Growth and Aggregation Regulate Clusters Structural Properties and Gel Time

Electronic Supplementary Information

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Calculation of the hydrodynamic radius of a cluster made of interpenetrating particles having different sizes

In the following, we will use Kirkwood-Riseman (KR) theory extended to the case of clusters with partially-overlapping primary particles having different size.

We will begin by considering the general formalism of KR theory. For colloidal particles, the interactions with the surrounding fluid can be described in the framework of Stokes equations, according to which is the linear relationship between the hydrodynamic force experience by a particle and its relative velocity. The KR approach consists in writing that for each particle in a cluster the hydrodynamic force equals:

$$\mathbf{F}_i = 6\pi\eta R_{P,i}\left(\mathbf{u}_i - \mathbf{v}_i\right) \tag{1}$$

where $\mathbf{F}_i$ is the force acting on the i^{th} particle, $\mathbf{u}_i$ is the i^{th} particle velocity and $\mathbf{v}_i$ is the fluid velocity at the center of the i^{th} particle. The fluid velocity is written as a combination of the unperturbed fluid velocity and of the perturbations due to all other particles in the cluster. Assuming that there the unperturbed velocity of the fluid is zero, one can write:

$$\mathbf{v}_i = \mathbf{v}_i' = \sum_{j=1\neq i}^{N} \mathbf{T}_{ij} \cdot \mathbf{F}_j \tag{2}$$

In Equation(2), the tensor $\mathbf{T}_{ij}$ provides the relationship between the force acting on particle j and the corresponding velocity perturbation caused by it at the center of particle i [1]. By combining the two previous equations, we obtain the following result:

$$\mathbf{F}_i = 6\pi\eta R_{P,i}\left(\mathbf{u}_i - \sum_{j=1\neq i}^{N} \mathbf{T}_{ij} \cdot \mathbf{F}_j\right) \tag{3}$$

By taking the angular average of Equation (3) (which amounts to considering the cluster as an isotropic object), and by summing over the total number of particles N in a cluster, we can obtain the following expression for the total hydrodynamic force acting on it:

$$\mathbf{F}_T = \sum_{i=1}^{N} \mathbf{F}_i = \sum_{i=1}^{N} \left[6\pi\eta R_{P,i} \left(\mathbf{u}_i - \sum_{j=1\neq i}^{N} \left\langle \mathbf{T}_{ij} \right\rangle \cdot \mathbf{F}_j \right) \right] = \sum_{i=1}^{N} 6\pi\eta R_{P,i} \mathbf{u} - \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1\neq i}^{N} 6\pi\eta R_{P,i} \left\langle \mathbf{T}_{ij} \right\rangle \mathbf{F}_T \tag{4}$$

The latter equation can be rearranged as follows:

$$\mathbf{F}_T = \frac{6\pi\eta \sum_{i=1}^{N} R_{P,i}}{1 + \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1\neq i}^{N} 6\pi\eta R_{P,i} \left\langle \mathbf{T}_{ij} \right\rangle} \mathbf{u} \tag{5}$$

This leads to the following expression for the hydrodynamic radius of a cluster:

$$R_H = \frac{\sum_{i=1}^{N} R_{P,i}}{1 + \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1\neq i}^{N} 6\pi\eta R_{P,i} \left\langle \mathbf{T}_{ij} \right\rangle} \tag{6}$$

The only open question about the above equation, is the necessity to use a suitable expression for the tensor $\mathbf{T}_{ij}$, valid for partially overlapping spheres with different sizes. This requires an extension of Rotne-Prager-Yamakawa tensor, valid for equal size particles [2]. Such an expression has been developed by Zuk et al.[3]:

$$\mathbf{T}_{ij}=\begin{cases}\dfrac{1}{8\pi\eta R_{ij}}\left(\left(1+\dfrac{R_{p,i}{}^{2}+R_{p,j}{}^{2}}{3R_{ij}^{2}}\right)\underline{\mathbf{I}}+\left(1-\dfrac{R_{p,i}{}^{2}+R_{p,j}{}^{2}}{R_{ij}^{2}}\right)\dfrac{\mathbf{R}_i\mathbf{R}_j}{R_{ij}^{2}}\right) & \text{for } R_{ij}\geq R_{p.i}+R_{p,j}\\ \dfrac{1}{6\pi\eta R_{p,i}R_{p,j}}\left(\left(\dfrac{16R_{ij}^{3}\left(R_{p,i}+R_{p,j}\right)-\left(\left(R_{p,i}-R_{p,j}\right)^{2}+3R_{ij}^{2}\right)^{2}}{32R_{ij}^{3}}\right)\underline{\mathbf{I}}+\left(\dfrac{3\left(\left(R_{p,i}-R_{p,j}\right)^{2}-R_{ij}^{2}\right)^{2}}{32R_{ij}^{3}}\right)\dfrac{\mathbf{R}_i\mathbf{R}_j}{R_{ij}^{2}}\right) & \text{for } R_{p,>}-R_{p,<}\leq R_{ij}\leq R_{p,i}+R_{p,j}\\ \dfrac{1}{6\pi\eta R_{p,>}}\underline{\mathbf{I}} & \text{for } R_{ij}\leq R_{p,>}-R_{p,<}\end{cases} \quad (7)$$

By performing the orientation average, we obtain the following final result:

$$\left\langle\mathbf{T}_{ij}\right\rangle=\begin{cases}\dfrac{1}{6\pi\eta R_{ij}}\underline{\mathbf{I}} & \text{for } R_{ij}\geq R_{p.i}+R_{p,j}\\ \dfrac{1}{6\pi\eta R_{p,i}R_{p,j}}\left(\dfrac{\left(R_{p,i}+R_{p,j}\right)}{2}-\dfrac{R_{ij}}{4}-\dfrac{\left(R_{p,i}-R_{p,j}\right)^{2}}{4R_{ij}}\right)\underline{\mathbf{I}} & \text{for } R_{p,>}-R_{p,<}\leq R_{ij}\leq R_{p,i}+R_{p,j}\\ \dfrac{1}{6\pi\eta R_{p,>}}\underline{\mathbf{I}} & \text{for } R_{ij}\leq R_{p,>}-R_{p,<}\end{cases} \quad (8)$$

When Equation (8) is substituted in Equation (6), we obtain the general expression used for the calculation of the hydrodynamic radius of the clusters generated by the Monte Carlo code developed in this work.

Convergence on N_{MAX}

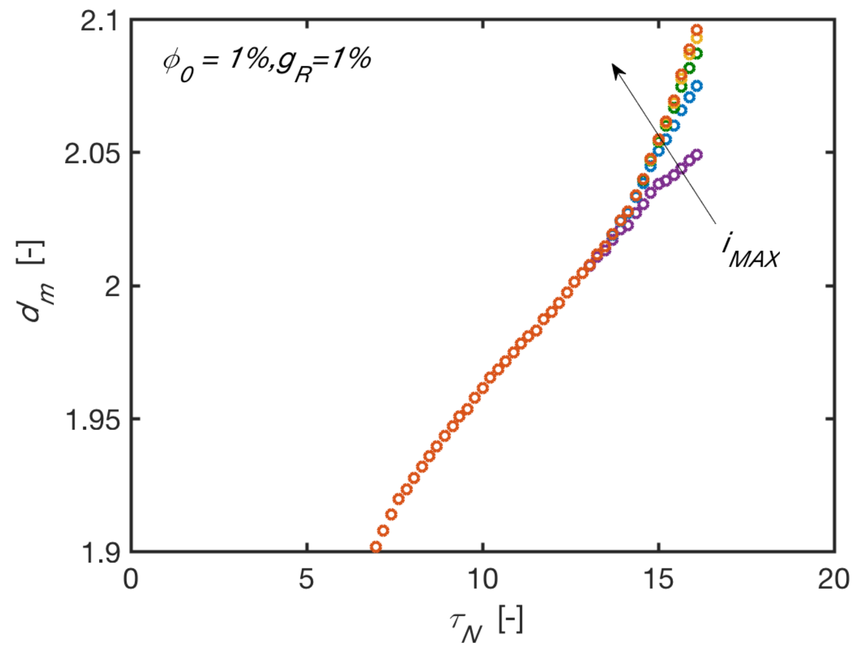

Figure S1 d_m vs τ_N in DLCA at $\phi_0 = 1\%$ and $g_R = 1.00\%$ for different values of i_{MAX}. Color code: violet $i_{MAX} = 1000$; blue $i_{MAX} = 2000$; green $i_{MAX} = 3000$; yellow $i_{MAX} = 4000$; red $i_{MAX} = 5000$.

As $i_{MAX} = 4000$ and $i_{MAX} = 5000$ are superimposed, $i_{MAX} = 5000$ has been selected as the upper boundary of cluster mass to be considered for the calculation of d_m

DLCA case – kinetic information

i) ϕ against τ_N

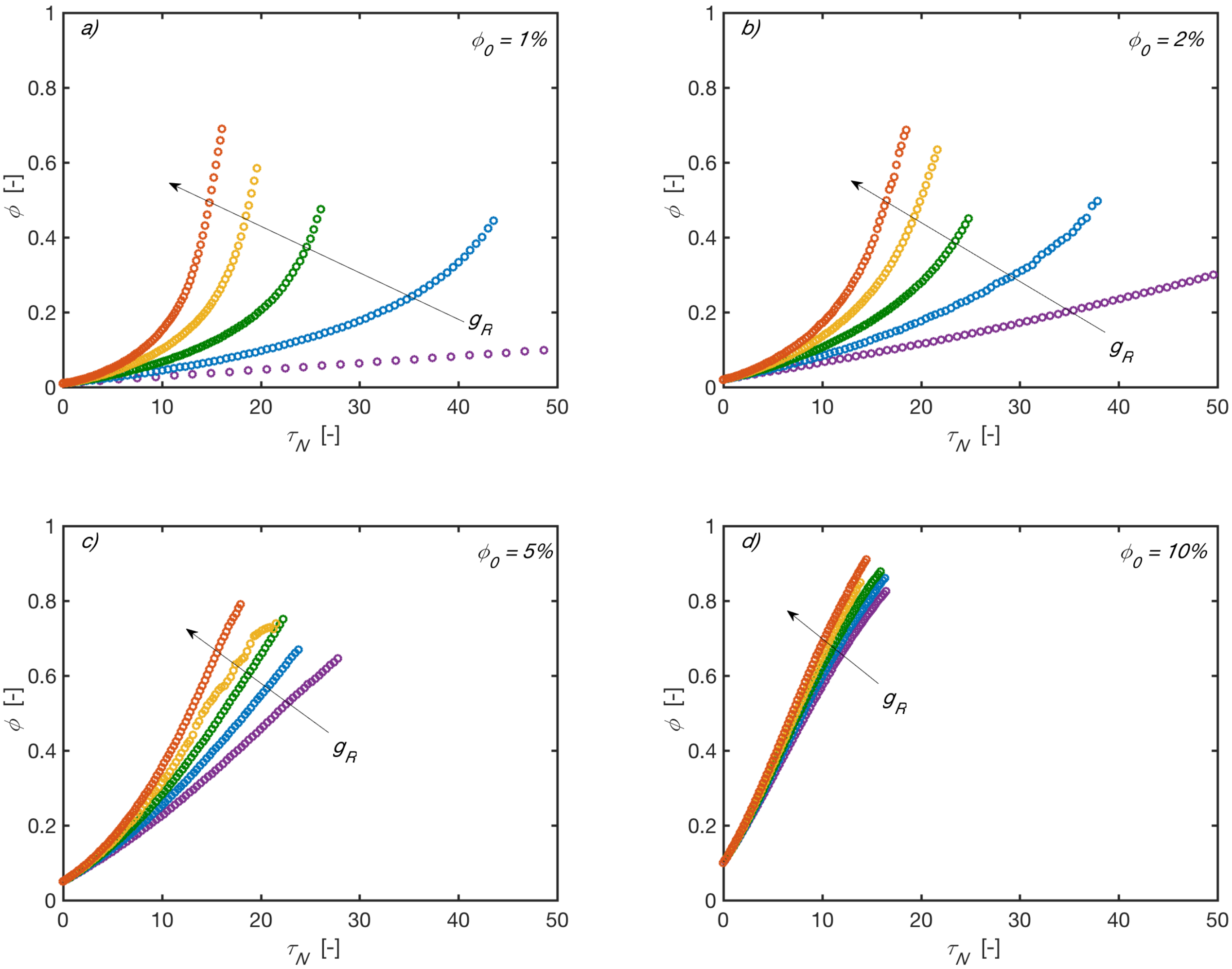

Figure S2 ϕ vs τ_N in DLCA at different ϕ_0 and g_R. Color code: violet $g_R = 0.00\%$; blue $g_R = 0.25\%$; green $g_R = 0.50\%$; yellow $g_R = 0.75\%$; red $g_R = 1.00\%$

ii) N_{AVE} against τ_N

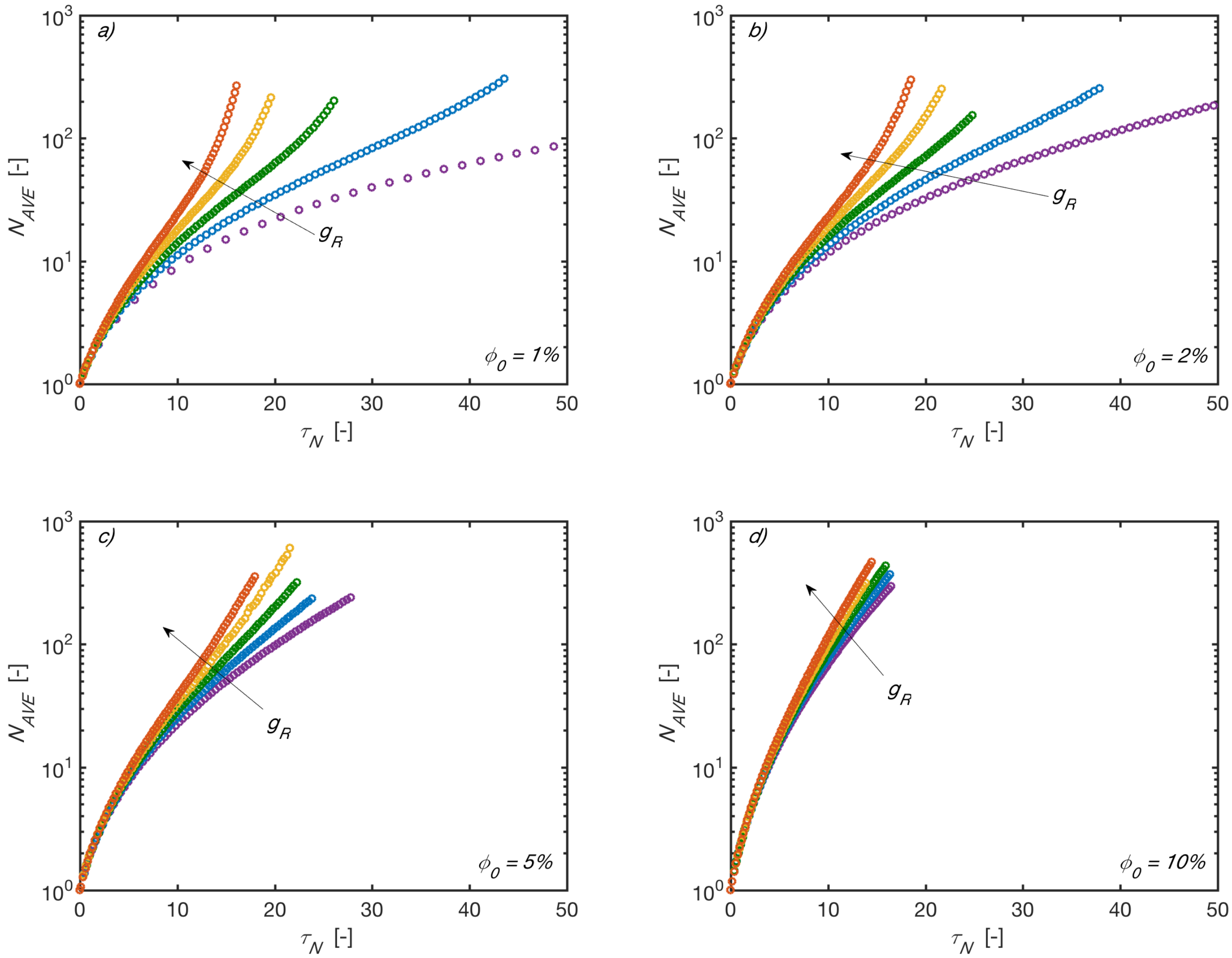

Figure S3 N_{AVE} vs τ_N in DLCA at different ϕ_0 and g_R. Color code: violet $g_R = 0.00\%$; blue $g_R = 0.25\%$; green $g_R = 0.50\%$; yellow $g_R = 0.75\%$; red $g_R = 1.00\%$

iii) ϕ_P against τ_N

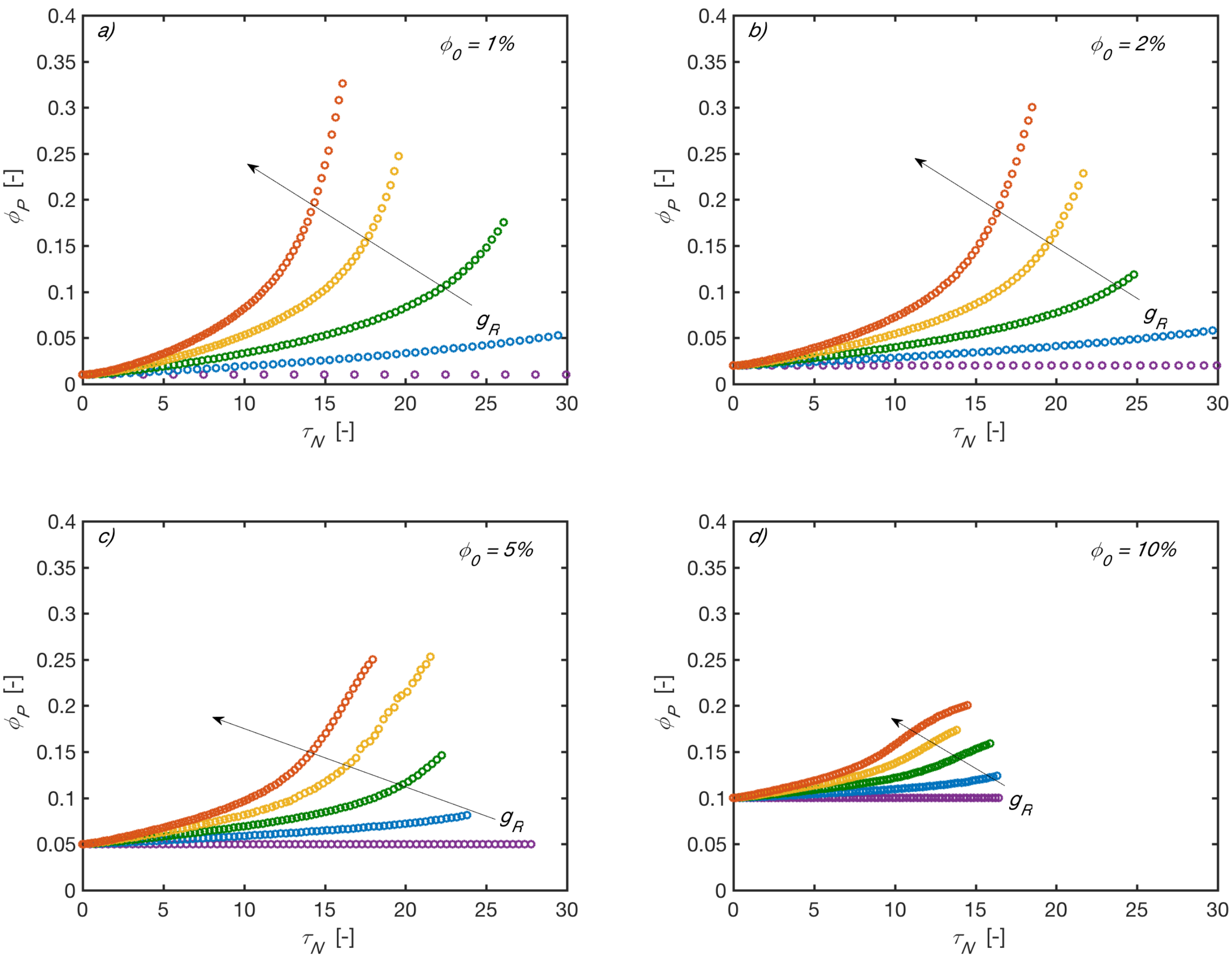

Figure S4 ϕ_P vs τ_N in DLCA at different ϕ_0 and g_R. Color code: violet $g_R = 0.00\%$; blue $g_R = 0.25\%$; green $g_R = 0.50\%$; yellow $g_R = 0.75\%$; red $g_R = 1.00\%$

RLCA case – kinetic information

i) ϕ against τ_N

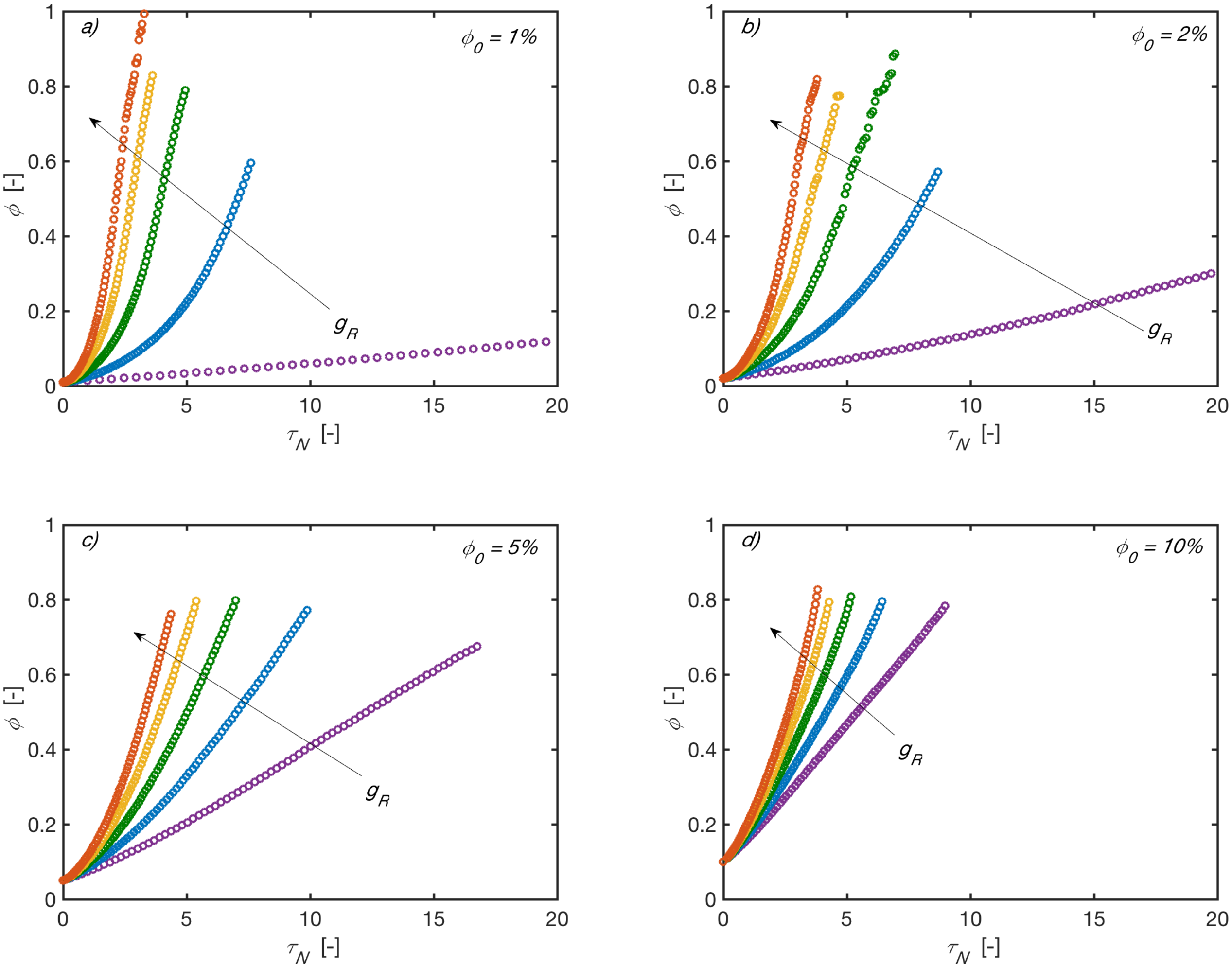

Figure S5 ϕ vs τ_N in RLCA with $p_S = 0.1$ at different ϕ_0 and g_R. Color code: violet $g_R = 0.00\%$; blue $g_R = 0.25\%$; green $g_R = 0.50\%$; yellow $g_R = 0.75\%$; red $g_R = 1.00\%$

ii) N_{AVE} against τ_N

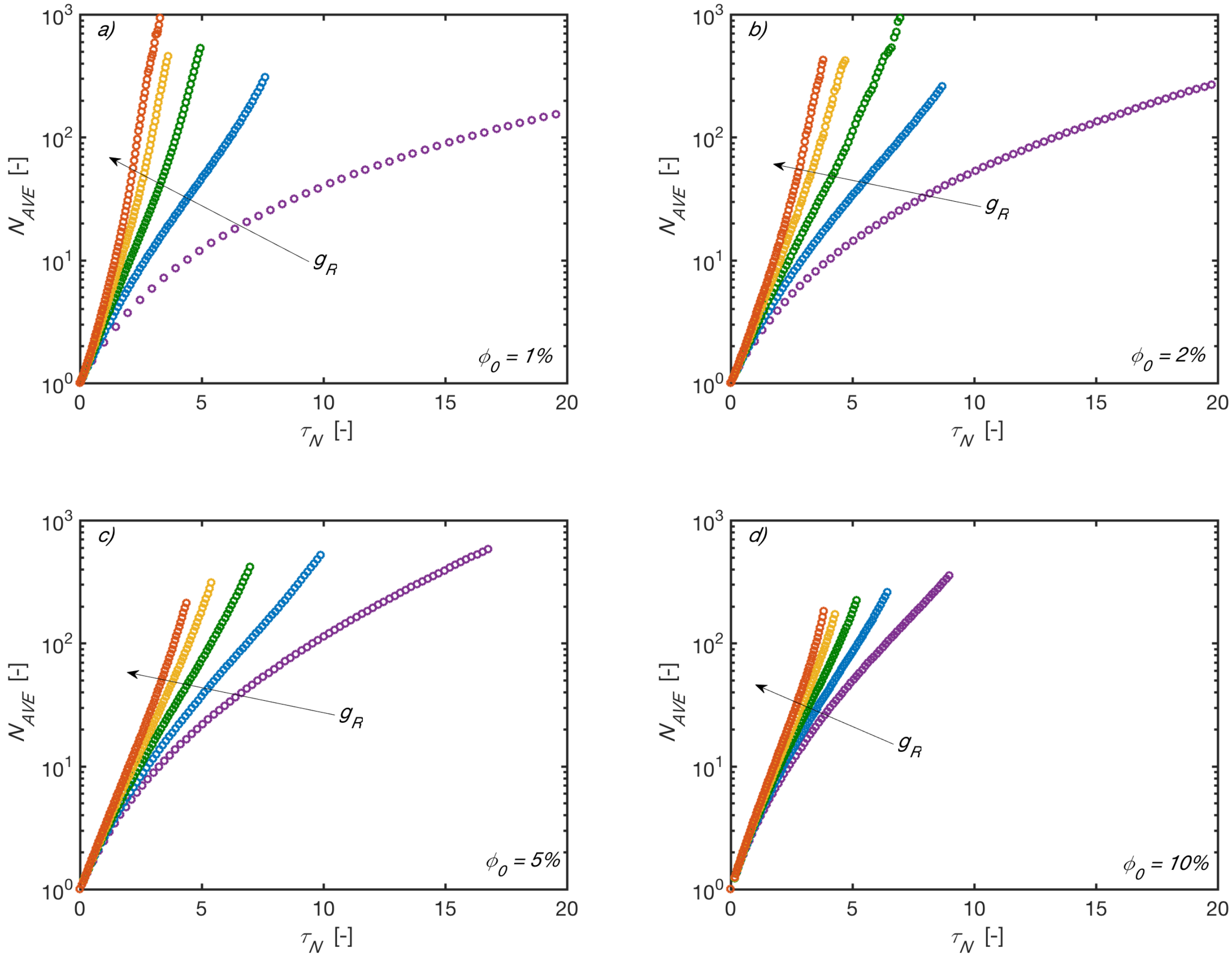

Figure S6 N_{AVE} vs τ_N in RLCA with $p_S = 0.1$ at different ϕ_0 and g_R. Color code: violet $g_R = 0.00\%$; blue $g_R = 0.25\%$; green $g_R = 0.50\%$; yellow $g_R = 0.75\%$; red $g_R = 1.00\%$

iii) ϕ_P against τ_N

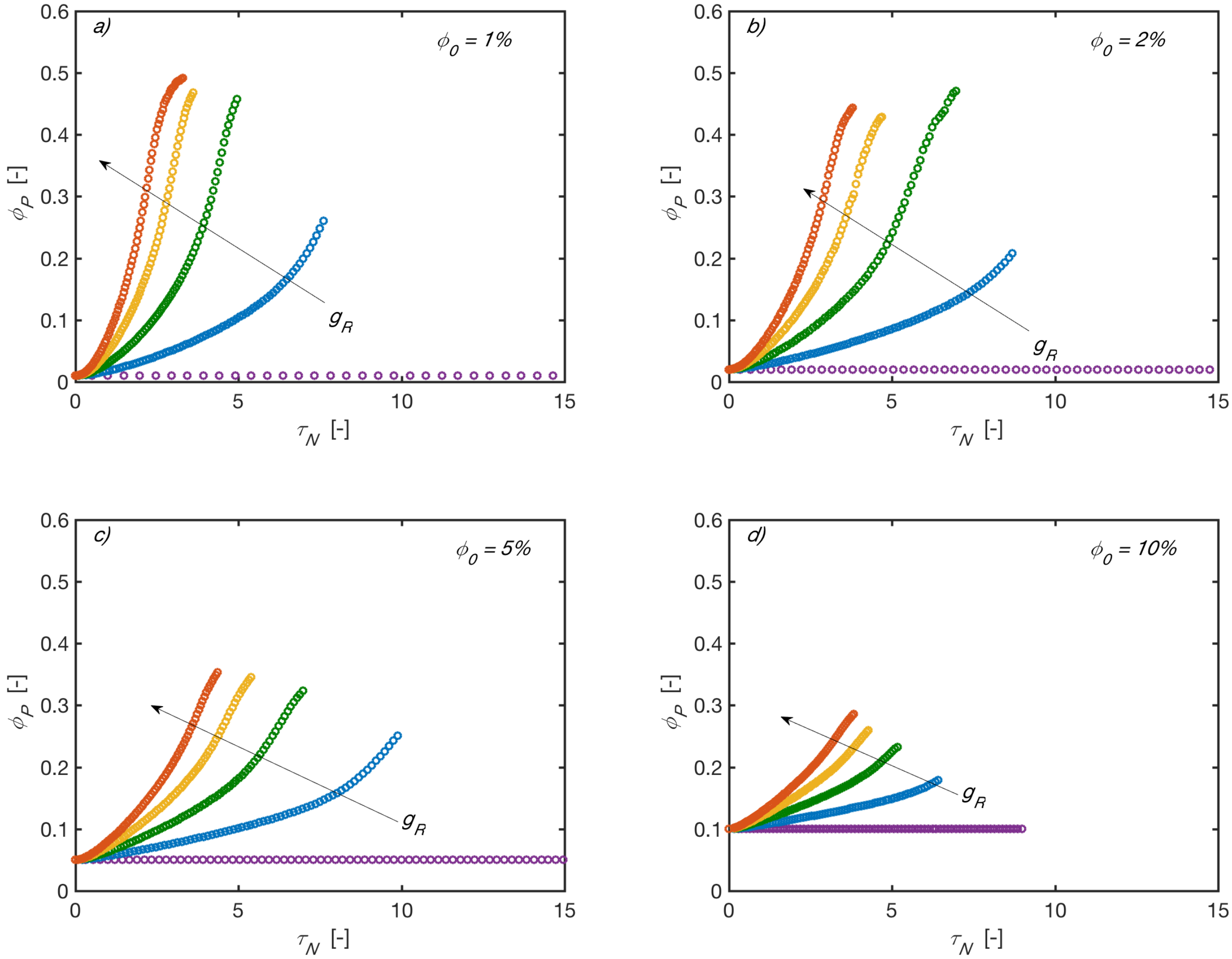

Figure S7 ϕ_P vs τ_N in RLCA at different ϕ_0 and g_R. Color code: violet $g_R = 0.00\%$; blue $g_R = 0.25\%$; green $g_R = 0.50\%$; yellow $g_R = 0.75\%$; red $g_R = 1.00\%$

References

1. Lattuada, M.; Wu, H.; Morbidelli, M. Hydrodynamic radius of fractal clusters. *Journal of Colloid and Interface Science* **2003,** *268* (1), 96-105.
2. Lazzari, S.; Jaquet, B.; Colonna, L.; Storti, G.; Lattuada, M.; Morbidelli, M. Interplay between Aggregation and Coalescence of Polymeric Particles: Experimental and Modeling Insights. *Langmuir* **2015,** *31* (34), 9296-9305.
3. Zuk, P. J.; Wajnryb, E.; Mizerski, K. A.; Szymczak, P. Rotne-Prager-Yamakawa approximation for different-sized particles in application to macromolecular bead models. *Journal of Fluid Mechanics* **2014,** *741*.