Quasi-Confined Colloidal Liquids - Structure and Dynamics

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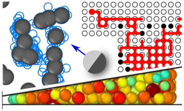
Der Wissenschaftsfonds.



Soft Matter

The hard physics of soft matter

H. Löwen, M. Watzlawek, C. N. Likos, M. Schmidt, A. Jusufi,
J. Dzubiella, C. von Ferber, E. Allahyarov, A. Thünemann, I. D'Amico^{+}

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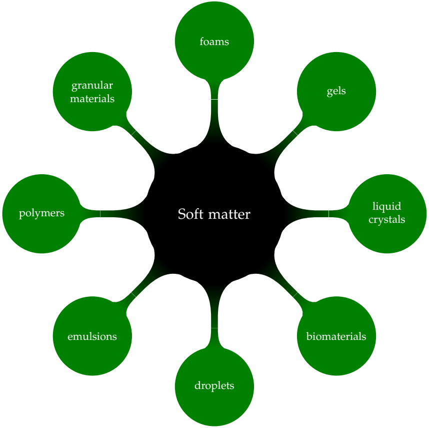
microscopic ($\lesssim 10\,\mathrm{nm}$)

↓

mesoscopic

↓

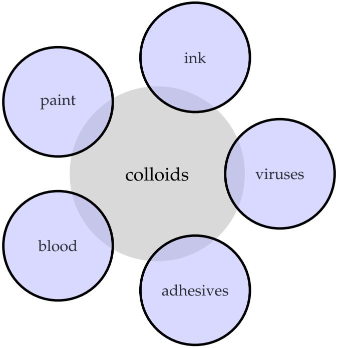
macroscopic ($\gtrsim 100\,\mu\mathrm{m}$)



- mechanical properties intermediate between solids and liquids
- easily deformable on macroscopic scale

Colloids

- solid particles embedded in a molecular liquid


colloids

paint

ink

viruses

blood

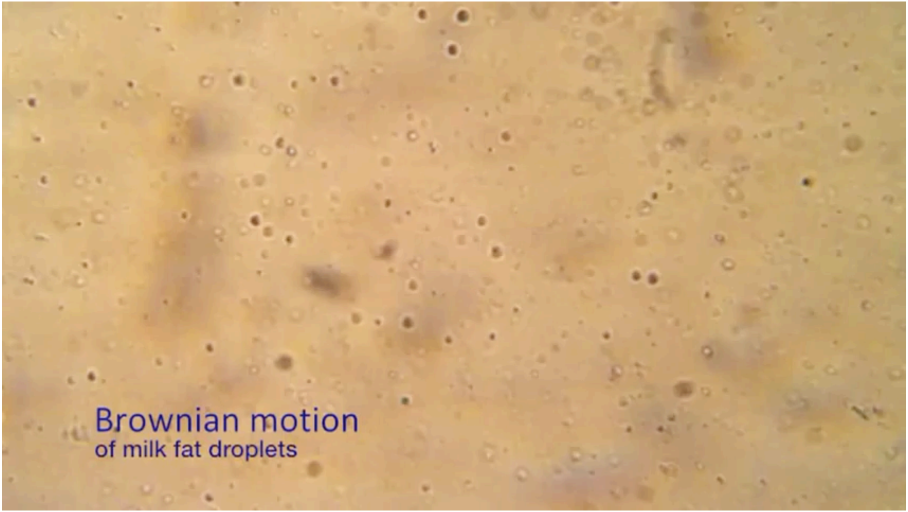
adhesives

- typical particle size:
  1 nm to 1µm

⇒ Brownian motion

I, Chedid [CC BY-SA 3.0]

Brownian Motion[1]



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[1] Stephen Curry (`https://www.youtube.com/watch?v=ernnQJwaKTs`) [CC BY]

Brownian Motion

A. Einstein
(1905)

R. Brown[1]
(1773-1858)

- micro-sized pollen in water
- erratic and agitated motion not connected to life

- collisions with solvent molecules, independent increments
  - mean displacement $\langle \mathbf{r}(t) \rangle = 0$ vanishes
  - mean square displacement $\langle \mathbf{r}(t)^2 \rangle = 6Dt$ related to diffusion coefficient

$\Rightarrow$ statistical interpretation of diffusion

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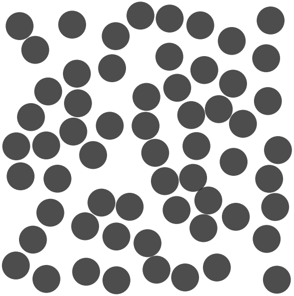
[1] Wellcome Library, London [CC BY 4.0]

Model System



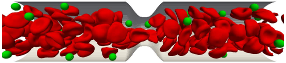
- 3D system
- monodisperse hard spheres with diameter σ
- impenetrable, no overlap
- packing fraction $\varphi = \pi n \sigma^3 / 6$

(Quasi-)Confinement

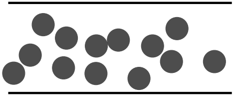
- confined fluids prevalent in nature and industrial applications:

Microfluidics[1]

Biophysics[2]

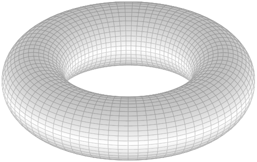


Slit geometry



$\Rightarrow$

Quasi-confinement



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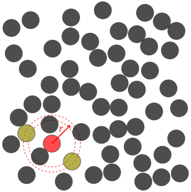
[1] M. Schlenk, E. Hofmann, S. Seibt, S. Rosenfeldt, L. Schrack et al., Parallel and perpendicular alignment of anisotropic particles in free liquid micro-jets and emerging micro-droplets, Langmuir 34, 16 (2018)

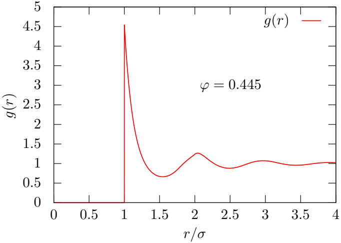
[2] C. Bächer, L. Schrack and S. Gekle, Clustering of microscopic particles in constricted blood flow, Phys. Rev. Fluids 2, 013102 (2017)

Liquid State Theory

- radial distribution function (RDF) $g(r)$: probability of finding particle at distance r from reference particle



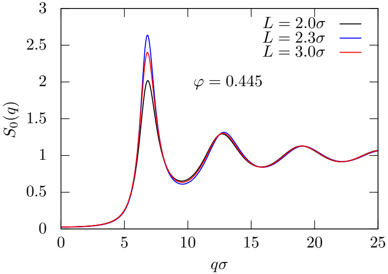
$$g(r) = h(r) + 1$$



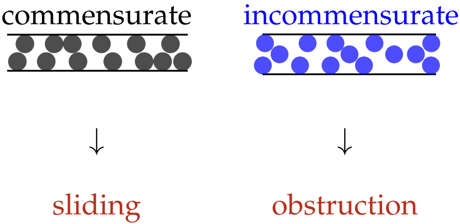
- $g(r < \sigma) = 0 \Rightarrow$ no particle overlap
- $g(r \to \infty) = 1 \Rightarrow$ no long-range order (ideal gas limit)
- peaks roughly in intervals of σ with decreasing intensity
- first peak $\Rightarrow$ first coordination sphere

Stucture of Quasi-Confined Liquids

- adapting established theory for RDF to quasi-confined liquids[1]
- $S_0(q)$: structure parallel to confinement
- Fourier transform (area density n_0): $\boxed{S_0(q) = 1 + \frac{n}{L} h_0(q)}$



- first peak: near-ordering of the fluid


commensurate

incommensurate

↓

↓

sliding

obstruction

⇒ non-monotonic behavior as a function of confinement length

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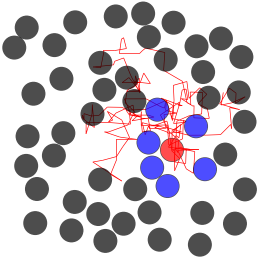
[1] C. Petersen, L. Schrack and T. Franosch, Static properties of quasi-confined hard-sphere fluids, J. Stat. Mech. 083216 (2019)

Dynamics of Colloids

- describe density dynamics
- cage effect: internal forces from cages of neighboring particles ⇒ non-linear feedback

Liquid



- cage breaking by particle motion

increasing $\xrightarrow{\hspace{3cm}}$ packing fraction

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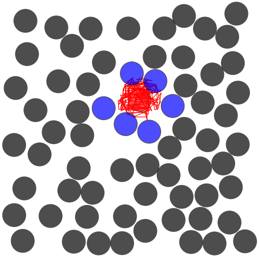
glass transition

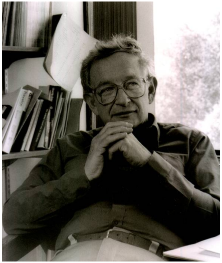
Glass



- trapped in cage by neighbors

Glass Transition

'The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition.' P. W. Anderson[1]



Nobel Prize 1977 for theoretical investigations of the electronic structure of magnetic and disordered systems

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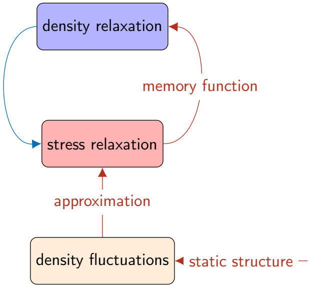
[1] P. Anderson, Through the Glass Lightly, Science 267, 1615 (1995)

Mode-Coupling Theory (MCT)

- first-principle theory without phenomenological assumptions ⇒ static quantities as input



density relaxation

memory function

stress relaxation

approximation

density fluctuations

static structure

- density dynamics described by *self-intermediate scattering function* (ISF)

$$\boxed{S^{(s)}(q,t) = \langle \underbrace{\rho^{(s)}(\mathbf{q},t)^*}_{\text{density mode}} \rho^{(s)}(\mathbf{q},0)\rangle}$$

- ISF characteristic function of random displacement ⇔ full probability distribution

⇒ elaborating MCT for (quasi-)confined colloidal liquids[1]

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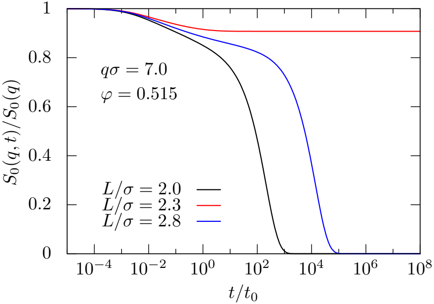
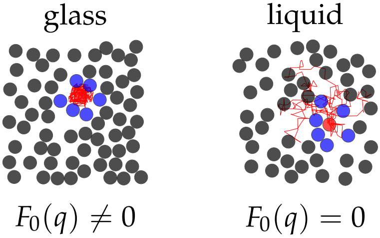
[1] L. Schrack and T. Franosch, Mode-coupling theory of the glass transition for colloidal liquids in slit geometry (under review)

Dynamics



- glass-form factor

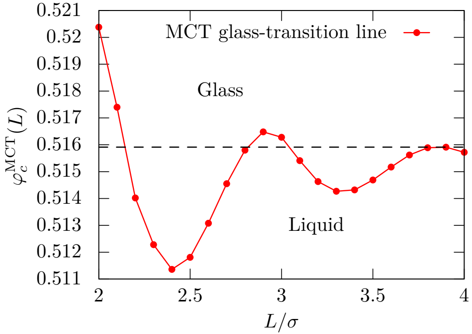
$$\boxed{F_0(q) = \lim_{t\to\infty} S_0(q,t)}$$



- solving integro-differential equation over 12 orders of magnitude
  $\Rightarrow$ efficient numerical algorithm
- short time: rattling within cage

Phase Diagram[1]

- glass-form factor to distinguish between liquid and glassy state



- non-monotonic behavior ⇒ reentrant phenomena
- commensurate vs. incommensurate packing
- comparison with simulations

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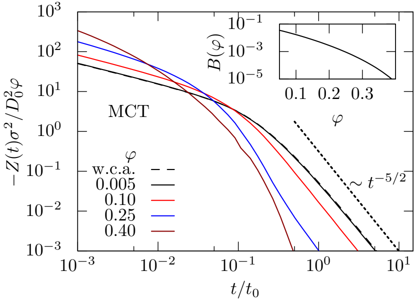
[1] L. Schrack, C. Petersen and T. Franosch, Dynamic properties of quasi-confined colloidal hard-sphere liquids near the glass transition (in preparation)

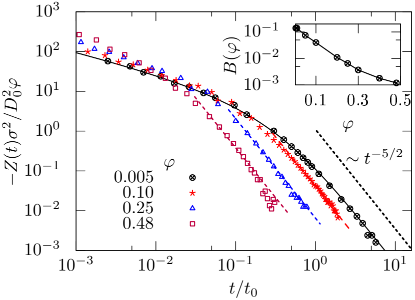
Excursus: Anti-Correlations of Dense Colloidal Suspensions[1]

- long-time behavior of velocity-autocorreation function (VACF) of dense colloidal suspensions

MCT



Simulation



- negative algebraic power-law decay instead of exponential decay

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[1] S. Mandal, L. Schrack, H. Löwen, M. Sperl, T. Franosch, Persistent Anti-Correlations in Brownian Dynamics Simulations of Dense Colloidal Suspensions Revealed by Noise Suppression, PRL 123, 168001 (2019)

Conclusions and Outlook

- quasi-confinement: extremely small periodic boundary conditions in one direction
- elaborate liquid state theory for static and mode-coupling theory for dynamic properties of quasi-confined colloidal liquids
- non-monotonic behavior as a function of confinement length
- comparison with simulations
- analyze further transport properties, e.g. mean-square displacement

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Thank you for your attention.