



Original Article

Gelation of Anisotropic Colloids with Short-Range Attraction

Dang Minh Triet^{1,*}, Truong Quoc Tuan², Tran Van Thien²

¹*School of Education, Can Tho University, Vietnam*

²*College of Natural Sciences, Can Tho University, Vietnam*

Received 10 January 2020

Revised 19 February 2020; Accepted 21 February 2020

Abstract: Colloidal gels are space-spanning networks that form solids at dilute particle volume fractions. The kinetic process of gelation is central to understand the flow of complex fluids. Here, we report a simulation study of colloidal gelation of anisotropic colloids with attractive Lennard-Jones potential. These forces quasi-model the critical Casimir effect far from the critical solvent fluctuations acting on colloidal patches. By tuning the depths of the patch-to-patch particle interactions and the selected colloidal patches, we dynamically arrest the colloids to form gels. We find that thermal density fluctuation is the key factor to activate colloidal cluster space spanning: the balance between clustering and break-up mechanism is important for the gelation process of anisotropic systems. These results open new opportunities for studying the structural modifications of colloidal gels formed by anisotropic particles, and shed light on non-equilibrium behavior of anisotropic colloidal building blocks.

Keywords: Gelation, anisotropic colloids, short-range attraction.

1. Introduction

Microscopically, colloidal gels are dilute space-spanning networks that form solids at dilute particle volume fraction [1], which allows to control the rheological properties of complex materials. In colloidal science, one can form these networks by aggregating attractive colloidal particles [2-4], measures the mechanics of these networks via the storage and loss moduli, and shows a strong time evolution of colloidal gel formation due to the complex energy landscape [5]. This network elasticity is essential in food industry and in biological systems such as cell cytoskeleton. The time evolution while quenching is crucial to measure the network elasticity and the structural modification of

*Corresponding author.

Email address: dmtriet@ctu.edu.vn

<https://doi.org/10.25073/2588-1124/vnumap.4451>

colloidal aggregates. Recently, Zaccone and coworkers [6] propose a microscopic model of master kinetic equations based on nonequilibrium statistical mechanics of the break-up and bonding of colloidal aggregates to evaluate the colloidal cluster size distribution and the relaxation time spectrum during the gelation process. In this paper, we simulate the aggregation process of colloidal gels composed of anisotropic material building blocks. These particles give rise to strongly directional bonds with a variety of patch-to-patch bond interactions. Using molecular dynamics simulations, we show that the kinetic process, particularly the clustering and breakup of colloidal aggregates, plays an essential role on gel formation induced by anisotropic colloids. These results open a new way to in-situ control the complex sub-nanometer structures in colloidal science.

2. Measurement of critical Casimir forces

To simulate the aggregation of attractive anisotropic colloids induced by patch-to-patch interactions, we obtain experimental potential parameters from confocal microscopy observations and extrapolate these parameters in a wider simulation range. We investigate a system of poly-*n*-isopropyl acrylamide (PNIPAM) particles with a diameter of $\sigma=500\text{nm}$ [7-9] suspended in a near-critical quasi binary solvent composed of 3-methylpyridine (3MP), water and heavy water [10, 11]. The solvent composition is close to, but slightly off the critical composition of the 3MP - water - heavy water system [12], allowing solvent density fluctuations to occur [7, 8, 13]. We choose this particular experimental system which has the particle refractive index matched to that of the solvent to directly image the particles and determine the particle pair correlation function $g(r)$, the probability of finding the number of particles around a particle in a given distance from its center, deep inside the bulk of the suspension. The index match also minimizes van der Waals forces to ensure that the only two relevant potentials acting on this system are the repulsive screened electrostatic and the attractive critical Casimir interactions.

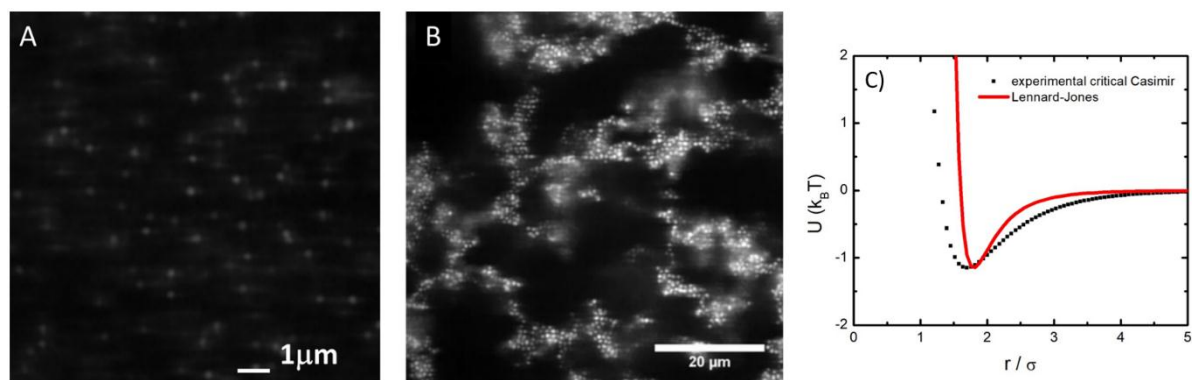


Figure 1. Confocal microscopy images of PNIPAM particles in a dilute state (volume fraction $\phi=2\%$ at room temperature (a), and in a gel state (volume fraction $\phi=6\%$) close to the solvent critical temperature (b). (c) Comparison between experimental critical Casimir and Lennard-Jones potentials. The experimental critical Casimir potential is determined from the particle pair correlation function.

To measure the critical Casimir particle pair potential, we heated a dilute suspension with a $\sim 2\%$ effective colloidal volume fraction just below the solvent phase separation temperature T_{cx} and let the system to equilibrate. After 30 minutes of waiting, we again heated the system to temperatures close to

the solvent critical temperature, and obtained thousand images of particle configurations at each temperature to determine the average pair correlation function. We determine effective pair potentials from experimental measurement of the temperature-dependent pair correlation function $g(r; T)$ in dilute solutions of spherical colloids using the Boltzmann relation $\beta U(r; T) \approx -\ln(g(r; T))$ and apply these interactions to the patches of the anisotropic colloids in this study. Figure 1.(a) shows a snapshot of PNIPAM particles obtained from a confocal microscope in a dilute limit and the experimental temperature dependent critical Casimir potential obtained from the particle pair correlation function. Detail of this measurement is well-documented in ref [9]. The depth of the compared Lennard-Jones potential obtained in this measurement is used as input for simulating the self-assembly of colloidal gels in the next sections.

3. Computational methods

To study the structural modification of gel networks with anisotropic colloids, one can employ Gibbs ensemble Monte Carlo simulations with precise potential forms. Such approach was successfully applied to study the phase behavior of gas-liquid-solid transitions of spherical colloids with short-range attractions [9]. However, in the case of anisotropic colloids, due to the complexity of the particle geometry and the interactions between the patches, standard Monte Carlo simulations are not computationally effective. Furthermore, to study the dynamics of gel formation especially when attraction strength is comparable to thermal activation energy, it requires a model that allows the particles to explore all possible degrees of freedom while clustering, and an appropriate attraction strength which allows colloidal aggregates to form and to breakup during gel formation. Thus, in this paper, we model the anisotropic particles as water-like molecules composing of a B-type particle at center and two A-type patches at edges (see fig. 2a) and implement the ELBA potential model [14] to these colloids. The ELBA potential model can be described by a single interaction site as a Lennard-Jones sphere embedded with a dipole. The total potential energy U_{ij} of an interacting pair of two sites i, j is given as $U_{ij} = U_{ij}^{LJ} + U_{ij}^{dip}$, where U_{ij}^{LJ} represents the Lennard-Jones term and U_{ij}^{dip} is the point dipole potential. In this study, we fix the point dipole term and vary the depths of Lennard-Jones potentials U_{ij}^{LJ} to mimick the increase of the attractive strength induced by the critical Casimir forces. We approached this method due to the fact that high attraction strengths at gelation states are experimentally difficult to obtain. We then consecutively apply these extrapolated potentials to all the patches of the colloids, including A-A, A-B, B-B patches. For simplicity, we only apply the attraction parts to one type of the patches. Fig. 2 (b) illustrates the depths and ranges of the implemented Lennard-Jones potentials. A stiffer attraction strength corresponds to a larger depth of these potentials. Molecular dynamics simulations were run for about 10800 molecules with the program LAMMPS [15] until the simulation systems reach steady states, as defined by the saturation of the potential energy curves at long simulation time (see fig. 2c the top two curves). The temperature was set at 300K. The system size was about $45 \times 45 \times 45 \text{ \AA}^3$. For each potential dataset, we simulated the system for ~ 5000 ps, the initial 2000ps was for equilibration, the last 2000ps was considered as production and we used data of the last 2000ps for analysis. At the highest attraction strength, due to the simulation time limit, we perform the molecular dynamic simulation (MD simulation) up to its quasi-stable state.

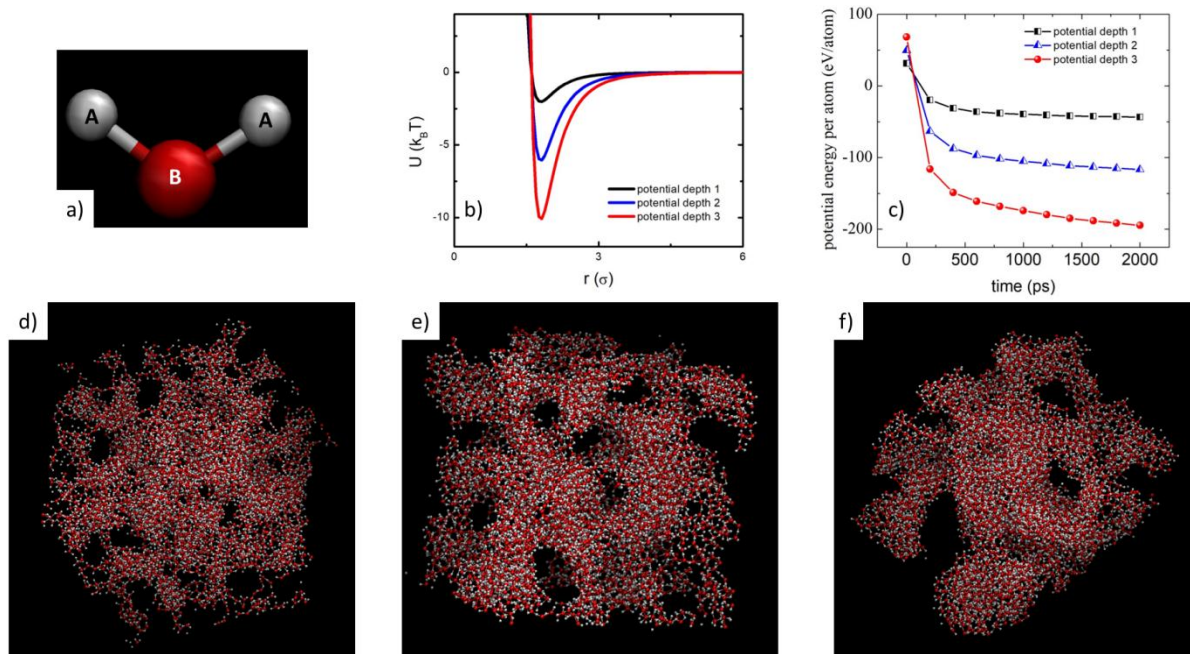


Figure 2. Structural modification of colloidal gels formed by anisotropic particles. (a) A sketch of an anisotropic particle with type *A* and type *B* patches. (b) Lennard-Jones pair potentials between colloidal patches. Higher depth of potential illustrates stronger attractions between colloidal patches. (c) Time evolution potential energy per atom of the simulation system. (d-f) Simulation snapshots of A-A interactions obtained at 3 different Lennard-Jones potential depth 1 (d), potential depth 2 (e), potential depth 3 (f) at 530ps. Stiffer and larger gel networks are obtained when increasing the attraction depths.

4. Results and discussion

4.1. Formation of attractive gels

To assemble a space-spanning colloidal network at number density $\sim 10\%$, we generated fcc crystal configurations where the center of each molecule was placed at the fcc lattice point, and applied three different Lennard-Jones potentials to *A-A*, *A-B*, *B-B* patches. During quenching, the systems melted from crystal states to form gels. The highest potential depth was chosen at around $10 k_B T$ equivalent to the highest potential depth we could obtain experimentally. At each potential, we ran about 2 million MD steps and exported about 4000 configurations for statistical analyses. Figures 2 (d-f) are simulation snapshots achieved at 530ps for all potential depths. As can be seen clearly, space spanning networks are completely formed at this time stamp, and these networks are distinct at the highest strength. These simulation snapshots qualitatively agree with our confocal microscopy observation (see fig. 1b).

We first investigated the pair correlation function during formation. Figure 3 shows the pair-correlation functions $g(r)$ of an attraction field equivalent to potential depth 1 of *A-A* patch-to-patch interaction (top) and $g(r)$ of *A-A* patch-to-patch interaction at various potential depths. As time evolves, the gel network becomes longer and stiffer: at stronger attraction equivalent to higher solvent temperatures close to the solvent phase separation point, the second peak of $g(r)$ is higher indicating a

higher degree of short-range order, the patch-to-patch attractions become more pronounced. Higher-order maxima correspond to the formation of molecule clusters. At this potential strength, the thermal activation potential barrier is comparable to the system configurational entropy allowing particle structural rearrangements, making the gel more compact and stronger over longer formation time [2]. Moreover, at the simulation time of $530ps$, at large particle separations, similar behaviors are also observed by increasing the potential depths (fig. 3 - bottom panel).

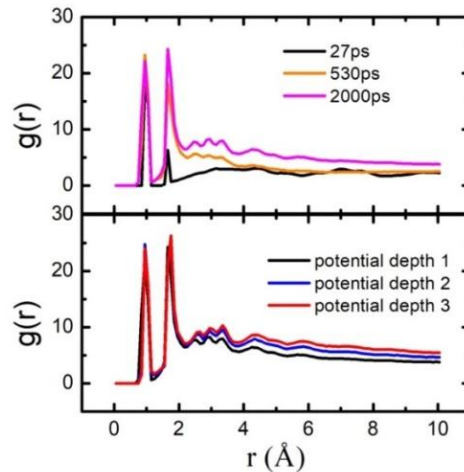


Figure 3. Pair-correlation functions of colloidal aggregates.

(Top) Time evolution of pair-correlation functions of an attraction field equivalent to *potential depth 1* of A-A patch-to-patch interaction. (Bottom) Pair-correlation functions of A-A patch-to-patch interaction at $530ps$ with all three potential depths.

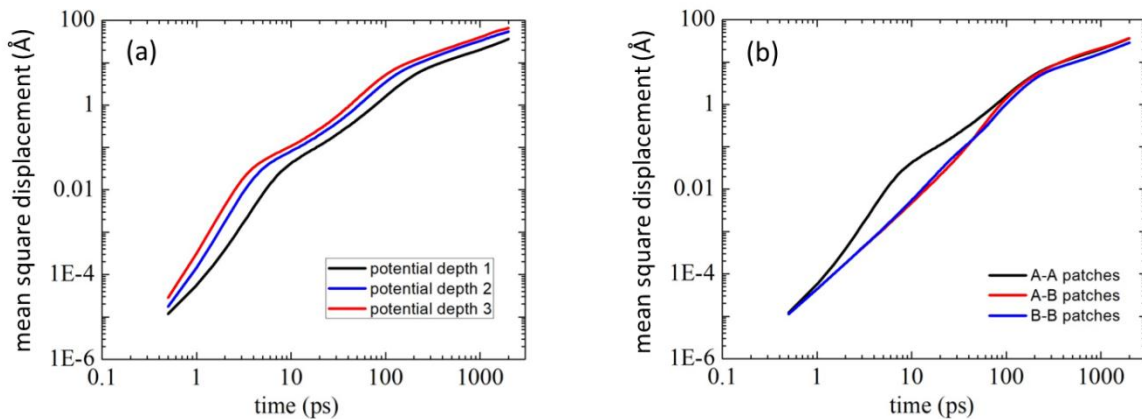


Figure 4. Mean-square displacement of attractive colloidal aggregates. (a) Distinct potential depths are applied to A-patches. (b) Potential depth 1 is applied to colloids with A-A, A-B, and B-B patches.

To further understand the gel dynamics, we follow the motion of particles over time and compute the particle mean-square displacement and plot this quantity for A-A patch-to-patch interaction for all three depths of potential in fig. 4(a) and for *potential depth 1* for A-A, A-B and B-B contributions. Beside the standard ballistic regime at the beginning and the diffusive regime at longer diffusion period (simulation time above $1000ps$), the anisotropic colloids experience a transition crystal-gel state

(from $\sim 10ps$ to $\sim 200ps$). This transition regime is even more pronounced when comparing different patch-to-patch interactions (fig. 4b), suggesting that A-A patch-to-patch interaction plays a major role in the cluster growth.

4.2. Model of gelation

To understand the structural origin of the gelation process, we study the time evolution of the system coordination numbers. In an ideal case, the coordination number is defined by counting the number of nearest neighbors around a single particle with a radius equal to the particle diameter. In this study, to measure the coordination number of anisotropic colloids, for each selected patch in a anisotropic particle, we only count the number of patches of other particles and ignore the trivial interaction between patches inside a particle. This method allows us to determine the essential role of colloidal patches while aggregating. To effectively follow the clustering process, we apply an attraction depth around $k_B T$ (potential depth 1) to the simulation system.

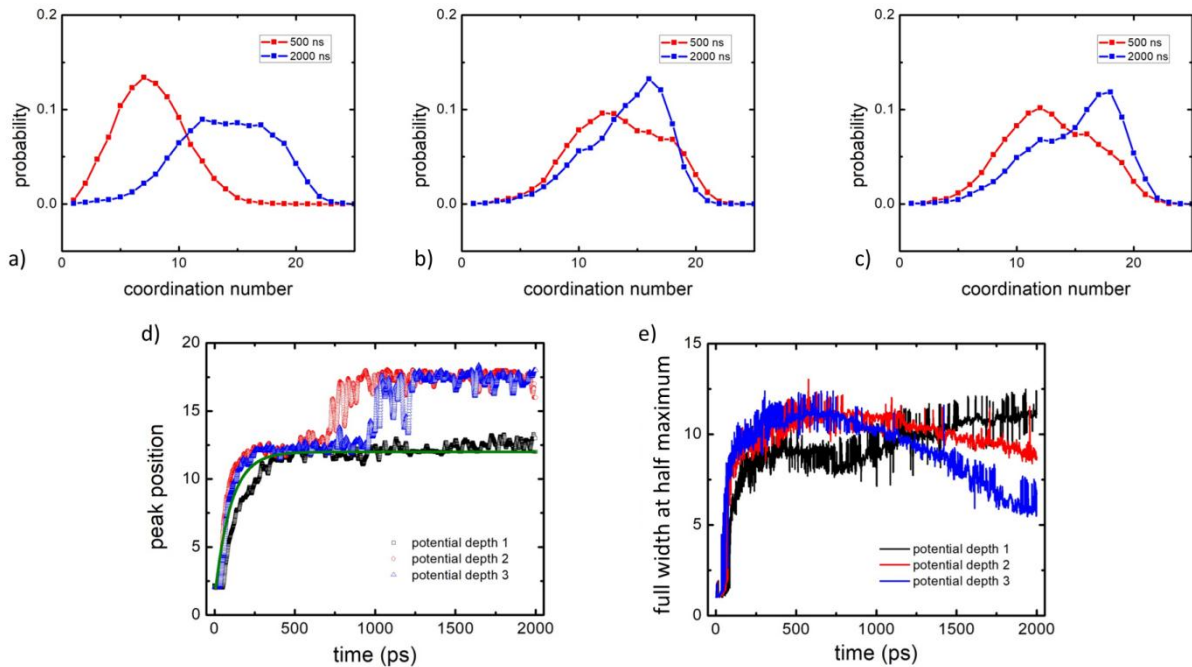


Figure 5. Coordination numbers of attractive gels. (a-c) Distribution of coordination numbers at 500 ps and 2000 ps for potential depth 1 (a), depth 2 (b), depth 3 (c). Peaks (d) and full-width half-width (e) of the coordination numbers as a function of simulation time.

As seen in fig. 5, while quenching, larger colloidal networks are formed: the coordination peaks shift towards higher values and the full-width half-width curves spread out significantly. Figures 5.a-c demonstrate the shift of the coordination number distributions towards higher values. This right shift is even more pronounced at higher attraction strengths (see fig. 5d for comparison between red and black symbols equivalent to systems quenched at the highest and lowest attraction potentials). We also observe a weak double peak of coordination numbers at the highest attractive potential in this study. This interesting behavior suggests that there should be a balance between clustering and particle breakup during gelation, meaning that the aggregates can be formed by physical or chemical bonds with binding energy V and may also break up due to thermal activation barrier. One can simply model

this cluster formation with cluster mass k and linear size R_k according to the general master kinetic equation [6]:

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i,j=1}^{i+j=k} K_{ij}^+ c_i c_j - c_k \sum_{i=1}^{\infty} K_{ik}^+ c_i - K_k^- c_k + \sum_{i=k+1}^{\infty} K_{ik}^- c_i \quad (1)$$

where c_i is the number concentration of clusters of i particles. K_{ij}^+ is the rate of aggregation of two clusters i and j , while K_{ij}^- is the rate of breaking up the $j+i$ cluster to two single clusters i and j . The first term can be considered as the “birth” of clusters with mass k , while the second term illustrates the “death” of clusters with mass k . The last two terms are the dynamical factors for the “death” and “birth” of k -clusters due to cluster breakup, respectively. To capture the time scale of the gelation formation, the peak positions of the coordination numbers were fitted with the theoretical master equation proposed in ref. [6]:

$$A(t) = (B - C)e^{-(K_{ij}^+)^{d_f}} e^{-K_{ij}^+(t-t_0)} + C \quad (2)$$

where $A(t)$ is the peak position of the coordination number, B is the initial peak value, C is the long-time value of $A(t)$, and $d_f = 2.1$ is the fractal dimension of this gelation system obtained by fitting the tail of the structure factor. Fig. 5d (green solid line) shows a quantitative agreement between the clustering theory of gelation and our simulations with the aggregation constant $K_{ij}^+ = 0.01$. The balance between these two processes are nicely captured by the broadening of the distribution of the coordination numbers (fig. 5d – green line). It is worth noting that eq. [2] fails to capture the full assembly kinetics of gels at high attraction strengths due to the anisotropy of the colloid building blocks and the depths of the potentials. At these depths of interactions, structural rearrangement is very limited so the balance between break-up and clustering happens out of the simulation time scale. The coordination number full-width half-width narrows down at long simulation time (fig. 5e) suggesting that the systems become more compact and arrested.

5. Conclusion

We have shown that the anisotropy of colloids offer new opportunities to study the kinetics of particle aggregation at finite bond energies: the particle interactions can be applied and controlled on specific patches of colloids on a molecular time scale. Furthermore, when the attraction strength is comparable to the thermal activation energy (at potential depth 1), the balance between clustering and break-up is the main mechanism leading to gel formation of anisotropic colloids. This provides new insight into the kinetics of out-of-equilibrium assembly and the relation between aggregate structures and attractive potential. In particular, we show that aging can strengthen colloidal aggregates due to restructuring processes that make the structure more compact. As time evolves, the gel network becomes strongly arrested and develops a stiffer gel networks.

Acknowledgments

This research is partly funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.01-2018.308 and partly by Can Tho University under the contract number T2018-68. MTD acknowledges prof. P. Schall at the University of Amsterdam and dr. J. Oldenziel at Stichting Science International in the Netherlands for supporting a high-performance computing system.

References

- [1] V. Trappe, P. Sandkhler, Colloidal gels – low-density disordered solid-like states, *Curr. Opin. Colloid Interface Sci.* 8 (2004) 494–500. <https://doi.org/10.1016/j.cocis.2004.01.002>
- [2] L. Cipelletti, S. Manley, R.C. Ball, D. Weitz, Universal Aging Features in the Restructuring of Fractal Colloidal Gels, *Phys. Rev. Lett.* 84 (2000) 2275–2278. <https://doi.org/10.1103/PhysRevLett.84.2275>
- [3] S. Manley, et al. Time-Dependent Strength of Colloidal Gels, *Phys. Rev. Lett.* 95 (2005) 48302. <https://doi.org/10.1103/PhysRevLett.95.048302>
- [4] S. Jabbari-Farouji, et al., High-bandwidth viscoelastic properties of aging colloidal glasses and gels, *Phys. Rev. E* 78 (2008) 61402. <https://doi.org/10.1103/PhysRevE.78.061402>
- [5] P.G. Debenedetti, F.H. Stillinger, Supercooled liquids and the glass transition, *Nature* 410 (2001) 259–267. <https://doi.org/10.1038/35065704>
- [6] A. Zaccone, H.H. Winter, M. Siebenbarger, M. Ballauff, Linking self-assembly, rheology, and gel transition in attractive colloids, *J. Rheol.* 58 (2014) 1219–1244. <https://doi.org/10.1122/1.4878838>
- [7] P.B. Shelke, V.D. Nguyen, A. V. Limaye & P. Schall, Controlling colloidal morphologies by critical casimir forces, *Adv. Mater.* 25 (2013) 1499–1503. <https://doi.org/10.1002/adma.201204458>
- [8] V.D. Nguyen, S. Faber, Z. Hu, G.H. Wegdam, P. Schall, Controlling colloidal phase transitions with critical Casimir forces, *Nat. Commun.* 4 (2013) 1584. <https://doi.org/10.1038/ncomms2597>
- [9] M.T. Dang, A.V. Verde, V.D. Nguyen, P.G. Bolhuis, P. Schall, Temperature-sensitive colloidal phase behavior induced by critical Casimir forces, *J. Chem. Phys.* 139 (2013) 94903. <https://doi.org/10.1063/1.4819896>
- [10] T. Narayanan, A. Kumar, E.S.R. Gopal, A new description regarding the approach to double criticality in quasi-binary liquid mixtures, *Phys. Lett. A* 155 (1991) 276–280. [https://doi.org/10.1016/0375-9601\(91\)90482-N](https://doi.org/10.1016/0375-9601(91)90482-N)
- [11] D. Beysens, T. Narayanan, Wetting-induced aggregation of colloids, *J. Stat. Phys.* 95 (1999) 997–1008. <https://doi.org/10.1023/A:1004506601807>
- [12] J.D. Cox, Phase relationships in the pyridine series. Part II. The miscibility of some pyridine homologues with deuterium oxide. *J. Chem. Soc.* (1952) 4606–4608. <https://doi.org/10.1039/JR9520004606>
- [13] C. Hertlein, L. Helden, A. Gambassi, S. Dietrich, C. Bechinger, Direct measurement of critical Casimir forces, *Nature* 451 (2008) 172–175. <https://doi.org/10.1038/nature06443>
- [14] M. Orsi, Comparative assessment of the ELBA coarse-grained model for water, *Mol. Phys.* 112 (2014) 1566–1576. <https://doi.org/10.1080/00268976.2013.844373>
- [15] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, *J. Comput. Phys.* 117 (1995) 1–19. <https://doi.org/10.1006/jcph.1995.1039>