First-principles predictor of the location of ergodic/non-ergodic transitions

P.E. Ramírez-González[a], R. Juárez-Maldonado[a], L. Yeomans-Reyna[b], M.A. Chávez-Rojo[c],
M. Chávez-Páez[a], A. Vizcarra-Rendón[d], and M. Medina-Noyola[a]

[a]*Instituto de Física "Manuel Sandoval Vallarta",*
Universidad Autónoma de San Luis Potosí, Álvaro
Obregón 64, 78000 San Luis Potosí, SLP, México
[b]*Departamento de Física, Universidad de Sonora, Boulevard Luis*
Encinas y Rosales, 83000 Hermosillo, Sonora, México.
[c]*Facultad de Ciencias Químicas, Universidad Autónoma de*
Chihuahua, Venustiano Carranza S/N, 31000 Chihuahua, Chih., México.
[d]*Unidad Académica de Física, Universidad*
Autónoma de Zacatecas, Paseo la Bufa y Calzada Solidaridad, 98600 Zacatecas, Zac., México.

This letter presents a remarkably simple approach to the first-principles determination of the ergodic/non-ergodic transition in monodisperse colloidal suspensions. It consists of an equation for the long-time asymptotic value γ of the mean squared displacement of the colloidal particles, whose finite real solutions signal the non-ergodic state, and determines the non-ergodic parameter $f(k)$. We illustrate its concrete application to three simple model colloidal systems, namely, hard-spheres, hard-spheres plus repulsive (screened Coulomb) Yukawa interaction, and hard-sphere plus attractive Yukawa tail. The results indicate that this is quite a competitive theory, similar in spirit to, but conceptually independent from, the well-known mode coupling theory.

Keywords: Colloidal dynamics; glass transition; dynamic arrest.

Esta carta presenta un método notablemente simple para la determinación, de primeros principios, de la transición ergódico/no-ergódico en suspensiones coloidales monodispersas. Dicho método consiste en una ecuación para el valor asintótico a tiempos largos, γ, del desplazamiento cuadrático medio de las partículas coloidales, cuyas soluciones reales finitas son sinónimo de no-ergodicidad, y determinan el parámetro no-ergódico $f(k)$. Ilustramos su aplicación concreta en tres modelos simples de sistemas coloidales, a saber, esferas duras, esferas duras con interacción de Yukawa repulsiva (Coulombica apantallada), y esferas duras con interacción de Yukawa atractiva (fuerzas de deplección). Los resultados indican que ésta es una teoría muy competitiva, similar en espíritu, pero conceptualmente diferente, a la bien conocida teoría de *acoplamiento de modos*.

Descriptores: Dinámica coloidal; transición vítrea; arresto dinámico.

PACS: 64.70.Pf; 61.20.Gy; 47.57.J-

The most basic and elementary information on the thermodynamic properties of a material is its phase diagram. The description of the gas-liquid transition provided by the van der Waals equation of state is the earliest and most paradigmatic example of the construction of a phase diagram starting from molecular considerations [1]. The most outstanding achievement of statistical mechanics, however, has been the establishing of the microscopic version of the second law of thermodynamics, which provides the basis for the systematic calculation, given the intermolecular forces, of phase diagrams, by the simple conceptual procedure of identifying the phase with the lowest free energy. This very fundamental principle permitted the development of the wide range of methods, approaches, techniques and applications of equilibrium statistical thermodynamics [2].

At the same time, one of the most obvious limitations of statistical mechanics has been its inability to identify an equally general and simple description of non-equilibrium states of matter, given the molecular interactions. From a practical and fundamental perspective, this is quite disturbing, given the fact that a large variety of the materials with which we actually interact in everyday life are not in their thermodynamic equilibrium state. Thus, it is permanently important to search for first-principles approaches to describe the most elementary properties of such "phases" and the transitions between them, even in the context of specific classes of non-equilibrium states. Perhaps the simplest of them refer to the states that result when kinetic barriers prevent a material from reaching its thermodynamically most stable state, thus being trapped in dynamically arrested states, such as glasses or gels. One would then like to have first-principles criteria to predict the location of the boundary between the ergodic fluid phase and such arrested non-ergodic states. Contrary to its thermodynamic analog, in this case we only have a single theory of this sort, namely, the mode coupling theory (MCT) of the ideal glass transition [3,4], some of whose predictions have found beautiful experimental confirmation [5,6]. Unfortunately, its criterion to decide in a practical manner if a system is in an ergodic or in an arrested state is obscured by the conceptual complexity of this theory and by the many other issues addressed [3]. Thus, the need exists for simpler and more straightforward approaches that focus on this specific and important issue. The main purpose of this communication is to illustrate the application, and to

outline the derivation, of a new first-principles prescription to locate the ergodic-non-ergodic transition in monodisperse colloidal dispersions in a remarkably practical and simple manner, completely independent of the MCT and its recent variants [7, 8].

This prescription consists of an equation for the basic "order parameter" of the transition from an equilibrium fluid phase to a glass or gel state, namely, the long-time asymptotic value,

$$\gamma \equiv \lim_{t \to \infty} \langle (\Delta x(t))^2 \rangle,$$

of the mean squared displacement (msd) of individual particles. In the arrested states, this parameter is finite, representing the localization of the particles, whereas in the ergodic phase it diverges. This equation reads

$$\frac{1}{\gamma} = \frac{1}{6\pi^2 n} \int_0^\infty dk k^4 \frac{[S(k) - 1]^2 \lambda^2(k)}{[\lambda(k)S(k) + k^2\gamma][\lambda(k) + k^2\gamma]}, \quad (1)$$

where $S(k)$ is the static structure factor of the system,

$$\lambda(k) \equiv [1 + (k/k_c)^2]^{-1},$$

with k_c being the position of the first minimum of $S(k)$, and n the particle number concentration. The very form of this criterion exhibits its simplicity: given the effective inter-particle forces, statistical thermodynamic methods allow one to determine $S(k)$, and the absence or existence of *finite* positive real solutions of this equation will indicate if the system remains in the ergodic phase or not (notice that $\gamma = \infty$ is always a solution, representing ergodic states). The next objective of this letter is to illustrate the practical application of this criterion, in the context of three simple model colloidal systems, and to explain very briefly its conceptual origin.
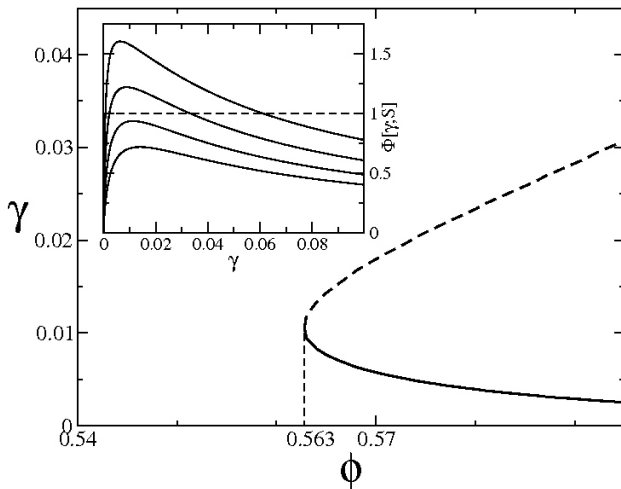

FIGURE 1. Real solutions γ to Eq. (1). Below $\phi_g = 0.563$, this equation has no real solutions. Above ϕ_g, two solutions appear, illustrated by the two branches that bifurcate at ϕ_g. The branch for which γ decreases with ϕ (solid line) corresponds to the physical solution of the glass state. In the inset we plot the functional $\Phi[\gamma; S]$ as a function of γ for $\phi = 0.50, 0.55, 0.60$, and 0.65 (from bottom to top).

To illustrate the use of this criterion, let us notice that γ times the right-hand side of Eq. (1) is a functional of $S(k)$ and an ordinary function of γ, which we denote by $\Phi[\gamma; S]$. Thus, for a fixed state [*i.e.*, fixed $S(k)$], this equation may be solved by plotting $\Phi[\gamma; S]$ as a function of γ, to see if it crosses unity, and for which value(s) of γ it does so; notice that this functional must vanish in the limits of large and small γ. This very simple procedure leads to the determination of the finite solutions of Eq. (1), as illustrated in Fig. 1 for the hard sphere (HS) system with the static structure factor $S(k)$ given by the Percus-Yevick (PY) approximation [9] with the Verlet-Weis (VW) correction [10]. The inset of Fig. 1 exhibits the dependence of the functional on γ for various volume fractions. Clearly, below a threshold value ϕ_g, $\Phi[\gamma; S]$ remains below 1.0 for all γ, and hence, there are no real solutions; thus, the system must be in the ergodic state for $\phi < \phi_g$. Above ϕ_g there are two real solutions, the smallest one corresponding to the glass state, since in the glass the msd must decrease with n. In this manner, we determine this threshold value to be $\phi_g = 0.563$. This quantitative prediction is closer to the experimental values than those of the original MCT or its extensions.

The criterion above emerges from the long-time asymptotic analysis [11] of the self-consistent generalized Langevin equation (SCGLE) theory of colloidal dynamics [12, 13]. This theory was originally developed to describe the dynamic properties of colloidal dispersions. Thus, it permits the calculation of properties such as the msd of the particles, or the intermediate scattering function $F(k, t)$ and its *self* component, $F_S(k, t)$ [14, 15], given the effective pair potential $u(r)$ between colloidal particles. The relaxation of $F(k, t)$ from its initial value $S(k)$ towards zero provides a description, in Fourier space, of the relaxation of the local concentration profile $n(\mathbf{r}, t)$ from an arbitrary initial profile $n_0(\mathbf{r})$ towards its equilibrium value n. In an ergodic fluid, this relaxation is complete, and hence, $F(k, t)$ relaxes to zero, whereas in a glass or a gel state, the initial concentration profile only evolves due to the local motion of the arrested particles, without the complete structural rearranging that would permit the full dissipation of the initial profile. Thus, in a non-ergodic state, $F(k, t)$ does not decay to zero, but to some finite value denoted by $f(k)S(k)$. From the long-time analysis mentioned above (and reviewed below), one can also derive [11] a remarkably simple expression for this experimentally important property. This expression reads

$$f(k) = \frac{\lambda(k)S(k)}{\lambda(k)S(k) + k^2\gamma}, \quad (2)$$

with γ being the physical solution to Eq. (1). Let us notice that this result only involves $S(k)$ and $\lambda(k)$ as static inputs. We may illustrate its use by applying it to the HS system above, for which we just found $\phi_g = 0.563$. Right at ϕ_g, there is only a single solution for γ, namely, $\gamma = 1.06 \times 10^{-2}\sigma^2$, with σ being the HS diameter. This solution for γ may then be employed in Eq. (2) to determine the

non-ergodic parameter $f(k)$. Fig. 2 compares this prediction for $f(k)$ with the experimental data from Ref. 5. A similar comparison is also included in this figure, corresponding to a higher volume fraction, $\phi = 0.58$, and to the experimental data of Ref. 6.

The next example refers to dispersions of charged colloidal particles, with effective pair potential modeled by the HS plus the repulsive screened Coulomb potential, $\beta u(r) = K \exp[-z(r/\sigma - 1)]/(r/\sigma)$ for $r > \sigma$. The interaction parameters z and K are, respectively, the inverse Debye screening length (in units of σ), and the intensity of

FIGURE 4. Theoretical glass transition line in the plane (T^*, ϕ) for the HSAY system, calculated with Eq. (1) (thick solid and dashed curve), and from the MCT (symbols, taken from Ref. 19). The lighter (solid and dashed) line corresponds to the freezing line, according to the HV criterium. The dotted curve corresponds to the spinodal line. The inset displays the same information in the (K, ϕ) plane.

the pair potential at hard-sphere contact (in units of the thermal energy $\beta^{-1} \equiv k_B T$). We employed as the static input of Eqs. (1) and (2) the experimentally-determined static structure factor of a sample with $\sigma = 272 nm$ and $\phi = 0.27$, provided in Ref. 6. For this, we used the hyper-netted chain approximation [2] to provide a smooth fit of the data, leading to $z = 3.14$ and $K = 11.56$. The solution to Eq. (1) is $\gamma = 0.00293\sigma^2$, and the results for $f(k)$ from Eq. (2) are compared with the corresponding experimental data in Fig. 3. Given that no fitting parameters are involved in the theoretically-predicted non-ergodic parameter $f(k)$ in Figs. 2 and 3, we consider that the overall quantitative accuracy of our theory is quite remarkable, and is certainly better than that of the MCT. Of course, one can easily determine the full liquid-glass "phase" diagram in the space (K, z, ϕ), but this is not discussed here.

The last illustrative example refers to another simple model of a colloidal dispersion, this time involving the hard-sphere plus an *attractive* Yukawa (HSAY) potential, $\beta u(r) = -K \exp[-z(r/\sigma - 1)]/(r/\sigma)$, modeling depletion forces [16]. In this case we only emphasize some qualitative aspects of the predictions of our theory, obtained using the mean spherical approximation (MSA) [17] for $S(k)$. Figure 4 presents the ergodic-non-ergodic transition line of this system for $z = 20$ in the plane (T^*, ϕ) of state parameters, with $T^* \equiv K^{-1}$ being a reduced temperature. For reference we also plot the line where the maximum of $S(k)$ reaches 2.85 (the freezing line, according to the Hansen-Verlet (HV) criterion [18]), as well as the spinodal curve. To illustrate the qualitative similarity between our results and those of the MCT, we have also included the MCT transition line [19]. The inset re-plots the same curves, now in the plane (K, ϕ), to illustrate the experimentally observed [16] shape of the glass
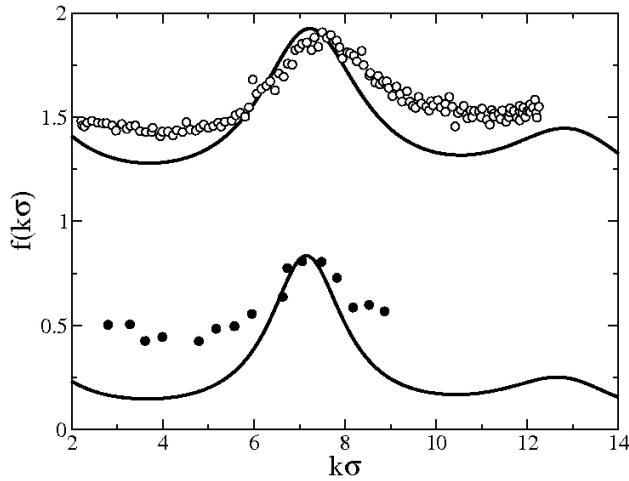

FIGURE 2. Non-ergodic parameter $f(k)$ (solid lines) calculated with Eqs. (1) and (2) for the HS system, with $S(k)$ given by the PY approximation with the VW correction, at the theoretically-predicted ideal glass transition, $\phi_g = 0.563$ (lower curve), and at the larger volume fraction $\phi = 0.58$ (upper curve, shifted upwards one unit, for visual clarity). Symbols are the experimental data from Ref. 5 (filled circles) and Ref. 6 (empty circles).
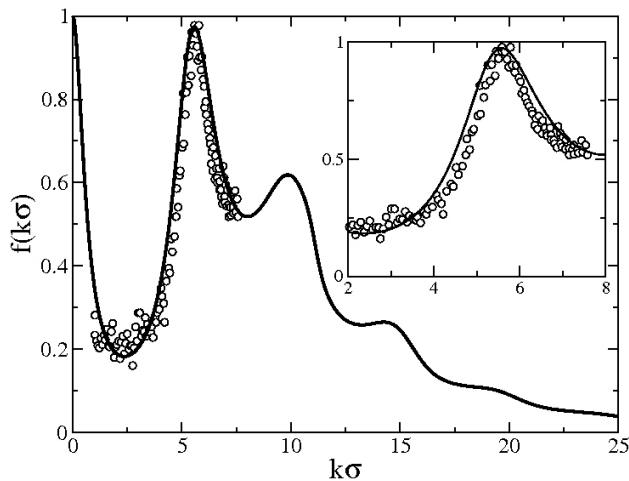

FIGURE 3. Theoretical prediction of the non-ergodic parameter $f(k)$ (solid line) calculated with Eqs. (1) and (2) for the hard-sphere plus the *screened* Coulomb tail, with $\phi = 0.27$, $z = 3.14$, and $K = 11.56$. The symbols are the experimental data from Ref. 6.
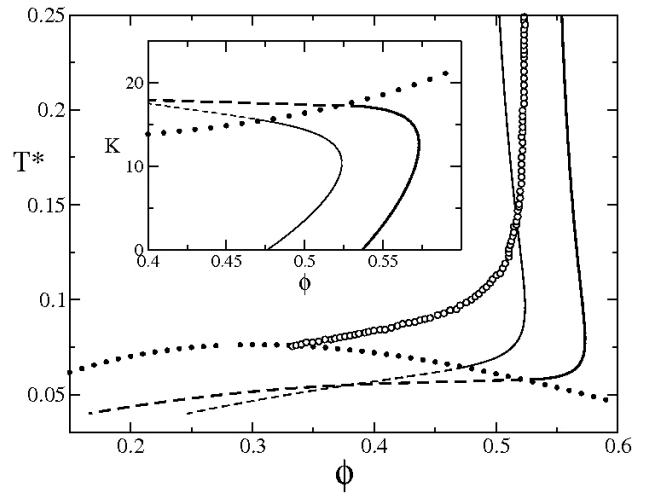
transition line at its high density end. This describes the re-entrant behavior of a system upon lowering its temperature at fixed volume fraction, from a hard-sphere glass to an ergodic state, followed by the re-entrance from the ergodic state to a second ("attractive") glass state.

This completes the illustration of the practical use of the general results in Eqs. (1) and (2). Let us now comment on their physical origin. Of course, the physics behind them is the physics behind the full self-consistent theory from which they derive. Hence, let us summarize the four distinct fundamental elements of this theory. The first consists of general memory-function expressions for $F(k,t)$ and $F_S(k,t)$ derived with the generalized Langevin equation (GLE) formalism [11,12], which in Laplace space read

$$F(k,z) = \frac{S(k)}{z + \frac{k^2 D_0 S^{-1}(k)}{1 + C(k,z)}}, \quad (3)$$

$$F_S(k,z) = \frac{1}{z + \frac{k^2 D_0}{1 + C_S(k,z)}}, \quad (4)$$

where D_0 is the free-diffusion coefficient, and $C(k,z)$ and $C_S(k,z)$ are the corresponding memory functions.

The second element is an approximate relation between collective and self-dynamics. We approximate the difference $[C(k,t) - C_S(k,t)]$ by its exact short-time/large-k limit, thus defining what we refer to as the "additive" Vineyard-like approximation [12],

$$C(k,t) = C_S(k,t) + [C^{SEXP}(k,t) - C_S^{SEXP}(k,t)]. \quad (5)$$

In this equation, $C^{SEXP}(k,t)$ and $C_S^{SEXP}(k,t)$ are the exact short-time expressions for these memory functions, which also define the so-called [15, 20] single exponential (SEXP) approximation, and for which well-established expressions, in terms of equilibrium structural properties, are available [11].

The third ingredient consists of the independent approximate determination of $F_S(k,t)$ [or $C_S(k,t)$]. One intuitively expects that these k-dependent self-diffusion properties should be simply related to the properties that describe the Brownian motion of individual particles, just like in the Gaussian approximation [14], which expresses $F_S(k,t)$ in terms of the mean-squared displacement $W(t)$ as $F_S(k,t) = \exp[-k^2 W(t)]$. We introduce an analogous approximate connection, but at the level of their respective memory functions. The memory function of $W(t)$ is the so-called time-dependent friction function $\Delta\zeta(t)$. This function, normalized by the solvent friction $\zeta_0 = k_B T/D_0$, is the large wave-vector limit of $C_S(k,t)$. Thus, we interpolate $C_S(k,t)$ between its two exact limits, namely,

$$C_S(k,t) = C_S^{SEXP}(k,t)$$
$$+ \left[\Delta\zeta^*(t) - C_S^{SEXP}(k,t)\right]\lambda(k), \quad (6)$$

where $\Delta\zeta^*(t) \equiv \Delta\zeta(t)/\zeta_0$. The fourth ingredient of our theory is a general expression for this property, also derived with

the GLE approach [21], namely,

$$\Delta\zeta^*(t) = \frac{D_0}{3(2\pi)^3 n}$$
$$\times \int d\mathbf{k} \left[\frac{k[S(k)-1]}{S(k)}\right]^2 F(k,t)F_S(k,t). \quad (7)$$

Equations (3)–(7) constitute the SCGLE theory of colloidal dynamics. Besides the unknown dynamic properties, it only involves the static structural properties $S(k)$, $C^{SEXP}(k,t)$ and $C_S^{SEXP}(k,t)$, determined by the methods of equilibrium statistical thermodynamics. Concerning the interpolating function $\lambda(k)$, phenomenological arguments were given [12] that led to the definition given above [immediately after Eq. (1)]. Although no fundamental basis is available for this choice of $\lambda(k)$, this definition is universal (in the sense that it is the same for any system or state), and renders the resulting self-consistent scheme free from any form of adjustable parameters.

The derivation of the results in Eqs. (1) and (2) from the SCGLE scheme in Eqs. (3)–(7) is rather straightforward. It consists of the assuming that the unknown dynamic properties $F(k,t)$, $F_S(k,t)$, $C(k,t)$, $C_S(k,t)$, and $\Delta\zeta^*(t)$, which in an ergodic state decay to zero, in a non-ergodic state decay to a finite asymptotic value, referred to as the non-ergodic parameters, denoted by $f(k)S(k)$, $f_S(k)$, $c(k)$, $c_S(k)$, and $\Delta\zeta^{*(\infty)}$. One then re-writes Eqs. (3)–(7) in terms of these asymptotic values plus a regular contribution that does decay to zero. Taking the long-time limit of the resulting equations leads to a system of five equations for these five unknown non-ergodic parameters. This system of equations can be reduced to a single equation for the scalar parameter $\Delta\zeta^{*(\infty)}$, which is precisely Eq. (1), with the parameter γ defined as $\gamma \equiv D_0/\Delta\zeta^{*(\infty)}$. That γ thus defined is the mean squared displacement, follows from the fact that the effective force on a tracer particle includes a term given by [21]

$$\zeta_0 \int_0^\infty \Delta\zeta^*(t-t')\mathbf{v}(t')dt';$$

in an arrested state, the non-ergodic part of $\Delta\zeta^*(t)$ generates a harmonic force whose elastic constant, given by $\zeta_0\Delta\zeta^{*(\infty)}$, is related to γ by the definition above, through the equipartition theorem. The other four equations for the non-ergodic parameters can then be used to express those quantities in terms of γ. The equation for the non-ergodic parameter $f(k)$ is precisely Eq. (2).

We have also solved numerically the full self-consistent theory for the systems discussed here. Of course, we confirmed, with this lengthier method, the quantitative results obtained in a much more economical manner from Eqs. (1) and (2). The numerical solution, however, provides the whole scenario of the relaxation processes. On the basis of such results, which we shall discuss separately, we may say that the general scenario of the glass transition provided by the

present theory is consistent with the available experimental data, and is quite similar to that provided by the MCT. We should point out, however, that for the HS system, our theory does not have to appeal to any sort of re-scaling of the volume fraction, as the MCT is forced to invoke due to its numerically low predicted glass transition volume fraction ($\phi_g = 0.52$). In fact, none of our theoretical results presented here involved any form of adjustable parameter. Thus, we conclude that in many respects, the present theory of dynamic arrest is a sound and competitive theoretical description of dynamic arrest in colloidal systems.

Acknowledgments

1. M.J. Klein, *Physica A* **73** (1974) 28.

2. D.A. McQuarrie *Statistical Mechanics*, Harper & Row (New York, 1973).

3. W. Götze, in *Liquids, Freezing and Glass Transition*, edited by J.P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991).

4. W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).

5. W. van Megen, S.M. Underwood, and P.N. Pusey, *Phys. Rev. Lett* **67** (1991) 1586.

6. Ch. Beck, W. Härtl, and R. Hempelmann, *J. Chem. Phys.* **111** (1999) 8209.

7. G. Szamel, *Phys. Rev. Lett.* **90** (2003) 228301.

8. J. Wu and J. Cao, *Phys. Rev. Lett.* **95** (2005) 078301.

9. J.K. Percus and G.J. Yevick, *Phys. Rev.* **110** (1957) 1.

10. L. Verlet and J.-J. Weis, *Phys. Rev. A* **5** (1972) 939.

11. L. Yeomans-Reyna *et al.*, submitted to *Phys. Rev. E* (2007).

12. L. Yeomans-Reyna and M. Medina-Noyola, *Phys. Rev. E* **62** (2000) 3382.

13. L. Yeomans-Reyna, H. Acuña-Campa, F. Guevara-Rodríguez and M. Medina-Noyola, *Phys. Rev. E* **67** (2003) 021108.

14. P.N. Pusey, in *Liquids, Freezing and the Glass transition*, edited by J.P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, Amsterdam, 1991).

15. G. Nägele, *Phys. Rep.* **272** (1996) 215.

16. K.M. Pham *et al.*, *Science* **296** (2002) 104.

17. J.S. Høye and L. Blum, *J. Stat. Phys.* **16** (1977) 399.

18. J.P. Hansen and L. Verlet, *Phys. Rev.* **184** (1969) 151.

19. J. Bergenholtz and M. Fuchs, *Phys. Rev. E* **59** (1999) 5706.

20. J.L. Arauz-Lara and M. Medina-Noyola, *Physica A* **122** (983) 547.

21. M. Medina-Noyola, *Faraday Discuss. Chem. Soc.* **83** (1987) 21.