Crystal nucleation of highly screened charged colloids

Cite as: J. Chem. Phys. 157, 154905 (2022); https://doi.org/10.1063/5.0117867
Submitted: 02 August 2022 • Accepted: 26 September 2022 • Accepted Manuscript Online: 26 September 2022 • Published Online: 20 October 2022

Marjolein de Jager and Laura Filion

COLLECTIONS

Paper published as part of the special topic on Nucleation: Current Understanding Approaching 150 Years After Gibbs

ARTICLES YOU MAY BE INTERESTED IN

Guiding the self-assembly of colloidal diamond
The Journal of Chemical Physics 157, 154503 (2022); https://doi.org/10.1063/5.0109377

Layering and capillary waves in the structure factor of liquid surfaces
The Journal of Chemical Physics 157, 154703 (2022); https://doi.org/10.1063/5.0118252

Self-assembly and complex formation of amphiphilic star and bottle-brush block copolymers
The Journal of Chemical Physics 157, 154904 (2022); https://doi.org/10.1063/5.0108479
Crystal nucleation of highly screened charged colloids

Cite as: J. Chem. Phys. 157, 154905 (2022); doi: 10.1063/5.0117867
Submitted: 2 August 2022 • Accepted: 26 September 2022 •
Published Online: 20 October 2022

Marjolein de Jager and Laura Filion

AFFILIATIONS
Soft Condensed Matter, Debye Institute of Nanomaterials Science, Utrecht University, Utrecht, Netherlands

Note: This paper is part of the JCP Special Topic on Nucleation: Current Understanding Approaching 150 Years After Gibbs.
Author to whom correspondence should be addressed: m.e.dejager@uu.nl

ABSTRACT
We study the nucleation of nearly hard charged colloidal particles. We use Monte Carlo simulations in combination with free-energy calculations to accurately predict the phase diagrams of these particles and map them via the freezing density to hard spheres, then we use umbrella sampling to explore the nucleation process. Surprisingly, we find that even very small amounts of charge repulsion can have a significant effect on the phase behavior. Specifically, we find that phase boundaries and nucleation barriers are mostly dependent on the Debye screening length and that even screening lengths as small as 2% of the particle diameter are sufficient to show marked differences in both. This work demonstrates clearly that even mildly charged colloids are not effectively hard spheres.

I. INTRODUCTION
Hard spheres are arguably the archetypical model system for studying colloidal self-assembly and have been instrumental in our understanding of, e.g., phase transitions, glassy behavior, and defects. Experimentally, hard spheres are typically realized as colloidal particles suspended in a solvent. However, in such systems, the colloids nearly always carry surface charges and are generally decorated with surface ligands. This raises an important fundamental question: When can colloids be seen as hard spheres?

This question is particularly crucial when addressing crystal nucleation of hard spheres, where a long-standing issue is the large discrepancy between predicted and experimentally observed nucleation rates. Since any induced repulsion between the particles will make the particles act as if they are slightly larger, a quantitative comparison to the true model requires a way to assign an effective packing fraction to the charged systems. From a historical perspective, the most common mapping involves assigning an effective diameter to the particles such that the freezing point matches that of hard spheres. Within Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the effective interaction potential is given by

$$\beta \phi (r) = \begin{cases} \beta \epsilon e^{-\kappa r (r/\sigma - 1)} & \text{for } r \geq \sigma, \\ \infty & \text{for } r < \sigma, \end{cases}$$

(1)

with contact value $\beta \epsilon = Z^2 \lambda_b/\sigma (1 + \kappa \sigma/2)^2$, where $Z$ is the charge of the colloids in electron charge, and $\beta = 1/k_B T$, with $k_B$ the

J. Chem. Phys. 157, 154905 (2022); doi: 10.1063/5.0117867
Published under an exclusive license by AIP Publishing
Boltzmann constant and \( T \) the temperature. Note that in the limit of zero charge (\( Z \to 0 \)) or infinite screening (\( \kappa \sigma \to \infty \)), the repulsive hard-core Yukawa potential of Eq. (1) reduces to the hard-sphere potential. This system has been extensively studied using experiments, simulations, and theory, and the bulk phase behavior is extremely well understood\(^{37,34} \). Here, we focus on systems with short screening lengths, i.e., ranging from 1% to 4% of the particle diameter—similar to those often considered as hard experimentally.\(^{1,12,25,27,26,44,45,55} \) For the contact values, we explore mainly \( \beta \epsilon = 8, 20, 39, \) and 81, which allows us to compare with the phase diagrams of Ref. 43. An overview of the potentials is shown in Fig. 1. Additionally, in Fig. 1, we display the WCA potential with \( \beta \epsilon = 40 \), which was previously shown to accurately replicate the nucleation behavior of hard spheres.\(^{30} \)

### III. EFFECTIVE PHASE BOUNDARIES

We start by mapping the highly screened hard-core Yukawa particles to hard spheres using an effective hard-sphere diameter via \( \eta_{\text{eff}}=\left(\eta_{\text{HS}}/\eta_{F}\right)\eta_{F} \), where \( \eta_{F} \) is the actual packing fraction and \( \eta_{\text{HS}} \) is the freezing packing fraction of hard spheres. To calculate the freezing and melting densities, we use free-energy calculations in combination with common-tangent constructions.\(^{33} \) We first compute the equation of state of the fluid and face-centered cubic (FCC) crystal phase using Monte Carlo (MC) simulations in the NPT-ensemble with \( N = 2048 \) particles. Additionally, to increase the accuracy of the equation of state, we use MC simulations in the NVT-ensemble combined with the virial equation, when the system does not “feel” the hard cores. In practice, this means that we only use the NVT-ensemble combined with the virial equation for systems with \( \beta \epsilon \geq 8 \). Next, we use thermodynamic integration of the equation of state to get the free energy as a function of the density.\(^{34} \) For the fluid phase, we use the ideal gas as a reference system. For the FCC phase, we integrate from a reference density for which we computed the free energy using Einstein integration with finite-size corrections.\(^{34,35,36} \)

A complete summary of all freezing and melting densities is given in Table I and the resulting effective melting packing fractions \( \eta_{\text{eff}} \) are shown Fig. 2(a). As expected, in the limit of zero charge (\( \beta \epsilon \to 0 \)), the melting density matches that of hard spheres. Surprisingly, however, this limit really requires nearly zero charge, with significant deviations appearing for contact values as low as \( \beta \epsilon = 1 \). For \( \beta \epsilon > 1.5 \), \( \eta_{\text{eff}} \) is nearly unaffected by changing \( \beta \epsilon \). As required, in the limit of infinite screening (\( 1/\kappa \sigma \to 0 \)), the system reduces to hard spheres.

However, as the screening length increases, \( \eta_{\text{eff}} \) steadily decreases. In the end, \( \eta_{\text{eff}} \) is comparable to \( \eta_{\text{HS}}^{40} = 0.543(1)^{34,35} \) only for the

### Table I. Freezing and melting packing fractions, \( \eta_{F} \) and \( \eta_{M} \), of various systems of near hard spheres with contact values \( \beta \epsilon \) and screening length \( 1/\kappa \sigma \).

The last two columns of the table give the effective hard-sphere melting packing fraction \( \eta_{\text{eff}}^{\text{HS}} = (\eta_{\text{HS}}^{\text{M}}/\eta_{F}) \eta_{F} \), with \( \eta_{\text{HS}}^{\text{M}} = 0.492(1) \), and effective hard-sphere diameter \( \kappa \sigma_{\text{eff}}/\kappa \sigma = (\eta_{\text{HS}}^{\text{M}}/\eta_{F})^{1/3} \).

| \( \beta \epsilon \) | \( 1/\kappa \sigma \) | \( \eta_{F} \) | \( \eta_{M} \) | \( \eta_{\text{eff}}^{\text{HS}} \) | \( \kappa \sigma_{\text{eff}}/\kappa \sigma \) |
|---|---|---|---|---|---|
| 8 | 0.01 | 0.458 | 0.505 | 0.542 | 1.024 |
| 20 | 0.01 | 0.446 | 0.491 | 0.542 | 1.033 |
| 39 | 0.01 | 0.437 | 0.482 | 0.542 | 1.040 |
| 81 | 0.01 | 0.429 | 0.472 | 0.541 | 1.047 |
| 8 | 0.02 | 0.432 | 0.473 | 0.538 | 1.044 |
| 20 | 0.02 | 0.410 | 0.449 | 0.538 | 1.063 |
| 39 | 0.02 | 0.395 | 0.432 | 0.538 | 1.076 |
| 81 | 0.02 | 0.380 | 0.415 | 0.538 | 1.090 |
| 8 | 0.03 | 0.412 | 0.447 | 0.534 | 1.061 |
| 20 | 0.03 | 0.381 | 0.414 | 0.534 | 1.089 |
| 39 | 0.03 | 0.361 | 0.393 | 0.535 | 1.108 |
| 81 | 0.03 | 0.341 | 0.371 | 0.535 | 1.130 |
| 8 | 0.04 | 0.396 | 0.426 | 0.530 | 1.075 |
| 20 | 0.04 | 0.358 | 0.386 | 0.530 | 1.111 |
| 39 | 0.04 | 0.334 | 0.360 | 0.531 | 1.138 |
| 81 | 0.04 | 0.310 | 0.334 | 0.531 | 1.167 |

\(^{a}\)Note that Pusey and van Megen used \( Z_{\text{eff}} = 0.494 \), whereas we use \( Z_{\text{eff}} = 0.492 \). Here, we have corrected these values for this difference.
The most significant differences between the structure of the hard spheres and the nearly hard spheres are the very slight broadening of the first peak of the $g(r)$ and the mild shrinking of the higher order peaks of the $S(q)$. These differences increase with increasing softness $(1/\kappa \sigma)$, essentially not existing when $1/\kappa \sigma = 0.01$.

V. NUCLEATION BARRIERS AND RATES

We now turn our attention to the nucleation behavior of these nearly hard particles. To study the crystal nucleation, we use MC simulations in the NPT-ensemble combined with umbrella sampling and measure the nucleation free-energy barriers. Following Refs. 22 and 30, we bias the simulation using the number of particles in the nucleus measured via the Ten Wolde order parameter $^{22}$ with cutoff values $d_c = 0.7$ and $\xi = 6$, see the supplementary material. We use a fixed radial cutoff $r_c$ to determine the nearest neighbors. It is chosen to be approximately the position of the first minimum of the radial distribution function for each state point.

We compute the nucleation barriers for the various hard-core Yukawa systems at a fixed effective packing fraction of the supersaturated fluid of $\eta^* = 1.088\eta_M$, which corresponds to hard spheres at a pressure of $\beta P^{\alpha}_c = 17.0$. The resulting nucleation barriers are shown in Fig. 4. For each system, we use $N = 10,976$, and Table II contains all other necessary information per system. Additionally, Table II gives the interfacial free energy, critical nucleus size, and barrier height obtained from fitting the nucleation barriers (see the supplementary material). Based on our estimates, the error in the barrier height is no more than $\lambda kT$. Looking at Fig. 4 and Table II, we see that, as expected and similar to $\eta_M^{\HS}$ in Fig. 1(b), the nucleation barriers are grouped together according to $1/\kappa \sigma$. Furthermore, we see that the systems with $1/\kappa \sigma = 0.01$ map well to hard spheres and that increasing $1/\kappa \sigma$, i.e., increasing the softness of the particles, increases the height of the nucleation barrier. This is not entirely surprising, as the supersaturation, see Table II, decreases with increasing $1/\kappa \sigma$.

Next, we compute the nucleation rates for these systems. The methods are explained in the supplementary material. To calculate the attachment rate, we select 10 independent configurations from the umbrella simulations of the windows on top of the barrier and start 10 independent kinetic MC simulations from each window.
FIG. 3. The effective structure for a fluid of hard spheres (gray, solid), WCA particles with $\beta \varepsilon = 40$ (black, dashed), and hard-core Yukawa particles with $\beta \varepsilon = 39$ and varying screening length $1/kappa$ (colors, dashing). (e)–(f) is removed, please change the highlighted part of the caption to: (a)–(d) The results for the fluids studied at the freezing packing fraction, and (e)–(h) the fluids studied at the melting packing fraction. Here (a)–(b), (e)–(f) show the radial distribution function $g(r)$, where the insets of (a), (e) zoom in on the first peak of the $g(r)$, and (b), (f) show the second peak. The figures (c)–(d), (g)–(h) show the structure factor $S(q)$, where the insets of (c), (g) zoom in on the first peak of the $S(q)$, and (d), (h) show the second to sixth peak with the inset zooming in on the sixth peak. Note that all horizontal axes are scaled by the effective hard-sphere diameter $\sigma_{eff}$, see Table I.
configuration. The resulting attachment and nucleation rates in terms of the long-time diffusion coefficient $D_l$ are given in Table III. The error in the attachment rate is $\sim 10\%$. Combining this with the $1k_B T$ error in the barrier height gives an error in the nucleation rate of approximately a factor 3. The nucleation rate found for the hard-spheres system agrees with the ones given in Refs. 3 and 22. Furthermore, notice that the nucleation rates of the systems with $\beta \epsilon = 81$ agree within the error given with the corresponding system of $\beta \epsilon = 8$. This further confirms the accuracy of our calculations, considering that these systems are mapped onto each other when scaled with the effective hard-sphere diameter. As expected from the increasing barrier height, we see that the nucleation rate decreases with increasing $1/\kappa \sigma$. This is interesting, as this is in the opposite direction of the deviations between experiments and simulations for hard spheres. The “softer” particles studied in experiments have even

![Image of a graph](image)

**FIG. 4.** Nucleation barriers of the FCC crystal of hard-core Yukawa particles with contact value $\beta \epsilon$ (colors) and screening length $1/\kappa \sigma$ (dashing) for a packing fraction of the supersaturated fluid of $\eta^* = 1.088 \eta_f$. The corresponding hard-sphere barrier is shown by a black solid line. For more information, see Table II.

**TABLE I.** Nucleation rate $k$ in terms of the long-time diffusion coefficient $D_l$ for a few of the systems of Table II. The third and fourth columns give the second derivative of the nucleation barrier and the attachment rate, both on top of the barrier, used for calculating $k$. The error in $k$ is approximately a factor 3.

| $\beta \epsilon$ | $1/\kappa \sigma \beta \Delta G^o (n^*)$ | $J_m^o/6D_l$ | $k \sigma^2/6D_l$ |
|------------------|--------------------------------------|----------------|-----------------|
| Hard spheres     | -1.2 x 10^{-3}                       | 2.1 x 10^{-3}  | 1.5 x 10^{-7}   |
| 8                | -1.1 x 10^{-3}                       | 2.5 x 10^{-3}  | 1.5 x 10^{-7}   |
| 81               | -1.2 x 10^{-3}                       | 6.6 x 10^{-3}  | 3.1 x 10^{-7}   |
| 8                | -1.1 x 10^{-3}                       | 2.8 x 10^{-3}  | 2.1 x 10^{-8}   |
| 8                | -8.0 x 10^{-4}                       | 3.0 x 10^{-3}  | 2.5 x 10^{-9}   |
| 8                | -6.1 x 10^{-4}                       | 3.3 x 10^{-3}  | 1.7 x 10^{-10}  |
| 81               | -6.2 x 10^{-4}                       | 4.9 x 10^{-3}  | 1.7 x 10^{-10}  |

**TABLE II.** Interfacial free energy $\beta \gamma \sigma^2$, critical nucleus size $n^*$, and barrier height $\beta \Delta G^*$ obtained from fitting to the nucleation barriers of Fig. 4. The third and fifth column give the cutoff radius $r_c/\sigma$, packing fraction $\eta^*$ of the supersaturated fluid, and pressure $\beta P_o^3$ used for the simulations, respectively. The sixth and seventh column give the density $\rho_c \sigma^3$ of the solid phase and supersaturation $|\beta \Delta \mu|$ used for fitting the barrier. The error in $|\beta \Delta G|$ is no more than 1.

| $\beta \epsilon$ | $1/\kappa \sigma$ | $r_c/\sigma$ | $\eta^*$ | $\beta P_o^3$ | $\rho_c \sigma^3$ | $|\beta \Delta \mu|$ | $\beta \gamma \sigma^2$ | $\beta \gamma \sigma^2 | r_c/\sigma | n^*$ | $\beta \Delta G^*$ |
|------------------|--------------------|--------------|----------|----------------|---------------------|----------------|-------------------|---------------------|----------------|------------------|
| Hard spheres     | 1.40               | 0.5352       | 17.0     | 1.136          | 0.536               | 0.58           | 0.53              | 101                 | 19.1            |
| 8                | 0.01               | 1.43         | 0.4985   | 16.0           | 1.053               | 0.531          | 0.53              | 103                 | 19.2            |
| 8                | 0.01               | 1.45         | 0.4853   | 15.6           | 1.026               | 0.536          | 0.53              | 102                 | 19.2            |
| 39               | 0.01               | 1.46         | 0.4757   | 15.2           | 1.005               | 0.530          | 0.53              | 108                 | 19.6            |
| 81               | 0.01               | 1.47         | 0.4662   | 15.0           | 0.986               | 0.540          | 0.52              | 102                 | 19.4            |
| 8                | 0.02               | 1.46         | 0.4699   | 15.4           | 0.983               | 0.494          | 0.57              | 116                 | 21.2            |
| 8                | 0.02               | 1.49         | 0.4461   | 14.6           | 0.934               | 0.499          | 0.52              | 116                 | 20.9            |
| 39               | 0.02               | 1.51         | 0.4298   | 14.1           | 0.901               | 0.502          | 0.52              | 114                 | 20.7            |
| 81               | 0.02               | 1.53         | 0.4131   | 13.5           | 0.866               | 0.495          | 0.51              | 118                 | 21.1            |
| 8                | 0.03               | 1.49         | 0.4477   | 15.1           | 0.927               | 0.452          | 0.52              | 142                 | 23.2            |
| 8                | 0.03               | 1.52         | 0.4150   | 14.0           | 0.860               | 0.462          | 0.50              | 142                 | 23.3            |
| 39               | 0.03               | 1.56         | 0.3932   | 13.2           | 0.815               | 0.458          | 0.49              | 137                 | 23.2            |
| 81               | 0.03               | 1.58         | 0.3706   | 12.4           | 0.769               | 0.460          | 0.47              | 141                 | 23.4            |
| 8                | 0.04               | 1.50         | 0.4304   | 15.1           | 0.882               | 0.411          | 0.50              | 172                 | 25.8            |
| 8                | 0.04               | 1.56         | 0.3902   | 13.7           | 0.801               | 0.430          | 0.48              | 162                 | 25.3            |
| 39               | 0.04               | 1.59         | 0.3630   | 12.6           | 0.746               | 0.424          | 0.45              | 168                 | 25.7            |
| 81               | 0.04               | 1.63         | 0.3366   | 11.6           | 0.692               | 0.425          | 0.42              | 154                 | 25.9            |
faster rates than those predicted for purely hard spheres, meaning that the discrepancy between experiments and simulations cannot be explained by softness due to charge.

The question remains, is there a different way of mapping to hard spheres that leads to a better agreement for the nucleation rates? One option would be to map the entire coexistence region; another, for these systems, this would lead to lower nucleation rates? One option would be to map the entire coexistence region; another, for these systems, this would lead to lower nucleation rates. Another common practice is to compare nucleation rates at fixed $\beta\sigma^2$ to even higher barriers and slower nucleation rates. However, for these systems, this would lead to lower $\eta$ and thus to even higher barriers and slower nucleation rates. Another common practice is to compare nucleation rates at fixed $\beta|\Delta\mu|$. Notice that the systems with $1/\kappa \sigma = 0.01$ in Table IV indeed have a $\beta|\Delta\mu|$ comparable to that of the hard-sphere system. Here, we also compute the nucleation barriers for $\beta\sigma = 8$ with $1/\kappa \sigma = 0.02, 0.03$, and 0.04 at $\beta|\Delta\mu| = 0.54$. The necessary information for each system is given in Table IV, and Fig. 5 shows the resulting nucleation barriers. Contrary to the mapping at equal effective packing fraction, we now see that increasing $1/\kappa \sigma$ decreases the height of the nucleation barrier, and again good agreement only occurs when $1/\kappa \sigma = 0.01$.

TABLE IV. Interfacial free energy $\beta\gamma\sigma^2$, critical nucleus size $n^*$, and barrier height $\beta\Delta G^*$ obtained from fitting the nucleation barriers of Fig. 5. The third-fifth column give the cutoff radius $r_c/\sigma$, packing fraction $\eta^*$ of the supersaturated fluid, and pressure $\beta P\sigma^2$ used for the simulations, respectively. The sixth and seventh columns give the density $\rho_\sigma^3$ of the solid phase and supersaturation $\beta|\Delta\mu|$ used for fitting the barrier. The error in $\beta\Delta G^*$ is no more than 1.

| $\beta\sigma$ | $1/\kappa \sigma$ | $r_c/\sigma$ | $\eta^*$ | $\beta P\sigma^2$ | $\rho_\sigma^3$ | $\beta|\Delta\mu|$ | $\beta\gamma\sigma^2$ | $\beta|\Delta G^*|$ | $n^*$ | $\beta\Delta G^*$ |
|---------------|-------------------|-------------|---------|------------------|-------------|-----------------|-----------------|-----------------|------|-----------------|
| Hard spheres  | 1.40              | 0.5352      | 17.0    | 1.136            | 0.536       | 0.58            | 0.53            | 101             | 19.1 |
| 8             | 0.01              | 1.43        | 0.4985  | 16.0             | 1.053       | 0.531           | 0.53            | 103             | 19.2 |
| 8             | 0.02              | 1.46        | 0.4724  | 15.8             | 0.988       | 0.532           | 0.51            | 93              | 18.0 |
| 8             | 0.03              | 1.48        | 0.4538  | 16.1             | 0.938       | 0.541           | 0.45            | 81              | 16.0 |
| 8             | 0.04              | 1.49        | 0.4399  | 16.7             | 0.900       | 0.541           | 0.41            | 69              | 14.8 |

VI. CONCLUSIONS

In conclusion, we demonstrated that for highly screened particles, the phase behavior is incredibly sensitive to even very small amounts of charge repulsion. Specifically, we show that, when mapped to hard spheres via the freezing densities, the effective phase boundaries depend sensitively on the screening length, playing a measurable role even for screening lengths as low as $1/\kappa \sigma = 0.02$. Even though the effect of this on the effective structure of the system is barely perceivable, the nucleation rate is extremely sensitive to the change. This begs the question: When can experimental systems be considered hard spheres? The results here suggest that the answer is when the effective melting density matches that of hard spheres.

SUPPLEMENTARY MATERIAL

In the supplementary material, we provide a more in-depth description on the specific methods used for obtaining the nucleation barriers and rates. This includes a description of the Ten Wolde order parameter, umbrella sampling, fitting the nucleation barrier to classical nucleation theory, and calculating the nucleation rate.

ACKNOWLEDGMENTS

We would like to thank Frank Smallenburg, Michiel Hermes, and Alfons van Blaaderen for many useful discussions. L.F. and M.d.J. acknowledge funding from the Vidi research program with Project No. VI.VIDI.192.102, which is financed by the Dutch Research Council (NWO).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Marjolein de Jager: Conceptualization (supporting); Formal analysis (lead); Methodology (lead); Software (lead); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal).
Laura Filion: Conceptualization (lead); Funding acquisition (lead); Supervision (lead); Writing – original draft (supporting); Writing – review & editing (equal).

DATA AVAILABILITY

An open data package containing the (analyzed) data and other means to reproduce the results of the simulations is available at: https://doi.org/10.24416/UU01-8F4XK2 (Ref. 58).

REFERENCES

1. J. L. Harland and W. Van Megen, Phys. Rev. E 55, 3054 (1997).
2. U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, and D. A. Weitz, Science 292, 258 (2001).
3. S. Auer and D. Frenkel, Nature 409, 1020 (2001).
4. A. Cacciuto, S. Auer, and D. Frenkel, Nature 428, 404 (2004).
5. S. Auer and D. Frenkel, Phys. Rev. Lett. 91, 015703 (2003).
6. S. Iacopini, T. Palberg, and H. J. Shöpe, J. Chem. Phys. 130, 084502 (2009).
7. A. L. Thorneywork, J. L. Abbott, D. G. A. L. Aarts, and R. P. A. Dullens, Phys. Rev. Lett. 118, 158001 (2017).
8. M. Gordon, J. H. Gibbs, and P. D. Fleming, J. Chem. Phys. 65, 2771 (1976).
9. R. J. Speedy, Mol. Phys. 95, 169 (1998).
10. E. Zaccarelli, S. M. Liddle, and W. C. K. Poon, Soft Matter 11, 324 (2015).
11. A. L. Thorneywork, R. Roth, D. G. A. L. Aarts, and R. P. A. Dullens, J. Chem. Phys. 140, 161106 (2014).
12. C. H. Bennett and B. J. Alder, J. Chem. Phys. 54, 4796 (1971).
13. P. N. Pusey, W. Van Megen, P. Bartlett, B. J. Ackerson, J. G. Rarity, and S. M. Underwood, Phys. Rev. Lett. 63, 2753 (1989).
14. S. Pronk and D. Frenkel, J. Phys. Chem. B 105, 6722 (2001).
15. S. Pronk and D. Frenkel, J. Chem. Phys. 110, 4589 (2000).
16. R. van der Meer, M. Dijkstra, and L. Filion, J. Chem. Phys. 146, 244905 (2017).
17. C. Simm, A. Heymann, A. Stipp, and T. Palberg, in Trends Colloid Interface Science (Springer, 2001), Vol. XX, p. 266.
18. K. Schätzle and B. J. Ackerson, Phys. Rev. E 48, 3766 (1993).
19. S. Auer and D. Frenkel, J. Chem. Phys. 120, 3015 (2004).
20. S. Auer and D. Frenkel, Adv. Comput. Simul. 173, 149 (2005).
21. E. Zaccarelli, C. Valeriani, E. Sanz, W. C. K. Poon, M. E. Cates, and P. N. Pusey, Phys. Rev. Lett. 103, 135704 (2009).
22. L. Filion, M. Hermes, R. Ni, and M. Dijkstra, J. Chem. Phys. 133, 244115 (2010).
23. T. Schilling, S. Dorosz, H. J. Shöpe, and G. Opletal, J. Phys.: Condens. Matter 23, 194120 (2011).
24. W. Wöhler and T. Schilling, Phys. Rev. Lett. 128, 238001 (2022).
25. P. N. Pusey and W. van Megen, Phys. Rev. Lett. 59, 2083 (1987).
26. S. M. Underwood, J. R. Taylor, and W. Van Megen, Langmuir 10, 3550 (1994).
27. T. Palberg, J. Phys.: Condens. Matter 11, R323 (1999).
28. C. P. Royall, W. C. K. Poon, and E. R. Weeks, Soft Matter 9, 17 (2013).
29. T. Kawasaki and H. Tanaka, Proc. Natl. Acad. Sci. U. S. A. 107, 14036 (2010).
30. L. Filion, R. Ni, D. Frenkel, and M. Dijkstra, J. Chem. Phys. 134, 134901 (2011).
31. J. Russo, A. C. Maggs, D. Bonn, and H. Tanaka, Soft Matter 9, 7369 (2013).
32. G. Fiorucci, G. M. Colli, J. T. Padding, and M. Dijkstra, J. Chem. Phys. 152, 064903 (2020).
33. S. Auer, W. Poon, and D. Frenkel, Phys. Rev. E 67, 020401 (2003).
34. D. Frenkel and B. Smit, Understanding Molecular Simulation: From Algorithms to Applications, 2nd ed. (Academic Press, San Diego, 2002).
35. J. M. Polson, E. Trizac, S. Pronk, and D. Frenkel, J. Chem. Phys. 112, 5339 (2000).
36. P. N. Pusey and W. Van Megen, Nature 320, 340 (1986).
37. S. Alexander, P. M. Chaikin, P. Grant, G. J. Morales, P. Pincus, and D. Hone, J. Chem. Phys. 80, 5776 (1984).
38. K. Kremer, M. O. Robbins, and G. S. Grest, Phys. Rev. Lett. 57, 2694 (1986).
39. M. O. Robbins, K. Kremer, and G. S. Grest, J. Chem. Phys. 88, 3286 (1988).
40. Y. Monovoukas and A. P. Gast, J. Colloid Interface Sci. 128, 533 (1989).
41. E. R. Sirota, H. D. Ou-Yang, S. K. Sinha, P. M. Chaikin, J. D. Axe, and Y. Fujii, Phys. Rev. Lett. 62, 1524 (1989).
42. Y. Hamaguchi, R. T. Farouki, and D. H. E. Dubin, Phys. Rev. E 56, 4671 (1997).
43. A.-P. Hynninen and M. Dijkstra, Phys. Rev. E 68, 021407 (2003).
44. A. Yethiraj and A. van Blaaderen, Nature 421, 513 (2003).
45. C. P. Royall, M. E. Leunissen, and A. van Blaaderen, J. Phys.: Condens. Matter 15, S3581 (2003).
46. M. F. Hsu, E. R. Dufresne, and D. A. Weitz, Langmuir 21, 4881 (2005).
47. C. P. Royall, M. E. Leunissen, A.-P. Hynninen, M. Dijkstra, and A. van Blaaderen, J. Chem. Phys. 124, 244706 (2006).
48. D. El Masri, P. van Oostrum, F. Smallenburg, T. Vissers, A. Ihmof, M. Dijkstra, and A. van Blaaderen, Soft Matter 7, 3462 (2011).
49. F. Smallenburg, N. Boon, M. Kater, M. Dijkstra, and R. van Roij, J. Chem. Phys. 134, 074505 (2011).
50. T. Kanai, N. Boon, P. J. Lu, E. Sloutskin, A. B. Schofield, F. Smallenburg, R. van Roij, M. Dijkstra, D. A. Weitz et al., Phys. Rev. E 91, 030301 (2015).
51. S. Arii and H. Tanaka, Nat. Phys. 13, 503 (2017).
52. M. Chaudhuri, E. Allahyarov, H. Löwen, S. U. Egelhaaf, and D. A. Weitz, Phys. Rev. Lett. 119, 128001 (2017).
53. K. van Gruijthuijsen, M. Obiols-Rabasa, M. Heinen, G. Nägele, and A. Stradner, Langmuir 29, 11199 (2013).
54. T. E. Kodger, R. E. Guerra, and J. Sprakel, Sci. Rep. 5, 14635 (2015).
55. M. Leunissen, Ph.D. thesis, 2007.
56. D. Frenkel and A. J. C. Ladd, J. Chem. Phys. 81, 3188 (1984).
57. P.-R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, Faraday Discuss. 104, 93 (1996).
58. M de Jager (2022). “Crystal nucleation of highly-screened charged colloids,” Utrecht University.