Molecular-Level Relation between Intra-Particle Glass Transition Temperature and Stability of Colloidal Suspensions

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Abstract

ABSTRACT: In many colloidal suspensions, the dispersed colloidal particles are amorphous solids resulting from vitrification. A crucial open problem is understanding how colloidal stability is affected by the intra-particle glass transition. By dealing with the latter process from a solid-state perspective, we estabilish a proportionality relation between the intra-particle glass transition temperature, T_{g}, and the Hamaker constant, A_{H}, of a generic suspension of nanoparticles. It follows that T_{g} can be used as a convenient parameter (alternative to A_{H}) for controlling the stability of colloidal systems. Within DLVO theory, we show that the novel relationship, connecting T_{g} to A_{H}, implies the critical coagulation ionic strength (CCIS) to be a monotonically decreasing function of T_{g}. We connect our predictions to recent experimental findings.

Suspensions of colloidal particles dispersed in a liquid solvent represent a paradigm of complex systems where the interplay between a hierarchy of physico-chemical effects across different length and time scales leads to fascinating mesoscopic behaviours, from fractal

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aggregation[1] to phase separation and phase transitions such as colloidal gelation,[2–6] vitrification and crystallization.[7]

The stability of a colloidal suspension with respect to the aggregation of the dispersed colloidal particles (a phenomenon also known as *coagulation*) is explained by classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory[8,9] in terms of a balance between attractive van der Waals (vdW) and repulsive electrostatic double-layer forces, respectively.[10] A loss of colloidal stability due to either addition of salt[8,9] or application of shear flow[11,12] can eventually result in the suspension coagulating rapidly, and into gel formation. The presence of ions in the solution, in particular, can lead to a compression of the double layer as a consequence of which attractive interactions among the colloids dominate the repulsive ones. The threshold of ionic strength above which a colloidal suspension is destabilized due to rapid particle aggregation is known as the *critical coagulation ionic strength* (CCIS).[13,14]

Much research in the last years has concerned the role played on the stability of colloidal suspensions by so-called non-DLVO forces which include, among others, hydration repulsion, hydrophobic interactions and protrusion forces[15]. Comparatively, less attention has been devoted to investigate the role played by the physical properties of the dispersed colloidal particles.

Apart from a few important exceptions (e.g. colloidal nanocrystals), most widely dispersed colloids, such as silica and polymer nanoparticles, are amorphous solids with an internal disordered structure. They indeed commonly result from a vitrification process, i. e. a glass transition, with the glass-transition temperature T_g being an important material property that characterizes the degree of mobility within the colloids[16]. Understanding how the intra-particle glass transition temperature T_g affects the stability of a colloidal suspension is a fundamental open question.

In recent experiments, Scott et al.[17] investigated the effect of adding salts on the stability of a series of suspensions of electrostatic-stabilized polymer nanoparticles spanning a wide range of T_g values. When adding the hydrophilic KCl salt, these authors found the CCIS to

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be a decreasing function of T_g. A more intricate effect was observed when adding hydrophobic salts. In all cases, an explanation for these findings was suggested in terms of the lifetime of ionic structuration within mobile surface layers, i.e. chiefly in terms of non-DLVO effects.[17]

In this Letter, we examine this fundamental question from a theoretical point of view. We consider a suspension (see the sketch in Fig. 1) whose dispersed colloids have a spherical shape and consist of many polymer chains, with same length and chemical structure, vitrified at a temperature T_g. The strength of the vdW attraction among the colloids is conveniently taken into account by the so-called Hamaker constant A_H[18], which is a material-dependent coefficient providing quantitative information on the London dispersion forces acting among the monomer units of the polymer chains inside each colloidal particle[18,19]. Following Zaccone and Terentjev[20], we address the intra-particle vitrification process from a solid-state perspective. We consider a temperature $T < T_g$ where the colloids are amorphous solids with a finite shear modulus $G > 0$, and identify T_g as the point at which a loss of mechanical stability (signaled by the vanishing of G) of the polymer chains results as a consequence of the reduction in the monomer connectivity driven by the Debye-Grüneisen thermal expansion. By supplementing this picture with basic condensed matter physics consideration about thermal expansion, we investigate the repercussions of the intra-particle melting on the Hamaker constant A_H of the suspension. We find A_H to be inversely proportional to the thermal expansion coefficient α_T and, at the same time, directly proportional to T_g. From the latter relation it follows that the intra-particle glass transition temperature T_g can be used as a convenient parameter (typically more easily accessible in experiments than the Hamaker constant A_H) to estimate the degree of stability of a colloidal suspension with respect to particle coagulation. In particular, wthin DLVO theory, we find that the novel relationship of direct proportionality between T_g and A_H, implies the CCIS to monotonically decrease as a function of T_g. We conclude the Letter discussing how our theoretical predictions can be connected to the recent experimental findings of Scott et al.[17]

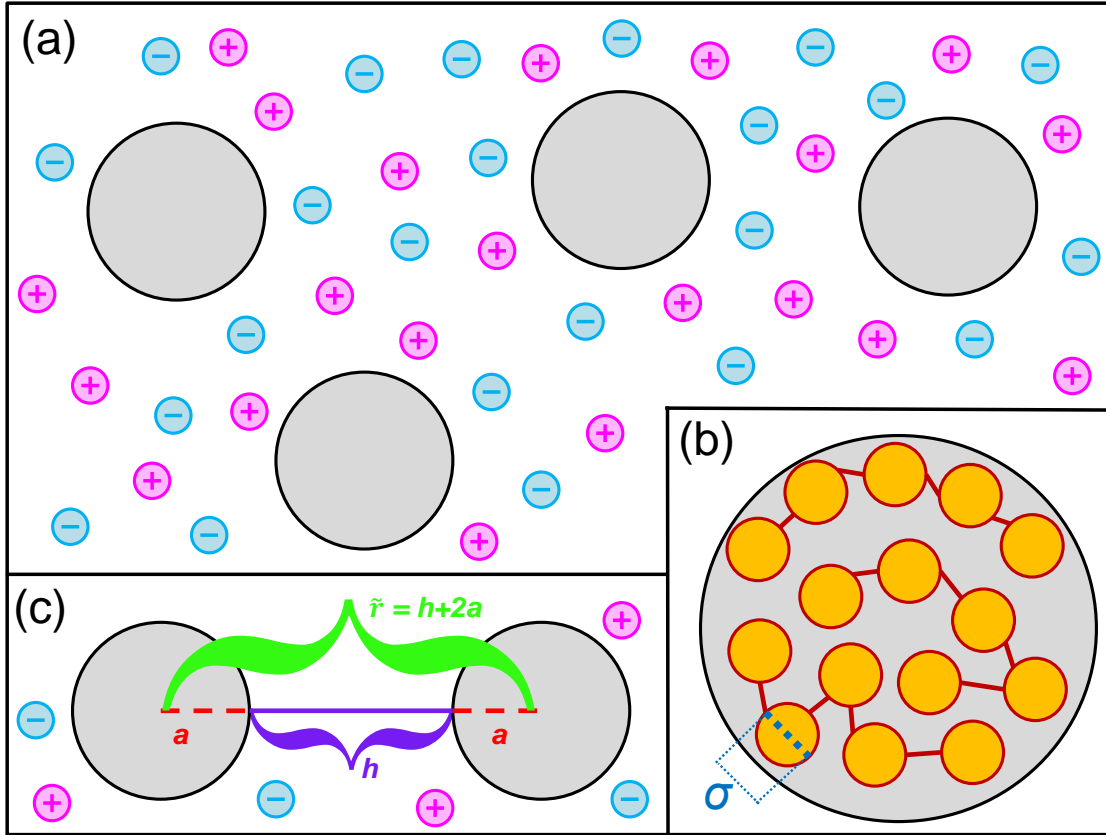A lot of research activity has been devoted to the general problem of the glass transition

Figure 1: (a) Sketch of the colloidal suspension considered in this Letter. Dispersed colloids have a spherical shape with radius a and, as showed in the zoom (b), consist of many polymer chains vitrified at a temperature T_g. The polymer chains have same length and chemical structure, and the monomer units inside each chain are spheres with diameter σ. Small magenta and light blue particles indicate positive and negative electrolytes, respectively, which are present in the solution. In (c) a zoom on two particles is considered. While h is the surface distance, $\tilde{r} = h + 2a$ is the center-to-center separation.

in the last decades[21,22]. While most available theories focus on the glass transition viewed "from the liquid", i.e. study the dynamical arrest occurring by further cooling a (supercooled) liquid, for many applications it is more useful to follow the alternative approach of Zaccone and Terentjev[20], which focuses on the glass transition viewed "from the solid", i. e. studying the melting of an amorphous solid into a liquid. This perspective allows one to deal with the vitrification phenomenon by means of the tools of solid state science, in particular the nonaffine response theory of glasses,[23] and to extract a (mechanical) signature of the glass transition from the temperature dependence of the low-frequency shear modulus G. More specifically, within nonaffine response theory, the shear modulus G of an amorphous solid can be analytically linked to the average number of intermolecular contacts per particle (e. g. a monomer subunit group in a polymer chain) z[24,25]. In turn, z can be connected to the absolute temperature T and the glass transition temperature T_{g} can be estimated by means of a generalized Born melting criterion[26] as the critical value of T at which G vanishes, i. e. $G(T_{\mathrm{g}}) = 0$[20].

In the presence of structural disorder, a solid lattice deforms under an applied strain very differently from well-ordered centrosymmetric crystals[27–30]. In the latter, indeed, the forces transmitted to every atom upon deformation by its bonded neighbors, cancel to zero. By contrast, due to the lack of local inversion symmetry, these forces do not balance in amorphous solids and can only be relaxed through a *nonaffine* displacement which adds to the *affine* one dictated by the macroscopic strain. In other words, as a consequence of the lattice disorder, atomic displacements in amorphous solids are strongly nonaffine. As nonaffine displacements are performed at the expense of the internal energy of the solid, the free energy of deformation of an amorphous solid under a shear strain γ, has to be expressed as $F(\gamma) = F_{\mathrm{A}}(\gamma) + F_{\mathrm{NA}}(\gamma)$, where $F_{\mathrm{A}}(\gamma)$ and $F_{\mathrm{NA}}(\gamma)$ are the affine contribution (provided by the framework of Born-Huang lattice dynamics[31]), and the nonaffine contribution, respectively. Starting from $F(\gamma)$, an analytic expression for the shear modulus G of an amorphous lattice can be derived by resorting to an eigenfunction decomposition of the nonaffine contribution.

This has been done, for example, by Lemaître and Maloney[32] and the result is given by $G = G_{\mathrm{A}} - G_{\mathrm{NA}} = G_{\mathrm{A}} - \sum_i \mathbf{f}_i^T \sum_j \mathbf{H}_{ij}^{-1} \mathbf{f}_j$, where $\mathbf{H}_{ij} = (\partial^2 \tilde{U}/\partial \mathbf{r}_i \partial \mathbf{r}_j)_{\gamma \to 0}$ represents the standard dynamical matrix of the solid[33], $\tilde{U}$ the internal energy of the system, and $\mathbf{f}_i$ the force per unit strain acting on the atoms due to the shear deformation[32]. As shown in Refs.[20,24,25], assuming central-force interactions, G can be evaluated analytically as

$$G = G_{\mathrm{A}} - G_{\mathrm{NA}} = \frac{2}{5\pi} \frac{\tilde{\kappa}}{R_0} \phi(z - z_c), \tag{1}$$

where ϕ is the packing fraction of the system, R_0 is the equilibrium lattice constant in the undeformed frame, and $\tilde{\kappa}$ is the lattice spring constant evaluated as $\tilde{\kappa} = \left(\partial^2 \tilde{U}/\partial \underline{u}_{ij}^2\right)_{R_0}$. The nonaffine contribution is encoded in Eq. (1) in the term proportional to z_c. More specifically, z_c is a rigidity threshold defining the critical coordination at which the system is no longer rigid, because all the lattice potential energy is "spent" on sustaining the nonaffine motions and no energy is left to support the elastic response to deformation. In general, z_c is proportional to the total number of degrees of freedom involved in the nonaffine energy relaxation, i. e. for purely central interactions in a d-dimensional space $z_c = 2d$. In the $d = 3$ case, it follows $z_c = 6$, consistently with purely central forces, $G \sim (z - 6)^{[24,27]}$.

It is worthwhile noticing that the direct contribution of thermal phonons to the elastic response is not included in the expression (1) of the shear modulus and will be neglected throughout this Letter, as for many materials it is very small compared with the contribution of nonaffinity[20].

The crucial effect which controls the temperature dependence of the shear modulus G of an amorphous solid is the change in the atomic connectivity z due to the Debye-Grüneisen thermal expansion. Upon approaching the glass transition temperature T_{g} from below, this effect is responsible for the loss of mechanical stability at $z = z_c$. When heated, the volume V of real molecular and atomic glasses increases. As a consequence, the atomic packing fraction ϕ decreases, an effect mediated by the thermal expansion coefficient defined as

$\alpha_T \equiv \frac{1}{V}(\partial V/\partial T) = -\frac{1}{\phi}(\partial \phi/\partial T)$. Integrating this relation, ϕ can be seen to evolve with T according to $\ln(1/\phi) = \alpha_T T + c$, with c an integration constant. The average intermolecular connectivity of the monomers z, instead, can be shown[20] to decrease while increasing T according to the relation

$$z(T) - z_c = \sqrt{\phi_c\left[e^{\alpha_T(T_g - T)} - 1\right]}, \tag{2}$$

where ϕ_c is the (critical) packing fraction, reached by the system at the glass transition. Insertion of Eq. (2) into Eq. (1), reveals T_g to correspond to the temperature at which the condition $z(T_g) = z_c$, causing the shear modulus G to vanish, is reached. In other words, T_g is the temperature at which the average number of total mechanical contacts on each atom z becomes just sufficient to compensate non-affine relaxation and the glass consequently ceases to be an elastic solid[20,24].

The theory depicted above can be employed to deal with the vitrification within the nanoparticles dispersed in a colloidal suspension. As already stated, we consider the case of colloidal particles consisting of several polymer chains, each composed of n monomer units with identical chemical structure. For this kind of systems, the framework of Zaccone and Terentjev allows one to find an estimate for the glass transition temperature T_g, by accounting for both covalent bonds along the chain and central-force London-van der Waals interactions. As noticed in Refs.[20,34], for these systems the critical packing fraction ϕ_c occupied by the monomers at the glass transition can be reasonably expressed as

$$\phi_c = \phi_c^* - \Lambda \cdot z_{co}, \tag{3}$$

where $z_{co} = 2(1-1/n)$ is the average connectivity due to intra-chain covalent bonds, ϕ_c^* is the maximum packing fraction occupied by the monomers at the glass transition in the absence of covalent bonds (i. e. in case $z_{co} = 0$), and Λ is a parameter expressing the effect of topological constraints due to covalent bonds on ϕ_c. It follows that, when the already mentioned relation $\ln\left(1/\phi\right) = \alpha_T T + c$ is evaluated at the glass transition (T_g, z_c, ϕ_c), after linearization, one

correctly obtains the Fox-Flory type[35] relation between T_g, thermal expansion and molecular weight:[20]

$$\alpha_T T_g \approx (1 - c - \phi_c^* + 2\Lambda) - \frac{2\Lambda}{n}. \tag{4}$$

When considering the values $n \approx 200$, $c \approx 0.48$, $\Lambda \approx 0.1$, $\alpha_T = 2 \cdot 10^{-4} \mathrm{K}^{-1}$, $\phi_c^* \approx 0.64$ (i. e. ϕ_c^* coinciding with the random close packing of a system of hard spheres[36–40]) as found in polymer glass[36,37,41] and $T_g = 383$ K, a $G(T)$ profile in agreement with experimental data of Ref.[42] follows from the insertion of Eq. (4) into the relations (2) and (3), and of the resulting expressions, in turn, into Eq. (1) (see e. g. Fig. 4 of Ref.[20]).

In this Letter, we show that Eq. (4) can be used to estimate how T_g affects the stability of a colloidal suspension. We recall that DLVO theory assumes the colloidal particles dispersed in a hosting solvent to interact through the pair potential[8,9]

$$V_{\mathrm{DLVO}}(h) = V_{\mathrm{vdW}}(h) + V_{\mathrm{R}}(h), \tag{5}$$

where the attractive vdW energy $V_{\mathrm{vdW}}(h)$ and repulsive electrostatic interaction energy $V_{\mathrm{R}}(h)$ are expressed as a function of the smallest surface separation distance h. The latter is given by (see Fig. 1(c)) $h = \tilde{r} - 2a$, where a is the radius of the spherical colloids and $\tilde{r}$ their center-to-center separation. In particular, the vdW attraction acting between two spherical colloids can be written as[18]

$$V_{\mathrm{vdW}}(h) = \frac{-A_{\mathrm{H}}}{12} \left(\frac{a^2}{h^2 + 2ah} + \frac{a^2}{(a+h)^2} + 2 \log \frac{h^2 + 2ah}{(a+h)^2} \right), \tag{6}$$

from which it is clear that the Hamaker constant A_{H} (being typically a positive quantity) measures how strong the attraction is among the dispersed colloids and hence contributes to quantifying the colloidal stability of the suspension. In the following, we prove that A_{H} can be quantitatively connected to the thermal expansion coefficient α_T and, consequently, derive a link between intra-particle glass transition temperature T_g and colloidal stability,

exploiting Eq. (4).

To establish a link between α_T and A_H, we focus on the interaction among monomers of different chains in each colloid and show how α_T can be computed once the non-covalent interaction pair potential $U(r)$ between two monomers separated by a distance r, is known. To start, we notice that α_T can be written in terms of the *linear* thermal expansion coefficient α_l, as $\alpha_T \approx 3\alpha_l$. In turn, α_l can be defined as

$$\alpha_l \equiv \frac{1}{\sigma}\frac{d\langle x \rangle}{dT}, \tag{7}$$

where σ is the hard-core diameter of a single monomer (see Fig. 1(b)), and $\langle x \rangle$ is the average displacement of the monomers from their equilibrium positions, i.e. $\langle x \rangle$ represents the average value of the quantity $x \equiv r - r_{\min}$ with $r_{\min}$ being the bonding minimum of $U(r)$. Albeit belonging to a glassy out-of-equilibrium state, each monomer can be safely assumed to be locally at thermal equilibrium, such that $\langle x \rangle$ can be evaluated in the Boltzmann ensemble as

$$\langle x \rangle \equiv \frac{\int_{-\infty}^{\infty} x\, e^{-\beta U(x)} dx}{\int_{-\infty}^{\infty} e^{-\beta U(x)} dx}, \tag{8}$$

where U is expressed as a function of x, and $\beta \equiv (k_B T)^{-1}$ is the Boltzmann factor.

As shown by Kittel[43], a convenient way to compute $\langle x \rangle$ from Eq. (8) is to consider a Taylor expansion of $U(x)$, which (up to fourth order) reads

$$U(x) = \zeta_2 x^2 - \zeta_3 x^3 - \zeta_4 x^4, \tag{9}$$

with ζ_2, ζ_3 and ζ_4 real and positive coefficients. By assuming that the cubic and quartic anharmonic correction terms in Eq. (9) are small compared to $k_B T$, it is possible to write $\int_{-\infty}^{\infty} x\, e^{-\beta U(x)} dx \approx \int_{-\infty}^{\infty} x\, e^{-\beta \zeta_2 x^2}(1 + \beta\zeta_3 x^3 + \beta\zeta_4 x^4)dx \approx (3\pi^{1/2}\zeta_3/4\zeta_2^{5/2})\beta^{-3/2}$ and

$\int_{-\infty}^{\infty} e^{-\beta U(x)} dx \approx (\pi/\beta\zeta_2)^{1/2}$, respectively. As a consequence, Eq. (8) becomes

$$\langle x \rangle = \frac{3}{4} \frac{\zeta_3}{\zeta_2^2} k_B T. \tag{10}$$

So, for a given non-covalent interaction pair potential $U(r)$, once the coefficients ζ_2 and ζ_3 in the Taylor expansion (9) are known, the average displacement of the monomers $\langle x \rangle$ can be estimated through Eq. (10) and the linear thermal expansion coefficient α_l can be in turn obtained by using Eq. (7). Finally, the thermal expansion coefficient α_T can be obtained as $\alpha_T = 3\alpha_l$.

In this Letter we assume that, within each colloidal particle, the non-covalent interaction pair potential $U(r)$ acting among monomers of different chains is dominated by attractive dispersion forces that decay as r^{-6}. A (simple) expression, derived by London, for these attractive dispersion forces reads as[44]

$$U_{\mathrm{L}}(r) \approx -\frac{3}{4} \frac{I \alpha_0^2}{r^6}, \tag{11}$$

where I and α_0 are the first ionization potential and the (material) polarizability, respectively. It follows that a good approximation for $U(r)$ is given by the Lennard-Jones potential $U_{\mathrm{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where σ is the hard-core diameter of each monomer (see Fig. 1(b)) and the identification $\epsilon \approx 3I\alpha_0^2/(16\sigma^6)$ is considered.

Once the non-covalent inter-monomer interaction potential $U_{\mathrm{LJ}}(r)$ is specified, we follow the method introduced by Kittel and recalled above to compute the thermal expansion coefficient α_T. We consider a Taylor expansion of U_{LJ} expressed as a function of $x \equiv r - r_{\min}$, with $r_{\min} = 2^{1/6}\sigma$ the single (physically meaningful) minimum of $U_{\mathrm{LJ}}(r)$. Up to third order, the expansion reads as

$$U_{\mathrm{LJ}}(x) \approx -\epsilon + \frac{36\epsilon}{\sigma^2} 2^{2/3} x^2 - \frac{756\epsilon}{\sigma^3} \sqrt{2} x^3. \tag{12}$$

By comparing Eq. (12) to Eq. (9), it follows that $2^{3/2}\sigma^2\zeta_2 = -36\epsilon$ and $\sigma^3\zeta_3 = 756\sqrt{2}\epsilon$, respectively, such that, from Eqs. (10) and (7) (and recalling $\alpha_T = 3\alpha_l$), one obtains

$$\alpha_T = \frac{7}{2^{5/6}}\frac{k_B\sigma^6}{I\alpha_0^2}. \tag{13}$$

Expression (13) can be exploited to connect α_T to the Hamaker constant A_H. According to the London-Hamaker formula[18], A_H can be written in terms of the parameters I and α_0 of the London potential (11) as

$$A_H = \frac{3\pi^2}{4}I\alpha_0^2\rho^2, \tag{14}$$

where ρ is the number of monomers per unit volume in the colloidal particles. From a comparison between Eq. (14) and Eq. (11), A_H can be clearly seen to measure the strength of attraction within the colloids. By using the definition of packing fraction of spheres $\phi = \frac{4}{3}\pi(\frac{\sigma}{2})^3\rho$, insertion of Eq. (14) into Eq. (13) leads to

$$\alpha_T = \frac{189}{2^{5/6}}\phi^2\frac{k_B}{A_H}, \tag{15}$$

such that, from Eq. (4) it follows

$$\frac{A_H}{k_BT_g} = K, \tag{16}$$

with

$$K = \frac{189}{2^{5/6}}\phi_c^2(1 - c - \phi_c + 2\Lambda)^{-1}. \tag{17}$$

In Eq. (17) we have neglected the last term on the r.h.s. of Eq. (4) as it is small for long ($n \approx 200$) chains, and evaluated ϕ at the glass transition. We recall that a reasonable expression for ϕ_c is given by Eq. (3).

   Equations (15) and (16) represent the main result of this Letter. They are molecular-level relationships, (to the best of our knowledge) never reported before, connecting α_T and T_g, respectively, to the Hamaker constant A_H of a colloidal suspension. From Eq. (6), it is clear

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that A_H controls the stability of a colloidal suspension as it quantifies the strength of the vdW attraction among the dispersed colloids. The effect of T_g on colloidal stability follows from the direct proportionality relation between T_g and A_H expressed by Eq. (16). From a physical point of view, a larger value of the intra-particle glass transition temperature T_g corresponds to a larger value of the Hamaker constant of the suspension and hence, from Eq. (14), to a larger cohesive energy of London dispersion forces between the polymer chains inside each colloid. Indeed, the larger T_g, the larger the amount of energy required to "break" the cohesive non-covalent interactions, which is necessary to "melt" the polymer glassy chains within the colloid particle. In this sense, both T_g and A_H are measures of the strength of the non-covalent London-vdW forces between monomers inside the colloid, and they must be related to each other. This quantitative relation has been provided in this Letter by Eqs.(15) and (16).

Equation (16) represents also a new way to estimate the Hamaker constant once the rheological $G(T)$ of the glassy polymer, from which the colloid particles are made, is known.

Equation (16) can be finally used to estimate how T_g affects the upper limit for salt addition beyond which particles begin to aggregate, i.e. how T_g affects the CCIS of colloidal suspensions. We recall that, following Derjaguin and Landau[8], the CCIS can be computed directly from the interaction energy profile (5) provided that an expression for the repulsive term $V_R(h)$ is known. A simple expression for $V_R(h)$ can be derived by using the Debye-Hückel approximation[13], according to which one writes

$$V_R(h) \approx V_{dl}(h) = 2\pi R \epsilon_0 \epsilon \psi_{dl}^2 e^{-\kappa h}, \tag{18}$$

where ϵ is the dielectric constant, ϵ_0 is the vacuum permittivity, ψ_{dl} is the diffuse-layer potential, and the inverse Debye length κ is defined in terms of the ionic strength I and the elementary charge q according to $\kappa^2 \equiv 2q^2 I/(k_B T \epsilon_0 \epsilon)$. The CCIS corresponds to the value
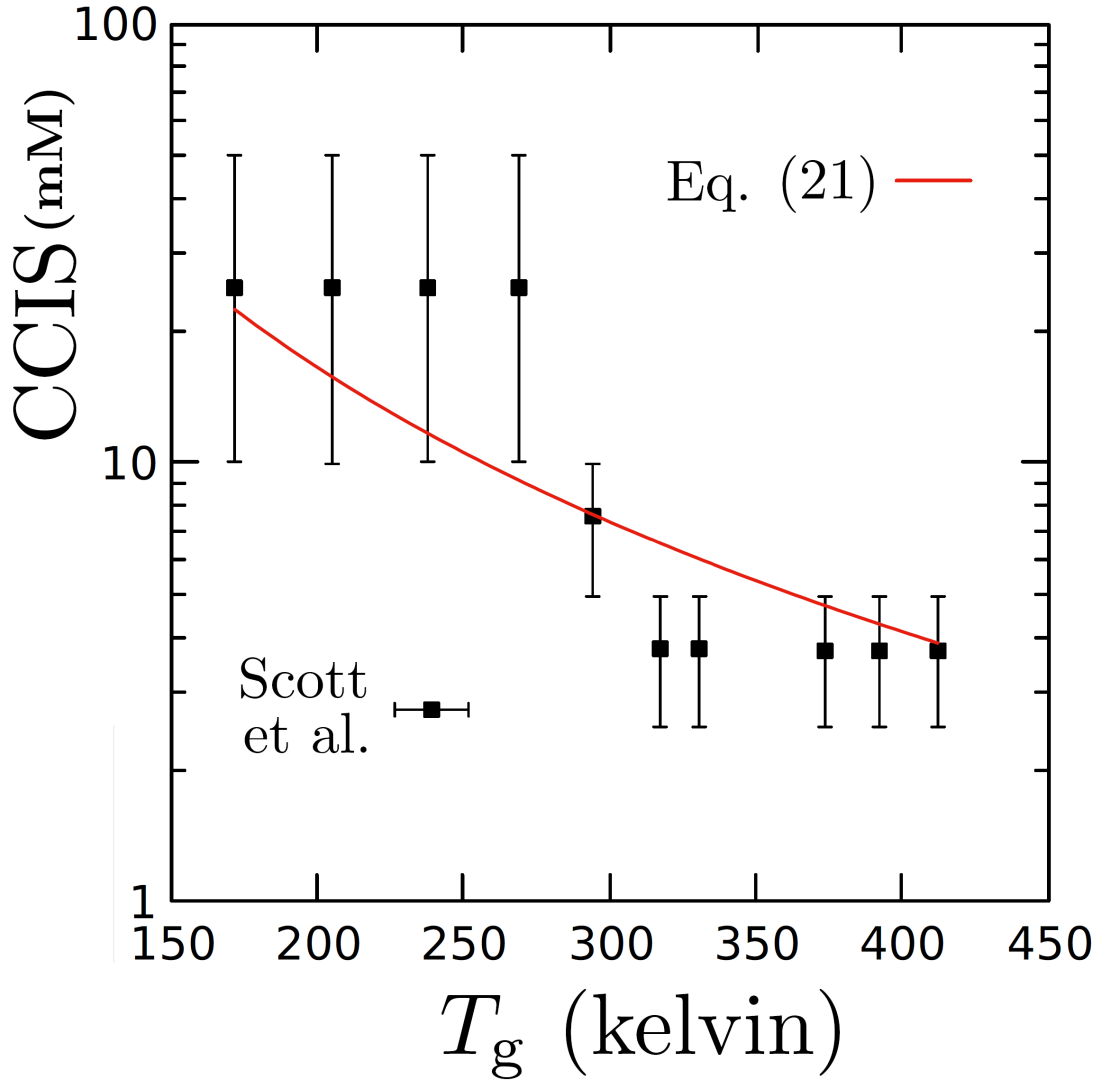
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Figure 2: Critical coagulation ionic strength (CCIS) as a function of the inter-particle glass transition temperature T_g. While points (and the corresponding error bars) are experimental data from Ref.[17], full line represents Eq. (21) with the proportionality constant obtained from a fit to experimental data. Both our theory and experiments from Scott et al. predict the CCIS to be a decreasing function of T_g. However, while theory predicts the decrease to be continuous and more gradual, the decrease in the experiments appears to be sharp. Data from Ref.[17] are obtained when adding KCl salt for which the CCIS coincide with the critical coagulation concentration (CCC).

of ionic strength I that satisfies the conditions

$$V_{\text{DLVO}}(h) = 0 \quad \text{and} \quad \frac{d V_{\text{DLVO}}(h)}{dh} = 0, \tag{19}$$

i. e. the CCIS represents the critical value of I at which there is no energy barrier against aggregation[8]. When the Debye-Hückel approximation (18) is used for the repulsive potential $V_{\text{R}}(h)$ and the Derjaguin approximation $a \gg h$[45] is considered in the attractive vdW potential (6), the conditions (19) lead to[13,14]

$$\text{CCIS} = \frac{72\pi}{e^2} \frac{1}{\lambda_B} \left(\frac{\epsilon\epsilon_0 \psi_{\text{dl}}^2}{A_{\text{H}}} \right)^2, \tag{20}$$

where e is the Neper's number and $\lambda_B \equiv q^2/(4\pi\epsilon\epsilon_0 k_B T)$ is the Bjerrum length. Upon inserting Eq. (16) into Eq. (20), the CCIS can be seen to vary as a function of the intra-particle glass transition temperature T_{g}, according to the relation

$$\text{CCIS} = \frac{72\pi}{e^2} \frac{K^{-2}}{\lambda_B} \left(\frac{\epsilon\epsilon_0 \psi_{\text{dl}}^2}{k_B T_{\text{g}}} \right)^2. \tag{21}$$

Equation (21) shows that the CCIS of a colloidal suspension decreases upon increasing T_{g}, with a law $\text{CCIS} \propto T_{\text{g}}^{-2}$. Moreover, Eq. (21) allows us to test our theory against the recent experimental results of Scott et al.[17] In particular, we consider data reported in Fig. 1 of Ref.[17] where the *critical coagulation concentration* (CCC), rather than the CCIS, of a suspension of electrostatic-stabilized polymer nanoparticles is measured by adding the hydrophilic KCl salt. In this case, the ionic strength I and the concentration c of the electrolytes present in the suspension are related by the condition[14] $I = z^2 c$, where z is the valency of the electrolytes. Since the ions resulting from the addition of the KCl salt have $z = 1$, the CCC and the CCIS coincide in this case.

A comparison between our theoretical prediction and the findings of Ref.[17] is presented in Fig. 2, where experimental data are plotted as symbols while Eq. (21) is represented

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by a full red line. The proportionality coefficient between CCIS and T_g^{-2} in Eq. (21) is obtained by a fit to the experimental data. Both our theory and experiments from Scott et al.[17] predict the CCIS to be a decreasing function of T_g. However, while theory predicts the decrease to be smooth, experiments rather display a sharper decrease, although this is difficult to ascertain due to the large error bars. Further investigation is required in the future to clarify this point and the possible influence of other effects that are not included in the above model. We hope this Letter will stimulate experimental and theoretical research along this line.

We observe that a different scaling between CCIS and A_H, namely CCIS $\propto A_H^{-2/3}$, can be obtained if the relationship $\sigma = \epsilon_0 \epsilon \kappa \psi_{dl}$, connecting the surface charge density σ to the diffuse-layer potential ψ_{dl}, is used into Eq. (18).[14] In this case, the proportionality relation CCIS $\propto T_g^{-2/3}$ can be derived from Eq. (16) . However at the moment we cannot say if this profile works better that of Eq. (21), given the large error bars in the experiments.

To conclude, in this Letter we theoretically investigated how the stability of a colloidal suspension with respect to coagulation is influenced by the glass-transition temperature, T_g, of the suspended colloidal particles. We started by identifying T_g with the point at which the glassy polymer chains within each colloid lose mechanical stability upon heating, as a consequence of the reduction of monomer connectivity driven by the Debye-Grüneisen thermal expansion. We supplemented this picture with basic solid-state science considerations about thermal expansion, and established two novel relationships connecting the Hamaker constant A_H of the suspension to the thermal expansion coefficient α_T and the intra-particle glass-transition temperature T_g, respectively. In particular, we found A_H to be directly proportional to T_g such that the latter quantity can be conveniently used as a key parameter (alternative to A_H) for controlling the stability of colloidal systems. The theory also provides an expression for the proportionality coefficient in terms of fundamental physical quantities. Finally, within DLVO theory, we derived the critical coagulation ionic strength (CCIS) to be a monotonically decreasing function of the T_g of the polymer.

The novel relations derived in this Letter may be useful for the design of colloidal materials whose stability can be tuned by varying the physical properties of the dispersed solid phase. For particles made of chemically complex materials, indeed, T_g is commonly a much more accessible quantity compared to the Hamaker constant.

In future studies, it will be of significant interest to investigate the stability of colloidal suspensions whose dispersed colloidal particles have not a single T_g but rather a distribution of glass-transition temperaures. In addition we aim to study the stability of suspensions whose dispersed particles have an internal crystal structure, as a function of the intra-particle melting temperature T_m. Analogously to the intra-particle glass transition temperature T_g, T_m can be connected to the thermal expansion coefficient α_T [46]. We furthermore plan to extend the theoretical framework presented in this Letter to predict the effect on colloidal stability of T_g in the presence of hydrophobic salts as those considered in Ref. [17] and to particles with non-spherical shape. [47]

Biographies

Acknowledgement

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