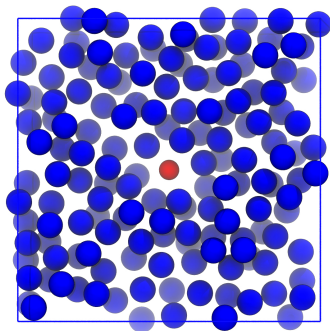# Liquids

MSE 421 - Ceriotti

A theory of the liquid state

- Very important for materials science: medium for synthesis, processing in the molten phase, models for glasses
- Liquids pose a huge challenge to modeling and theoretical description
  - atoms are disordered, so no way to invoke a harmonic approximation
  - atoms are strongly interacting, so cannot invoke independent particles approximations

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Classical statistical mechanics

- Atoms are treated as classical particles following the Hamiltonian

$$H = K(\mathbf{p}) + U(\mathbf{r}) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U(\{\mathbf{r}_i\})$$

  with positions $\mathbf{r} = \{\mathbf{r}_i\}$ and momenta $\mathbf{p} = \{\mathbf{p}_i\}$

- The potential is a complicated, non-linear function of all coordinates

- The partition function factors in a free-particle part (consider the classical limit of the quantum counterpart) and one that depends on U

$$Q = Q_{\mathbf{p}} Q_{\mathbf{r}} = \frac{1}{N!} \left[\frac{h}{\sqrt{2\pi m k_B T}} \right]^{3N} \int \mathsf{d}^N \{\mathbf{r}_i\} \, e^{-\beta U(\{\mathbf{r}_i\})}$$

- The probability of observing a given configuration of the atoms is just

$$P(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{Q_{\mathbf{r}}} e^{-\beta U(\{\mathbf{r}_i\})}$$

Reduced distribution functions

- We can always marginalize P with respect to some of the atoms. Take for instance single-particle marginal

- Since all atoms are statistically equivalent, it is more convenient to define a *generic* distribution function, summed over all particle indices

$$P^{(1)}(\mathbf{r}_1) = \int d^{N-1}(\mathbf{r}_2, \ldots) P(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$\rho^{(1)}(\mathbf{r}) = \sum_i P^{(1)}(\mathbf{r}_i) = N P^{(1)}(\mathbf{r}_1 = \mathbf{r}) \underset{\text{if no external potential}}{=} N \cdot \frac{1}{V} = \rho$$

- Two-particle case

$$P^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \int d^{N-2}(\mathbf{r}_3, \ldots) P(\mathbf{r}_1, \ldots, \mathbf{r}_N),$$

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \sum_{i \neq j} P^{(2)}(\mathbf{r}_i, \mathbf{r}_j) = N(N-1) P^{(2)}(\mathbf{r}_1 = \mathbf{r}, \mathbf{r}_2 = \mathbf{r}')$$

- for an ideal gas, $\rho^{(2)} = \frac{N(N-1)}{V^2} = \left(1 - N^{-1}\right) \rho^2$

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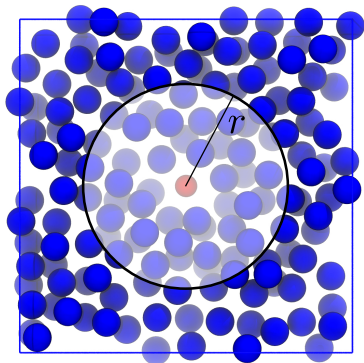
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The pair correlation function

- In an isotropic medium, $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ depends only on $r = |\mathbf{r} - \mathbf{r}'|$
- We can define a normalized version of $\rho^{(2)}$, that indicates the probability of finding a particle at distance r from the origin, conditional on having one particle at 0. This is called the pair correlation function $g(r)$.
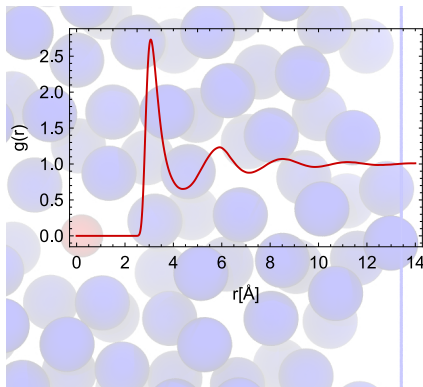
$$g(r) = \rho^{(2)}(\mathbf{0}, \mathbf{r})/\rho^2$$

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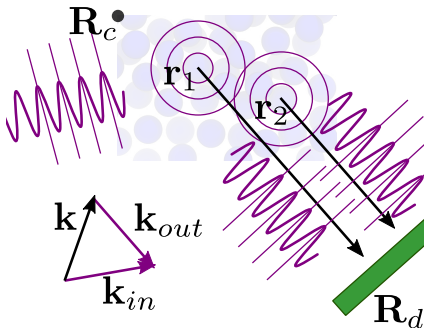$$g(r) = \rho^{(2)}(\mathbf{0}, \mathbf{r})/\rho^2$$

Scattering from a liquid/1

- Consider the scattering of X-rays (or, similarly, neutrons) from the atoms.
- Scattering is nearly elastic, so $k_{in} = k_{out}$. Define $\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{in}$.
- The amplitude of the waves scattered by an atom at position $\mathbf{r}_i$ relative to the center of the sample $\mathbf{R}_c$ reads

$$A_i \propto e^{i\mathbf{k}_{in}(\mathbf{R}_c+\mathbf{r}_i)} \, e^{i\mathbf{k}_{out}(\mathbf{R}_d-(\mathbf{R}_c+\mathbf{r}_i))} = e^{i(\mathbf{k}_{in}-\mathbf{k}_{out})\mathbf{R}_c} \, e^{i\mathbf{k}_{out}\mathbf{R}_d} \, e^{i(\mathbf{k}_{in}-\mathbf{k}_{out})\mathbf{r}_i} = \phi e^{-i\mathbf{k}\mathbf{r}_i}$$

- The amplitude (collected at $\mathbf{R}_d$) also includes a k dependent atomic form factor $f(k)$, which we ignore here

Scattering from a liquid/2

- The intensity collected at the detector is the square modulus of the total amplitude (structure factor $S(\mathbf{k})$)
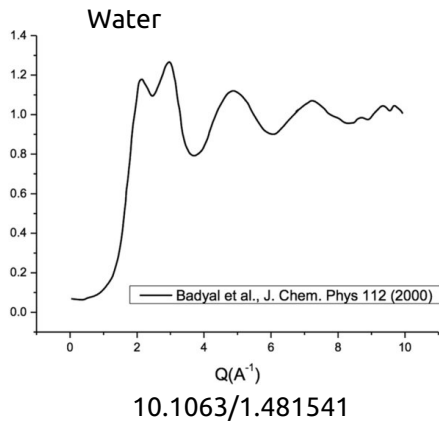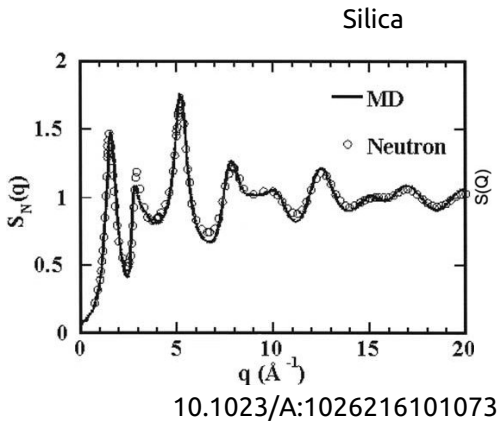
$$I \propto \left\langle \left| \sum_i A_i \right|^2 \right\rangle \propto |\phi|^2 \left\langle \sum_{ij} e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle \propto N + \sum_{i \neq j} \left\langle e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle =$$

$$= N + N(N-1) \left\langle e^{i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2)} \right\rangle = N S(\mathbf{k})$$

- The average can be computed as an integral over the generic pair correlation function. δ-like contribution for $k = 0$ can be removed by defining $h(r) = g(r) - 1$

$$S(\mathbf{k}) = 1 + \frac{V}{N} \int d\mathbf{r} \rho^{(2)}(\mathbf{0}, \mathbf{r}) e^{i\mathbf{k}\mathbf{r}} = 1 + \rho \int d\mathbf{r} g(r) e^{i\mathbf{k}\mathbf{r}}$$

$$S(k) = 1 + 2\pi\rho \int dr r^2 g(r) \, d\theta \sin\theta e^{ikr\cos\theta} = 1 + 2\pi\rho \int dr r^2 g(r) \frac{e^{-ikr} - e^{ikr}}{-ikr} =$$

$$= 1 + 4\pi\rho \int dr g(r) \frac{r}{k} \sin kr \sim 1 + \rho V \delta(\mathbf{k}) + \frac{4\pi\rho}{k} \int dr h(r) \, r \sin kr$$

Silica

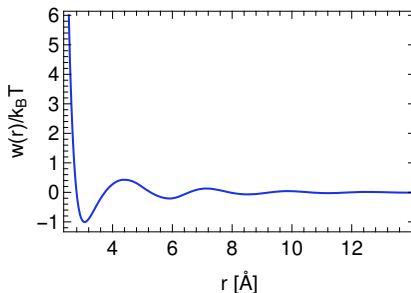Water

10.1023/A:1026216101073

10.1063/1.481541

Reversible work theorem

- How much work should be made to bring two atoms in the fluid, initially far from each other, at a distance r?

$$w(R) = -\int_{path} \langle \mathbf{f} \rangle \cdot d\mathbf{r} = -\int_{\infty}^{R} \langle \mathbf{f} \rangle \cdot \hat{\mathbf{u}} dr = -\int_{\infty}^{R} \cdot \left\langle -\frac{\partial U(\mathbf{0}, \mathbf{r}, \ldots)}{\partial \mathbf{r}} \right\rangle_{|\mathbf{r}|=r} dr$$

$$\left\langle -\frac{\partial U(\mathbf{0}, \mathbf{r}, \ldots)}{\partial \mathbf{r}} \right\rangle_{|\mathbf{r}|=r} = \frac{\int d\mathbf{r}_3 \ldots d\mathbf{r}_N - \frac{\partial U(\mathbf{0}, \mathbf{r}, \ldots)}{\partial \mathbf{r}} e^{-\beta U(\mathbf{0}, \mathbf{r})}}{\int d\mathbf{r}_3 \ldots d\mathbf{r}_N e^{-\beta U(\mathbf{0}, \mathbf{r}, \ldots)}} =$$
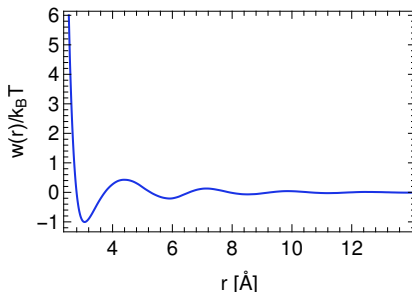

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... integrating by parts (or checking by substitution)

$$\left\langle -\frac{\partial U(\mathbf{0}, \mathbf{r}, \ldots)}{\partial \mathbf{r}} \right\rangle_{|\mathbf{r}|=r} = \frac{1}{\beta} \frac{\partial}{\partial \mathbf{r}} \ln \int d\mathbf{r}_3 \ldots d\mathbf{r}_N e^{-\beta U(\mathbf{0}, \mathbf{r}, \ldots)}$$
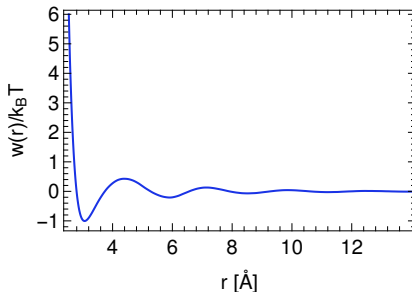

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. . . since we can add any constant in the log ($\partial K/\partial \mathbf{r} = 0$)

$$= \frac{1}{\beta} \frac{\partial}{\partial \mathbf{r}_1} \ln \frac{N(N-1)}{Q\rho^2} \int d\mathbf{r}_3 \ldots d\mathbf{r}_N e^{-\beta U(\mathbf{0}, \mathbf{r}, \ldots)} = \frac{1}{\beta} \frac{\partial}{\partial \mathbf{r}} \ln \frac{\rho^{(2)}(\mathbf{0}, \mathbf{r})}{\rho^2}$$
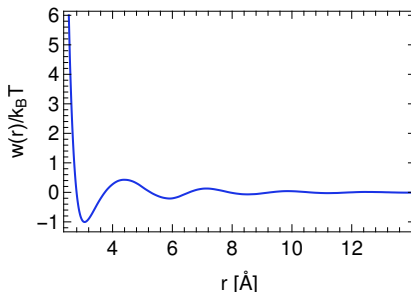

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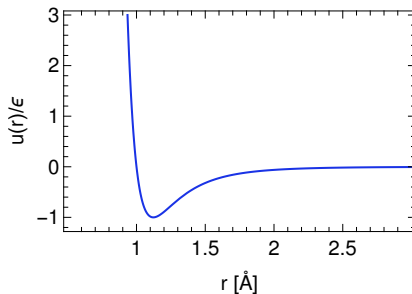

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Pair potentials & thermodynamic properties

- Consider the case in which $U(\{\mathbf{r}_i\}) = \frac{1}{2}\sum_{i\neq j} u(|\mathbf{r}_i - \mathbf{r}_j|)$ (a pair potential)
- We can compute explicitly the thermal average of the internal energy $\langle U \rangle$ based on the pair correlation function

$$\langle U \rangle = \int d\{\mathbf{r}_i\} \sum_{i\neq j} u(|\mathbf{r}_i - \mathbf{r}_j|) \frac{e^{-\beta U}}{2Q} = N(N-1) \int d\{\mathbf{r}_i\} u(|\mathbf{r}_1 - \mathbf{r}_2|) \frac{e^{-\beta U}}{2Q}$$

$$= \frac{1}{2} \int d\mathbf{r}' d\mathbf{r}\, u(|\mathbf{r}|)\, \rho^{(2)}(\mathbf{0}, \mathbf{r}) = \frac{1}{2} N\rho \int dr\, 4\pi r^2 g(r) u(r)$$

- This combines with the ideal gas term $\langle K \rangle = 3Nk_B T/2$ to give $\langle E \rangle$

Dilute limit and virial coefficients

- Now write $w(r) = u(r) + \Delta w$. We consider Δw to be small in the dilute limit, so we can write

$$\frac{\langle U \rangle}{N} \sim \frac{\rho}{2} \int dr \, 4\pi r^2 u(r) \, e^{-\beta u(r)} (1 + \mathcal{O}(\rho)) = \frac{\langle E \rangle - \langle E_{\text{ideal gas}} \rangle}{N} = \frac{\Delta E}{N}$$

- We can obtain the free energy by integrating over β [remember: $\langle E \rangle = -\partial \ln Q / \partial \beta$ and $\ln Q = -\beta A$]

$$\frac{\partial \beta \Delta A / N}{\partial \beta} = \frac{\rho}{2} \int d\mathbf{r} \, u(r) \, e^{-\beta u(r)} + \mathcal{O}(\rho^2)$$

- We can compute the equation of state [remember: $p = -\partial A / \partial V = \rho^2 \partial (A/N) / \partial \rho$, and for an ideal gas $\beta p = \rho$]

$$\beta p = \rho + \rho^2 \frac{\partial \beta \Delta A / N}{\partial \rho} = \rho + \rho^2 \underbrace{\int dr \, 4\pi r^2 \left[1 - e^{-\beta u(r)} \right]}_{\text{second virial coefficient}} + \mathcal{O}(\rho^3)$$

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