# Forward Scattering and Compressibility

Group Seminar – 24.11.2010

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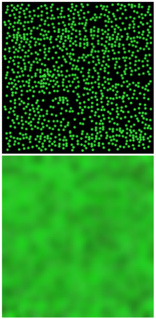
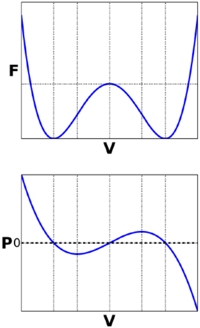


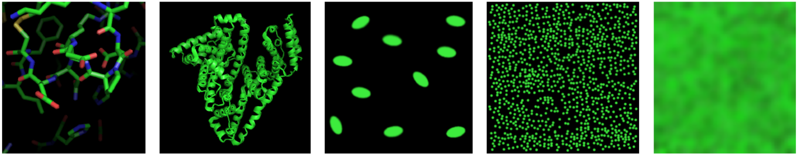
## Outline

- Scattering at low $q$
- Compressibility $\chi_T$
- Virial Expansion
- Applications



# Scattering and Length Scale

Scattering probes density autocorrelations at $\lambda \approx \frac{2\pi}{q}$



$q \approx \mathrm{nm}^{-1}$

$q \approx \mu\mathrm{m}^{-1}$

smaller $q$ $\Leftrightarrow$ smaller "resolution"

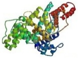
# Scattering and Structure Factor

$$\rho(r) = \sum_{j=1}^{N} f_j\,\delta(r - r_j) \qquad \text{scattering density}$$

$$\begin{aligned}
I(q) &= \mathcal{FT}[\langle \rho(r')\rho(r+r')\rangle] \qquad \text{scattering intensity} \\
&= \left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} f_j(q) f_k(q) \exp(iq(r_j - r_k)) \right\rangle \\
&\overset{(*)}{=} N\,f_{\mathrm{inc}}^2(q) + N\,f_{\mathrm{coh}}^2(q) S(q) \qquad \mid (*) : \text{decoupling approx.}
\end{aligned}$$

$$f_{\mathrm{coh}}(q) = \langle f_j(q) \rangle \;, \quad f_{\mathrm{inc}}^2(q) = \langle f_j^2(q) \rangle - \langle f_j(q) \rangle^2$$

$$S(q) = \frac{1}{N} \left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} \exp(iq(r_j - r_k)) \right\rangle \qquad \text{structure factor}$$



# Structure Factor $S(q)$ and Pair Correlation Function $g(r)$

$$
\begin{aligned}
\color{red}{S(q)} &= \frac{1}{N}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} \exp(iq(r_j - r_k)) \right\rangle \\
&= 1 + \frac{1}{N}\int \mathrm{d}r\, \exp(-iqr) \underbrace{\left\langle \sum_{j}\sum_{k\neq j} \delta(r + r_j - r_k)) \right\rangle}_{V\rho^2 g(r)} \\
&= 1 + \rho \int \mathrm{d}r\, \exp(-iqr)(g(r) - 1) \quad + \quad \frac{\rho}{V}\delta(q) \\
&\xrightarrow[q\to 0]{} 1 + \rho \int_0^{r_{\mathrm{corr,max}}} \mathrm{d}r (g(r) - 1) \qquad \left[\text{valid, if } q \ll \frac{2\pi}{r_{\mathrm{corr,max}}}\right]
\end{aligned}
$$

# Forward Scattering: $S(q \rightarrow 0)$

finite and fixed scattering volume $V \Rightarrow \rho = \frac{\langle N \rangle}{V}$

$$\begin{aligned}
S(q \rightarrow 0) &= 1 + \rho \int \mathrm{d}r (g(r) - 1) \\
&= 1 + \frac{1}{\langle N \rangle} \int \mathrm{d}r \left( \left\langle \sum_j \sum_{k \neq j} \delta(r + r_j - r_k)) \right\rangle - \rho \langle N \rangle \right) \\
&= 1 + \frac{\langle N^2 \rangle - \langle N \rangle}{\langle N \rangle} - \langle N \rangle = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{\langle \Delta N^2 \rangle}{\langle N \rangle}
\end{aligned}$$

⇒ for $q \rightarrow 0$, i.e. $q \ll 2\pi / r_{\mathrm{corr,max}}$:
number of particles in scattering volume relevant, not positions

⇒ fluctuations in $N$ important

# Thermodynamics and Fluctuations

## subsystem in bigger reservoir

total energy / free energy / enthalpy conserved

$$\Rightarrow \quad \begin{cases} \text{equilibrium maximizes total entropy } S_t = S_r + S_s \\ \text{propability for fluctuation with } \Delta S_t : \quad p \propto \exp(\Delta S_t / k_B) \end{cases}$$

fluctuation in variables $x_j$ small → Taylos series:

$$\Delta S_t \;=\; \sum_j \underbrace{\left.\frac{\partial S_t}{\partial x_j}\right|_{eq}}_{=0} \Delta x_j + \frac{1}{2} \sum_{j,k} \underbrace{\left.\frac{\partial^2 S_t}{\partial x_j \partial x_k}\right|_{eq}}_{<0} \Delta x_j \Delta x_k$$

now: look at number fluctuation $\Delta N = N - N_{eq}$ in subsystem

# Thermodynamics and Fluctuations

$$\begin{aligned} \Delta S_t &= \frac{1}{2}\left( \left.\frac{\partial^2 S_r}{\partial N^2}\right|_{eq} + \left.\frac{\partial^2 S_s}{\partial N^2}\right|_{eq} \right) (\Delta N)^2 \\ &\approx \frac{1}{2} \left.\frac{\partial^2 S_s}{\partial N^2}\right|_{eq} (\Delta N)^2 \end{aligned}$$

$$\Rightarrow \quad p \;\propto\; \exp(\Delta S_t / k_B) = \exp\left( \frac{1}{2k_B} \left.\frac{\partial^2 S_s}{\partial N^2}\right|_{eq} (\Delta N)^2 \right)$$

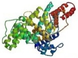
$$\begin{aligned} \Rightarrow \langle (\Delta N)^2 \rangle &= k_B \left.\frac{\partial^2 S_s}{\partial N^2}\right|_{eq}^{-1} = k_B T \left.\frac{\partial \mu}{\partial N}\right|_{T,V}^{-1} = \langle N \rangle \rho k_B T \left.\frac{\partial P}{\partial V}\right|_{T,N}^{-1} \\ &= \langle N \rangle \rho k_B T \chi_T \end{aligned}$$

# Compressibility Equation

$$S(q \rightarrow 0) = 1 + \rho \int \mathrm{d}r (g(r) - 1) = \frac{\langle \Delta N^2 \rangle}{\langle N \rangle} = \rho k_B T \chi_T$$

### compressibility equation connects

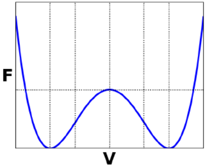
- microscopics: pair correlation function $g(r)$
- thermodynamics: isothermal compressibility $\chi_T$
- experiment: forward scattering $S(q \rightarrow 0)$



# Why Measure Compressibility?

**thermodynamic potential: free energy**
$F(T, V, N) = U - TS = -k_B T \ln(Z_N)$

- description of system in terms of the chosen state varibles $(T, V, N)$
- connects to statistical description via the partition function
  $Z_N = \frac{1}{N!\Lambda^{3N}} \int \mathrm{d}r^N \exp(-\beta V(r))$
- involves and produces all thermodynamic system parameters



# Why Measure Compressibility?

thermodynamic potential: free energy

$$F(T,V,N) = U - TS = -k_B T \ln(Z_N)$$

- description of system

equation of state: $P(T,V,N) = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$

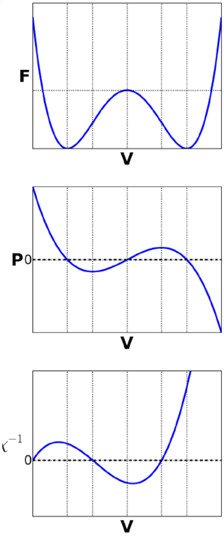
⇒ alternative description of system

isothermal compressibility:

$$\chi(T,V,N) = -\left(V\left.\frac{\partial P}{\partial V}\right|_{T,N}\right)^{-1}$$

- connects directly to scattering experiment

⇒ provides information on system behavior

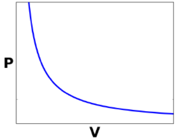


# Ideal Gas: Dilute Solutions

## Ideal Gas:

- no interactions $V(r) = 0$

$$
\begin{aligned}
Z_N &= \frac{V^N}{N!\Lambda^{3N}} \\
F &= Nk_B T(\ln(\Lambda^3\rho) - 1) \\
\beta P &= \frac{N}{V} = \rho \\
\frac{\beta}{\chi} &= \frac{N}{V} = \rho
\end{aligned}
$$



## Forward Scattering

$$
\begin{aligned}
I(q \to 0) &= N\, f_{coh}^2\, S(q \to 0) \\
&= N\, f_{coh}^2\, \rho\, k_B T\, \chi \\
&= N\, f_{coh}^2
\end{aligned}
$$

Information from $N\, f_{coh}$:

- molecular weight $M_w$
- molecular volume $v_p$
- number density / concentration
- constituents of particles

# Real Gas: Virial Expansion

interactions $V(r) \neq 0 \quad \Rightarrow \quad P(\rho) = k_B T \sum_{j=0}^{n} B_j \, \rho^j$

## Pertubation from ideal gas

with Mayer-function as parameter: $f(r) = \exp(-\beta V(r)) - 1$

$$\begin{aligned} Z_N &= \frac{1}{N!\Lambda^{3N}} \int \mathrm{d}r^N \prod_{j>k} \exp(-\beta V(r_{jk})) \\ &= \frac{1}{N!\Lambda^{3N}} \int \mathrm{d}r^N \prod_{j>k} (1 + f(r_{jk})) \\ &= \frac{1}{N!\Lambda^{3N}} \int \mathrm{d}r^N \left( 1 + \sum_{j>k} f(r_{jk}) + \mathcal{O}(f^2) \right) \end{aligned}$$

# Real Gas: Virial Expansion

$$\text{interactions } V(r) \neq 0 \quad \Rightarrow \quad P(\rho) = k_B T \sum_{j=0}^{n} B_j \, \rho^j$$

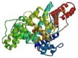
## Pertubation from ideal gas

with Mayer-function as parameter: $f(r) = \exp(-\beta V(r)) - 1$

$$\begin{aligned} Z_N &= \frac{1}{N!\Lambda^{3N}} \int \mathrm{d}r^N \left( 1 + \sum_{j>k} f(r_{jk}) + \mathcal{O}(f^2) \right) \\ &\approx \frac{V^N}{N!\Lambda^{3N}} \left( 1 + B_2 \frac{N(N-1)}{2V} \right) \end{aligned}$$

## Second virial coefficient

$$B_2 = -2\pi \int_0^\infty \mathrm{d}R \, R^2 \left(\exp(-\beta V(R)) - 1\right)$$



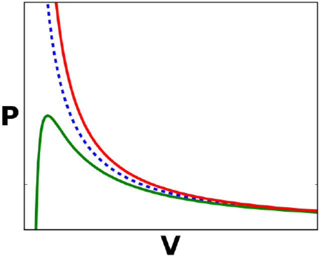
# Real Gas: Virial Expansion up to Second Order

## Real Gas:

- (pairwise) interactions

$$\beta P \approx \rho + B_2\rho^2$$
$$\frac{\beta}{\chi_T} \approx \rho + 2B_2\rho^2$$

$$\frac{1}{I(q \to 0)} = \frac{1}{N\,f_{coh}^2\,S(Q \to 0)} \approx \frac{1}{N\,f_{coh}^2}(1 + 2B_2\rho)$$



- dilute limit as in ideal gas
- measurement of 2nd virial coefficient $B_2$

→ information on interaction

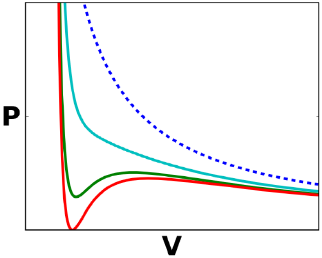
# Real Gas: van der Waals equation

## Real Gas:

- interactions → $P = P(\rho)$
- excluded volume due to particle volume

$$\beta P = \frac{\rho}{1-b\rho} - \beta a \rho^2$$

$$I(q \to 0) \quad \propto \quad \chi_T(\rho)$$
$$\chi_T(\text{spinodal}) \quad \to \quad \infty$$



- measurement of spinodal

→ information on phase diagram

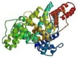
# Remark: Polydispersity / Incoherent Scattering

$$I(q) \overset{(*)}{=} N\, f_{\mathrm{inc}}^2(q) + N\, f_{\mathrm{coh}}^2(q) S(q) \qquad \mid (*) : \text{decoupling approx.}$$

$$f_{\mathrm{coh}}(q) = \langle f_j(q) \rangle \ , \quad f_{\mathrm{inc}}^2(q) = \langle f_j^2(q) \rangle - \langle f_j(q) \rangle^2$$

### Is $f_{\mathrm{inc}}^2$ negligible for $I(q \to 0)$?

- rotational polydispersity: for $q \ll 2\pi D_{\mathrm{particle}}$, $f_{\mathrm{inc}}$ vanishes (Rayleigh-scatterer)
- oligomerization: not negligible, since scattering amplitude remains different also for small $q$
  Example BSA: dimerfraction around 20 %
  $f_{\mathrm{coh}}^2(q \to 0) = (0.8 \cdot f_0 + 0.2 \cdot 2f_0)^2 = 1.44 f_0^2$
  $f_{\mathrm{inc}}^2(q \to 0) = 0.8 \cdot f_0^2 + 0.2 \cdot 4f_0 - f_{\mathrm{coh}}^2 \approx 0.16 f_0^2 \approx 0.1 f_{\mathrm{coh}}^2$



# Summary

## compressibility yields information on

- system phase behavior,
- particle interaction and
- particle properties

$\chi \searrow \quad \Rightarrow$ repulsion
$\chi \nearrow \quad \Rightarrow$ attraction
$\chi \rightarrow \infty \Rightarrow$ spinodal

## forward scattering probes compressibility

- compressibility equation:
  $$S(q \rightarrow 0) = 1 + \rho \int \mathrm{d}r(g(r) - 1) = \frac{\langle \Delta N^2 \rangle}{\langle N \rangle} = \rho k_B T \chi_T$$
- valid for $q \ll 2\pi / r_{\mathrm{corr,max}}$
- for negligible polydispersity / incoherent scattering:
  $I(q \rightarrow 0) \propto S(q \rightarrow 0)$

forward scattering, e.g. light scattering and (U)SAXS, provides information on the thermodynamics of the system

# Literature

Detailed derivations of the discussed relations can be found in:

- J.-P. Hansen, I.R. McDonald: Theory of simple liquids, 3rd Edition, Academic Press, 2006.