Eq. (6) in the case of $\phi_T = 0$. For frequencies lying in the range $\tau_D^{-1} < \omega \ll \beta_0$, the leading term of the Eq. (8) yields

$$\beta^{-1}(\omega) \simeq \beta_0^{-1} \left(\tau_D \omega\right)^{-\left(\frac{1-\delta}{2}\right)} . \tag{9}$$

The inverse Laplace transform of (9) can be performed by using the Tauberian theorem [27]. One then obtains the memory function

$$\zeta(t) \simeq \frac{1}{\beta_0 \tau_D} \frac{1}{\Gamma(\frac{1-\delta}{2})} \left(\frac{t}{\tau_D}\right)^{-\left(\frac{1+\delta}{2}\right)} , \tag{10}$$

where $\Gamma(b)$ is Euler's gamma function. After substituting (10) into (6) with $\phi_T = 0$ and using the inverse Laplace transform of Eq. (7), one arrives at the non-Markovian diffusion equation

$$\frac{\partial \rho}{\partial t} = \frac{D_0}{\tau_D \Gamma(\frac{1-\delta}{2})} \int_0^t \left(\frac{t-t'}{\tau_D} \right)^{-\left(\frac{1+\delta}{2}\right)} \nabla^2 \rho(\mathbf{r}, t') dt', \tag{11}$$

which is similar to the one previously derived in Ref. [27].

It is important to realize that equation (11) can be recast in the form of a fractional diffusion equation [37] by Laplace transforming it and multiplying the result by $(s\tau_D)^{-1}$. Then, taking the time derivative of the inverse Laplace transform of the resulting expression, one obtains

$$\frac{\partial \rho}{\partial t}(\mathbf{r}, t) = {}_0D_t^{1-\hat{\alpha}} D_0 \nabla^2 \rho(\mathbf{r}, t), \tag{12}$$

in which the exponent is $\hat{\alpha} = (3-\delta)/2$, with $1 < \delta < 3$ and the integro-differential operator

$${}_0D_t^{1-\hat{\alpha}} A(t') = \Gamma^{-1}(\hat{\alpha}) \frac{\partial}{\partial t} \int_0^t \left(\frac{\tau_D}{t-t'} \right)^{(1-\hat{\alpha})} A(t') dt' \tag{13}$$

entering Eq. (12) is the zero order Riemann-Liouville operator [37]. This feature demonstrates that our method based on a scaling of the memory function and a description using fractional derivatives leads to an identical kinetic equation.

The value of the exponent δ characterizing the properties of the viscoelastic medium can in general be obtained by analyzing the hydrodynamic effects [8]. For simplicity, we will show how this exponent may be inferred from the evolution in time of the MSD

$$\langle r^2 \rangle(t) = \int r^2 \rho(\mathbf{r}, t) d\mathbf{r}. \tag{14}$$

The evolution equation for $\langle r^2 \rangle(t)$ follows by taking the time derivative of Eq. (14) and then using Eq. (11). After integrating by parts, one obtains

$$\frac{d\langle r^2 \rangle(t)}{dt} = \frac{D_0}{(1-\delta)\Gamma(\frac{1-\delta}{2})} \left(\frac{t}{\tau_D} \right)^{\frac{1-\delta}{2}}, \tag{15}$$

whose solution is

$$\langle r^2 \rangle(t) \simeq t^{\frac{3-\delta}{2}}. \tag{16}$$

Equation (16) can now be compared with the experimental result $\langle r^2 \rangle_{exp} \simeq t^{\frac{3}{4}}$, obtained for a Brownian particle in the intracellular medium [6], yielding $\delta = 3/2$. In view of Eq. (9), the mobility is given by $\beta(\omega) \simeq \omega^{-\frac{1}{4}}$. Since $\beta(\omega) \propto \eta_{eff}(\omega)$ with $\eta_{eff}(\omega)$ the effective viscosity of the medium and $G''_{MSD}(\omega) \simeq \omega \eta_{eff}$, it follows that our result is in good agreement with the experimental result $G''_{MSD} \sim \omega^{\frac{3}{4}}$, reported in Ref. [13].

IV. SCALING OF THE MSD IN CLUSTER-CLUSTER AGGREGATION

Cluster-cluster aggregation in a viscoelastic medium at high temperatures can be viewed as a d-dimensional random walk (RW) in the space of cluster sizes x, [10]. Below, we present some arguments which lead to the recovery of the experimentally justified result given by Eq. (16) also at the level of clusters' RW.

A coupling of late-time growing and mechanical relaxation conditions has been proposed in Ref. [10] in order to properly describe the clusters' RW in the fluctuating viscoelastic medium. The role of MSD for such RW is played by the average radius of the clusters but squared, ${R_{av}}^2(t)$, which scales with the time t as [9, 10, 21]

$${R_{av}}^2(t) \sim t^{2/(d+1)}. \tag{17}$$

According to Ref. [10], and based on the above scaling relation, for a planar geometry the value of the exponent of the MSD is $\nu_{MSD} = 2/3$, which is the harmonic mean of two other exponents obtained for $d = 1$ and $d = 3$, namely $\nu_{MSD} = 1$ and $\nu_{MSD} = 1/2$, respectively. This is due to some physical interpretation that the harmonic mean well describes an optimal (excluded-volume involving [34]) kinetic pathway for a clustering thereby intro-

duced, which ultimately favors $d = 2$. This interpretation is in accordance with soft-glass matter-organization conditions which favor characteristic exponents less than 3/4, see Ref. [31] and references therein. If we, however, take an arithmetic instead of the harmonic mean, and apply it to both extreme exponents, $\nu_{MSD} = 1$ and $\nu_{MSD} = 1/2$, which looks like a customary fitting procedure applied by experimenters, cf. Ref. [1], we finally arrive at the arithmetic-mean exponent: ${\nu_{MSD}}^{AM} = 3/4$, which is characteristic of the viscoelastic matter relaxation (under late-stage growing conditions) [9, 10]. This relation supports the general view offered by the present study.

The scaling formula (17) can be used to obtain the particle MSD of specific concentrated colloidal systems. For example, in the case of the sol-gel continuous phase transition reported in Ref. [38] the exponent of the initial and final phases can be acceptably well-reproduced by taking into account the pivotal role of clusters' surface $x^{(d-1)/d}$, [10, 11, 21]. In our model, the characteristic exponent ν_{char} of these phases correspond to $\nu_{char} = 1$ for $d = 1$ (no surface) and $\nu_{char} = 0.66$ for $d = 2$ (a planar geometry) which is very close to the measured 0.7, see Figure **4** of Ref. [38]. Thereby, experiment and theory show almost the same exponents values under which the same dynamic behavior, i.e. a passage from a diffusive (sol) to some subdiffusive (gel) state can be seen [10]. This is also confirmed by relaxation measurements, cf. Figure **3** of the review [38] and our considerations below.

The MSD R^2_{av} introduced in Eq.(17) can be further related with the creep compliance $\kappa(t)$, defined by the average strain to be assigned to a probe particle immersed in the viscoelastic medium (e.g., the cytoskeleton), divided by the corresponding shear stress [31, 36]

$$R^2_{av}(t) \propto \kappa(t), \tag{18}$$

In the microrheological high-temperature environment considered in Ref. [10], we have made an attempt to define in a phenomenological way the inverse of κ, namely κ^{-1}, as

the internal matrix stress $\sigma_M(t)$ accumulated within the inter-cluster spaces of the matrix, assuming that in the late-stage growing conditions the average strain can be set constant. Taking this relation to be valid, the creep compliance for our high T clustering viscoelastic system satisfies $\kappa(t) \simeq {\sigma_M}^{-2}(t)$, which after taking into account Eqs. (17) and (18) leads to

$$\sigma_M(t) \propto t^{-1/(d+1)}, \tag{19}$$

i.e. a slightly modified result than while entirely based on the before applied phenomenology [10]. From this relation, it follows that the scaling of the internal matrix stress will, in general, be a function of the relevant degree of freedom, d -the space dimension, in the same way as the MSD.

V. COMPARISON WITH EXPERIMENTS

A. The cytoskeleton response: fast-slow crossover of the complex shear modulus

Recent experiments measuring the viscoelastic response of the cytoskeleton through its complex shear modulus $G''(\omega)$ have shown a crossover from the scaling behaviour $G''(\omega) \sim \omega^{3/4}$ for large values of the frequency to an almost constant value for low frequencies [1]. These experiments were performed by attaching a magnetic bead to the cytoskeleton network and then applying a periodic magnetic field that exerts a torque on the particle [1].

This crossover can be explained by means of the theory presented in section **II** if one assumes that the total force exerted on the attached probe particle can be modelled by means of the harmonic force $\mathbf{F}(\mathbf{r}) = -\omega_0^2\mathbf{r}$ with ω_0 a characteristic frequency, and that in Eq. (10) $\delta = 3/2$.

From our description one may show that the complex shear modulus is related with

$\langle \hat{\mathbf{r}}^2 \rangle(\omega)$, through the well-known expression [31]

$$G''(\omega) = \frac{k_B T}{\pi a} \frac{1}{\omega \langle \hat{r}^2 \rangle}, \tag{20}$$

where we have used the relation $\eta(\omega) = \eta_0 \hat{\zeta}^{-1}(\omega)$ obtained after taking the Laplace transform of Eq. (6) and using (7). From the resulting equation we can obtain the MSD

$$\langle \hat{r}^2 \rangle(\omega) = \frac{k_B T}{\pi a \eta_0} \frac{1}{\omega} \left(2\omega_0^2 \beta_0^{-1} + \tau_D^{-1/4} \omega^{3/4} \right)^{-1}. \tag{21}$$

Substituting now this expression into Eq. (20), one finds the complex shear modulus of a probe particle attached to the network

$$G''(\omega) = \eta_0 \left(2\omega_0^2 \beta_0^{-1} + \tau_D^{-1/4} \omega^{3/4} \right). \tag{22}$$

As shown in Figure **1**, our result (22) is in good agreement with the experiments reported in Ref. [1]. The linear model introduced in this subsection proves to be adequate in order to reproduce experiments performed at constant temperature. The effect of temperature can be incorporated into the description by taking into account entropic effects in the local equilibrium distribution function (3) [16, 17] and through the dependence on T of the relaxation time τ_D, [14, 35].

B. Brownian motion in a solution of giant micelles

We will now proceed to analyze the behavior of the MSD of a particle undergoing Brownian motion in a semidilute solution of worm-like micelles [39]. The host fluid will be modelled as a structured viscoelastic medium acting on the particle with the non-linear force

$$F^{el}(x) = -\nabla \phi = F_0 \cos(\lambda^{-1} x), \tag{23}$$

where F_0 is the amplitude of the force, considering the one-dimensional case for simplicity. λ can be interpreted as the characteritic distance between the particle and the cage formed by the micelles.

In order to describe the experimental results for the MSD reported in [39], we will approximate $\rho(\mathbf{r}, t+z)$ through: $\rho(\mathbf{r}, t+z) \simeq \rho(\mathbf{r}, t)+(\partial\rho/\partial t)(t)z+O(z^2)$. This approximation takes into account that for the subdiffusive processes we are considering here, the relaxation of the system is not exponential and thus no clear separation of times scales can be assumed. As a consequence, at larger times the dynamics of the system remains non-Markovian, but with time-dependent coefficients [27]. Thus, keeping the lowest order term of the expansion and substituting the resulting expression into (6), one obtains

$$\frac{\partial}{\partial t}\rho(x,t) = \tilde{D}(t)\frac{\partial^2}{\partial x^2}\rho(x,t) + \tilde{\zeta}(t)F_0\frac{\partial}{\partial x}\left[\,\rho(x,t)\cos\left(\lambda^{-1}x\right)\right], \tag{24}$$

where we have introduced the time-dependent coefficients

$$\tilde{\zeta}(t) = \int_0^t \zeta(z)dz \quad and \quad \tilde{D}(t) = k_B T\tilde{\zeta}(t), \tag{25}$$

where the memory function $\zeta(t)$ is given by Eq. (10). From Eq. (24) we obtain the evolution equation for the MSD

$$\frac{d}{d\tau}\langle x^2\rangle = 2D_0 - 2\frac{F_0 D_0}{k_B T}\langle x\cos\left(\lambda^{-1}x\right)\rangle, \tag{26}$$

where we have introduced the new variable $\tau(t) = \int \tilde{\zeta}(t)dt$. This equation implies that the effects due to the non-linear elastic force on the behaviour of the MSD appear through the average work $\langle xF^{el}\rangle$ which this force exerts over the particle [17]. Since the solution of Eq. (24) with F^{el} given by (23) cannot be obtained analytically, the average $\langle x\cos(x/\lambda)\rangle$ cannot be explicitly computed. However, we will assume small deviations with respect to the average value of the position of the particle, and then use the following expansion around

the mean value $\langle x\rangle(\tau)$: $\langle f\left(x\right)\rangle \simeq f\left(\langle x\rangle\right) + O\left(\langle x^2 - \langle x\rangle^2\rangle\right)$. The resulting equation is

$$\frac{d}{d\tau}\langle x^2\rangle(\tau) = 2D_0 - 2\frac{F_0 D_0}{k_B T}\langle x\rangle(\tau)\cos\left[\lambda^{-1}\langle x\rangle(\tau)\right], \tag{27}$$

which must be solved together with the approximated evolution equation for $\langle x\rangle(\tau)$

$$\frac{d}{d\tau}\langle x\rangle(\tau) = -\frac{F_0 D_0}{k_B T}\cos\left[\lambda^{-1}\langle x\rangle(\tau)\right]. \tag{28}$$

Integrating Eqs. (27) and (28) one can obtain the following expression for the MSD

$$\langle x^2\rangle(t) \simeq \langle x^2\rangle(t_0) + 2D_0\tau(t) + 4\lambda^2\tanh\left[\frac{F_0 D_0}{2\lambda k_B T}\tau(t)\right]^2, \tag{29}$$

where t_0 is a cut-off time, $\tau(t) = \frac{4}{(3-\delta)(\delta-1)}\Gamma^{-1}\left[(\delta-1)/2\right]\tau_D^{(\delta-1)/2}t^{(3-\delta)/2}$ and, for convenience, we have taken the first term of the expansion of $\arctan(x)^2 \simeq x^2$ with $x = \tanh[\frac{F_0 D_0}{2\lambda k_B T}\tau(t)]$. The behaviour of the MSD (29) as a function of time (solid line) is shown in Figure **2**, and compared with experimental data (circles) taken from Ref. [39]. We have used the following values for the parameters: $D_0 \simeq 3\cdot 10^{-5}\mu m^2 s^{-1}$, $k_B T \simeq 4.2\cdot 10^{-6} gr\mu m^2 s^{-2}$, $F_0 \simeq 0.5 gr\mu m\, s^{-2}$, $\tau_D \simeq 0.1s$ and $\lambda \simeq 8\cdot 10^{-3}\mu m$. From Figure **2** we may conclude that the expression for the MSD we have obtained agrees with microrheological experiments [39] within the time interval represented. Notice that the plateau is a signature of the existence of cage effects, which in our model become manifest at the maximum value of the elastic force F^{el}. The exponent characterizing the memory function of the solution of giant micelles is $\delta = 9/5$, which differs from that of our previous example.

VI. DISCUSSION

In this article, we have proposed a thermo-kinetic approach to analyze anomalous diffusion of particles and clusters in systems having a viscoelastic response. A non-Markovian diffusion

equation has been derived from the entropy production at the mesoscale related to the diffusion process.

Using hydrodynamic arguments, we have obtained an expression for the memory function which obeys a power law in frequencies and leads to the scaling behaviour of the mean square displacement of the Brownian particle.

Cluster-cluster aggregation in the viscoelastic medium considered as a d-dimensional random walk in the space of cluster sizes x has also been analyzed [9, 23]. The role of MSD for such a RW, played by the average radius of the clusters but squared, has been used to argue that the time dependence of the matrix stress and the creep compliance of the colloid-type system could scale with a law depending on the relevant degree of freedom, d -the space dimension of the Brownian particle. Moreover, we have shown that the characteristic exponent 3/4 of the MSD can be obtained by applying an arithmetic mean to both extreme exponents ($d = 1$ and $d = 3$). This procedure coincides well with the one followed when obtaining the exponents from experimental data [1, 31].

As particular cases of our general formalism, we have studied the dynamics of a particle attached to the cytoskeleton and of a Brownian particle moving through a semidilute solution of giant worm-like micelles. In the first case, we have explained the crossover of the complex shear modulus of the cytoskeleton observed in experiments in terms of an harmonic-force model. In the second case, we have analyzed the dynamics of a Brownian particle moving through a semidilute solution of giant worm-like micelles by proposing a nonlinear force model that takes cage effects into account. The good agreement between experiment and theory, shown through Figures **1** and **2**, allows one to conclude that the theoretical approach we have proposed in this article can explain the behaviour observed in microrheological experiments [1, 13, 31, 39].

Our study suggests for the possibility of providing justifications of experimental results on diffusion in a viscoelastic medium in terms of a Smoluchowski description [8, 23]. The theory proposed may constitute a useful tool ready for examining the dynamics of the soft-matter systems at a mesoscale.

Acknowledgments

This work was supported by UNAM-DGAPA under the grant IN-108006 (ISH), and by DGICYT of the Spanish Government under Grant No. FIS2005-01299. (Dis)ordered aggregation and Smoluchowski type dynamics aspects concerned with the present study are subject to a MNiI grant 2P03B 03225(2003-2006) regulations and AG's participation therein. A short-visit ESF/StochDyn grant is acknowledged too. Thanks go to Prof. R. Rodríguez, Dr. Adam Danch and Dr. Jacek Siódmiak for discussions and careful reading of this manuscript.

---

[1] Deng, L.; *et al.* **2006**, *Nature Materials*, **2006**, *5*, 636.

[2] Vekilov, P. G.; Alexander, J. I. D. *Chem. Rev.* **2000**, *100*, 2061.

[3] Oxtoby, D. W. *Philos. Trans. R. Soc. A* **2003**, *36*, 419.

[4] Wong, I. Y.; *et al. Phys. Rev. Lett.* **2004**, *92*, 178101.

[5] Lau, A. W. C.; Hoffman, B. D.; Davies, A.; Crocker, J. C.; Lubensky, T. C. *Phys. Rev. Lett.* **2003**, *91*, 198101.

[6] Salman, H.; Gil, Y.; Granek, R.; Elbaum, M. *Chem. Phys.* **2002**, *248*, 389.

[7] Storm, C.; Pastore J. J.; MacKintosh, F. C.; Lubensky, T. C.; Janmey, P. A. *Nature* **2005**,

435, 191.

[8] Santamaría-Holek, I. ; Rubí, J. M. *J. Chem. Phys.* **2006**, *125*, 064907.

[9] Gadomski, A. *Nonlinear Phenomena in Complex Systems (NPCS)* **2000**, *3*, 321.

[10] Gadomski, A.; Rubí, J. M.; Łuczka, J.; Ausloos, M. *Chem. Phys.* **2005**, *310*, 153.

[11] Gasser, U.; Weeks, E. R.; Schofield, A.; Pusey, P. N.; Weitz, D. A. *Science* **2001**, *292*, 258.

[12] Tanaka, H.; Nishikawa, Y. *Phys. Rev. Lett.* **2005**, *95*, 078103.

[13] Gisler, T.; Weitz, D. A. *Phys. Rev. Lett.* **1999**, *82*, 1606.

[14] Santamaría-Holek, I.; Rubí J. M.; Pérez-Madrid, A. *New J. Phys.* **2005**, *7*, 35.

[15] Vainstein, M. H.; Costa, I. V. L.; Morgado, R. ; Oliveira, F. A. *Europhys. Lett.* **2006**, *73*, 726.

[16] Reguera, D.; Rubí, J. M. *Phys. Rev. E* **2001**, *64*, 061106.

[17] Reguera D.; *et al. Phys. Rev. Lett.* **2006**, *96*, 130603.

[18] Gadomski, A.; Siódmiak, J; Santamaría-Holek, I.; Rubí, J. M.; Ausloos, M. *Acta Phys. Pol. B* **2005**, *36*, 1537.

[19] Reguera, D.; Vilar J. M. G.; Rubí, J. M. *J. Phys. Chem. B* **2005**, *109*, 21502.

[20] Vilar, J. M. G.; Rubí, J. M. *Proc. Natl. Acad. Sci.* **2001**, *98*, 11081.

[21] Gadomski, A. *Physica A* **1999**, *274*, 325.

[22] Tanaka, H.; Nishikawa, Y.; Koyama, T. *J. Phys.: Condens. Matter* **2005**, *17* L143.

[23] Gadomski, A. *Physica A* **2007** *373*, 43.

[24] Ausloos, M.; Lambiotte, R. *Phys. Rev. E.* **2006**, *73*, 011105.

[25] Zwanzig R. *Phys. Rev.* **1961**, *124*, 983.

[26] Trimper, S.; Zabrocki K.; Schulz, M. *Phys. Rev. E.* **2004**, *70*, 056133.

[27] Balescu, R. *Statistical dynamics*; Imperial College Press, Singapore, 1997.

[28] de Groot, S. R.; Mazur, P. *Non-equilibrium Thermodynamics*; Dover, New York, 1984.

[29] Tanaka, S.; Maki, S.; Ataka, M. cond-mat/0605617.

[30] Łuczka, J. *Physica A* **1999**, *274*, 200.

[31] Mason, T. G.; Gisler, T.; Kroy, K.; Frey, E.; Weitz, D. A. *J. Rheol.* **2000**, *44*, 917.

[32] Landau, L. D.; Lifshitz, L. *Fluid Mechanics*; Pergammon Press, Oxford, 1981.

[33] Pérez-Madrid, A.; Rubí J. M.; Bedeaux, D. *Physica A* **1990**, *163*, 778.

[34] Danch, A.; Osoba, W.; Stelzer, F. *Eur. Polymer J.* **2003**, *39*, 2051.

[35] Todd, B. *Phys. Rev. E* **2005**, *72*, 041204.

[36] Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley & Sons, New York, 1980.

[37] Metzler, R.; Klafter, J. *Physics Reports* **2000**, *339*, 1.

[38] Scheffold, F.; *et al. Progress in Colloid & Polymer Science* **2004**, *123*, 141.

[39] Bellour, M.; Skouri, M.; Munch, J. P.; Hébraud, P. *Eur. Phys. J. E* **2002**, *8*, 431.

Figure 1.

Complex shear modulus of the cytoskeleton as a function of frequency for the case of a magnetic bead attached to the cytoskeleton network. An oscillatory magnetic field was applied in order to measure the response of the material. Circles represent experimental data taken from Ref. [1] whereas the solid line a fit of the data obtained from Eq. (22), for $a = 2.25 \cdot 10^{-6} m$, $\beta \simeq 1 \cdot 10^{6} s^{-1}$, $\eta_0 \simeq 1 \cdot 10^{-3} kg m^{-1} s^{-1}$, $\omega_0 \simeq 1.77 \cdot 10^{-4} s^{-1}$ and $\tau_D \simeq 4 \cdot 10^{-5} s$.

Figure 2.

The MSD of a polystyrene particle in a semidilute solution of worm-like micelles as a function of time(23). The black circles are experimental data obtained by means of diffusing wave spectroscopy techniques, and taken from Ref. [39]. The solid line was obtained with Eq. (29). The values of the parameters are given in the text.

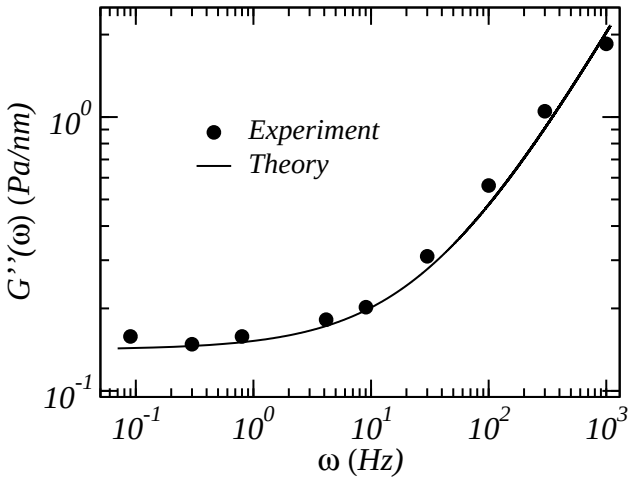

Figure 1.

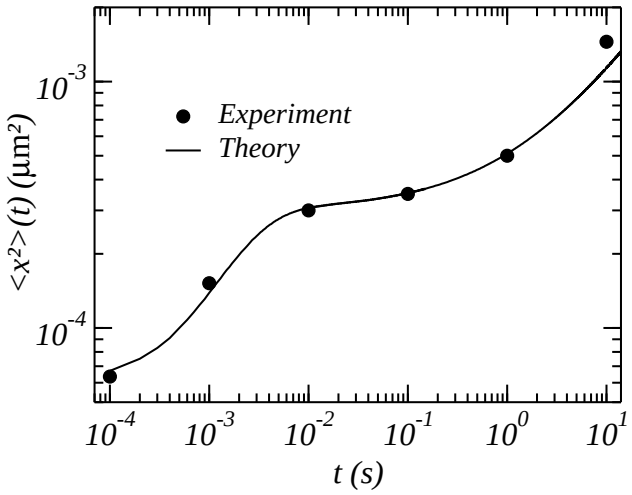

Figure 2