Static Properties of Liquids: Thermodynamics, Structure and beyond?

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Spatial correlations

Thermodynamics

Scattering experiments

https://en.wikipedia.org/wiki/Formation_skydiving

Spatial correlations

Radial distribution function

$$g(r) = \frac{1}{4\pi N r^2 \rho_0} \sum_{j=1}^{N} \sum_{\substack{i=1 \\ i \neq j}}^{N} \delta(r - r_{ij})$$

Total correlation function

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

N-body correlation function

$$P_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n) = \frac{1}{\mathcal{Z}_N} \int \cdots \int e^{-\beta U(\vec{q}_1 \cdots \vec{q}_N)} \mathrm{d}\vec{q}_{n+1} \cdots \mathrm{d}\vec{q}_N,$$

$$\rho_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n) = \frac{N!}{(N-n)!} P_N^{(n)}(\vec{q}_1 \cdots \vec{q}_n).$$

Spatial correlations

Density - density correlations function

$$H(r,r') = \langle (\rho(r) - \langle \rho(r) \rangle)(\rho(r') - \langle \rho(r') \rangle) \rangle$$

Direct correlation function

$$h(r,r') = \boxed{c(r,r') +} \int dr'' c(r,r'') \rho_1(r'') h(r'',r')$$

Functional

function

$$f(\mathbf{z}) = \sum_{i=1}^{n} a_i z_i,$$

$$\mathrm{d}f = \sum_{i=1}^{n} a_i \, \mathrm{d}z_i$$

$$\frac{\partial f}{\partial z_i} = a_i$$

functional

$$F[u] = \int a(x) u(x) \mathrm{d}x,$$

$$\delta F = \int a(x) \delta u(x) \mathrm{d}x$$

$$\frac{\delta F}{\delta u(x)} = a(x)$$

Functional derivatives: *Ideal gas in external field*

Hamiltonian

$$H(r^N, p^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} \phi(r)$$

Partition function

$$Q(\beta, V, z) = \sum_{i=1}^{N} e^{\beta\mu N} \frac{1}{h^{3N} N!} \int e^{-\beta[\sum_{i=1}^{N} \frac{p_i^2}{2m}]} dp_1 \ldots dp_N \int e^{-\beta[\sum_{i=1}^{N} \phi(r)]} dr_1 \ldots dr_N$$

$$= \sum_{N=0}^{\infty} z^N \frac{1}{N!} [Z(\beta, V, 1)]^N = e^{zZ(\beta, V, 1)}$$

we know that $e^x = \sum_{i=0}^{N} \frac{x_i^N}{N_i!}$

similarly we can write, $\sum_{i=0}^{N} \frac{(zZ(\beta,V,1))^N}{N!} = e^{zZ(\beta,V,1)}$

$$\ln Q(\beta, V, z) = z \frac{1}{\lambda^3} \int e^{-\beta\phi(\mathbf{r})} d\mathbf{r}$$

grand potential $\Omega(\beta, V, z) = -k_B T \ln Q(\beta, V, z)$

$$\beta\Omega(\beta, V, z) = -\frac{1}{\lambda^3} \int e^{-\beta u(\mathbf{r})} d\mathbf{r} = \beta\mathbf{\Omega}[\mathbf{u}]$$

Functional derivatives: *Ideal gas in external field*

First derivative

$$\beta\delta\Omega[u] = -\frac{1}{\lambda^3}\int e^{-\beta u(\mathbf{r})}\beta\delta u(r)dr$$

$$\frac{\delta\Omega[u]}{\delta u(r)} = -\rho_1(r)$$

Second derivative

$$\begin{aligned}\frac{\delta^2\Omega[u]}{\delta u(r)\delta u(r')} &= -\delta\rho_1(r) \\ &= -\beta\frac{1}{\lambda^3}e^{\beta u(r)}\delta u(r) \\ &= -\beta\int\rho_1(r)\delta(r-r')\delta u(r')dr \\ &= -\beta\rho_1(r)\delta(r-r') < 0\end{aligned}$$

We know that

$$\rho_1(r) = \left\langle \sum_{i=1} N\delta(r-r_i)\right\rangle = \frac{1}{\lambda^3}e^{\beta u(r)}$$

$$\int_{-\infty}^{\infty} g(x)\delta(x-x_0)dx = g(x_0).$$

Functional derivatives: *Interacting particles in external field*

Hamiltonian

$$H(r^N, p^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(r^N)$$
$$= \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} \phi(r) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} H(r_{ij})$$

Partition function

$$Q(\beta, V, z) = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{1}{h^{3N} N!} \int e^{-\beta[\sum_{i=1}^{N} \frac{p_i^2}{2m}]} dp_1 ... dp_N \int e^{-\beta[\sum_{i=1}^{N} \phi(r)]} dr_1 ... dr_N \int e^{-\beta[\sum_{i=1}^{N}\sum_{j\geq i}^{N} H(r_{ij})} dr_1 ... dr_N$$

$$e^{-\beta\Omega[u]} = \sum_{N=0}^{\infty} \frac{1}{N!\lambda^{3N}} e^{\beta\mu N} \int ... \int e^{-\beta\sum_{N=1}^{\infty} \phi(r_i) dr_1 ... dr_N}$$
$$= \sum_{N=0}^{\infty} \frac{1}{N!\lambda^{3N}} e^{\beta\mu \int \rho(r) dr1 ... dr_N} \int ... \int e^{-\beta\sum_{N=1}^{\infty} \phi(r_i) dr_1 ... dr_N}$$
$$= \sum_{N=0}^{\infty} \frac{1}{N!\lambda^{3N}} \int ... \int e^{\beta \int \rho(r) u(r) dr1 ... dr_N}$$

Functional derivatives: *Interacting particles in external field*

First derivative

$$e^{-\beta\Omega[u]}(-\beta\frac{\delta\Omega[u]}{\delta u(r')}) = \sum_{N=0}^{\infty}\frac{1}{\lambda^{3N}N!}\int...\int e^{\beta\int\rho(r)u(r)dr1...dr_N}(\beta\frac{\delta}{\delta u(r')}\int\rho(r)u(r)dr1...dr_N)$$

$$= \sum_{N=0}^{\infty}\frac{1}{\lambda^{3N}N!}\int...\int e^{\beta\int\rho(r)u(r)dr1...dr_N}(\beta\int\rho(r)\frac{\delta u(r)}{\delta u(r')}dr1...dr_N)$$

$$= \sum_{N=0}^{\infty}\frac{1}{\lambda^{3N}N!}\int...\int e^{\beta\int\rho(r)u(r)dr1...dr_N}(\beta\int\rho(r)\delta(r-r')dr1...dr_N)$$

$$= \sum_{N=0}^{\infty}\frac{1}{\lambda^{3N}N!}\int...\int e^{\beta\int\rho(r)u(r)dr1...dr_N}(\beta\int\rho(r')dr^N)$$

$$\frac{\delta\Omega[u]}{\delta u(r')} = -\frac{\sum_{N=0}^{\infty}\frac{1}{\lambda^{3N}N!}\int...\int e^{\beta\int\rho(r)u(r)dr1...dr_N}(\int\rho(r')dr^N)}{e^{-\beta\Omega[u]}}$$

$$= -\langle\rho_1(r')\rangle$$

Functional derivatives: *Interacting particles in external field*

Second derivative

$$\frac{\delta^2\Omega[u]}{\delta u(r')\delta u(r'')} = -\beta e^{\beta\Omega}\frac{\delta\Omega[u]}{\delta u(r'')}\sum_{N=0}^{\infty} e^{\beta\mu N}\int\dots\int e^{-\beta\sum_{N=1}^{\infty}\phi(r_i)}\rho(r')dr_1\dots dr_N$$

$$- e^{\beta\Omega}\sum_{N=0}^{\infty} e^{\beta\mu N}\int\dots\int e^{-\beta\sum_{N=1}^{\infty}\phi(r_i)}\rho(r')dr_1\dots dr_N(\beta\int\rho(r)\frac{\delta u(r)}{\delta u(r'')}dr)$$

$$= -\beta\frac{\delta\Omega}{\delta u(r'')}\frac{\delta\Omega}{\delta u(r')} - e^{\beta\Omega}\sum_{N=0}^{\infty} e^{\beta\mu N}\int\dots\int e^{-\beta\sum_{N=1}^{\infty}\phi(r_i)}\rho(r')dr_1\dots dr_N(\beta\int\rho(r'')dr)$$

$$= \beta(\langle\rho(r')\rho(r'')\rangle - \langle\rho(r')\rangle\langle\rho(r'')\rangle$$

Relationship between spatial correlations and thermodynamics

derivatives	Ideal	interacting
$\frac{\delta\Omega[u]}{\delta u(r)}$	$-\rho_1(r)$	-$\langle\rho_1(r)\rangle = -\rho_1(r)$
$\frac{\delta^2\Omega[u]}{\delta u(r)\delta u(r')}$	$\rho_1(r)\delta(r-r')$	$-\beta\langle\rho_1(r)\rho_1(r')\rangle\langle\rho_1(r)\rangle\langle\rho_1(r')\rangle$

Understanding Hydration

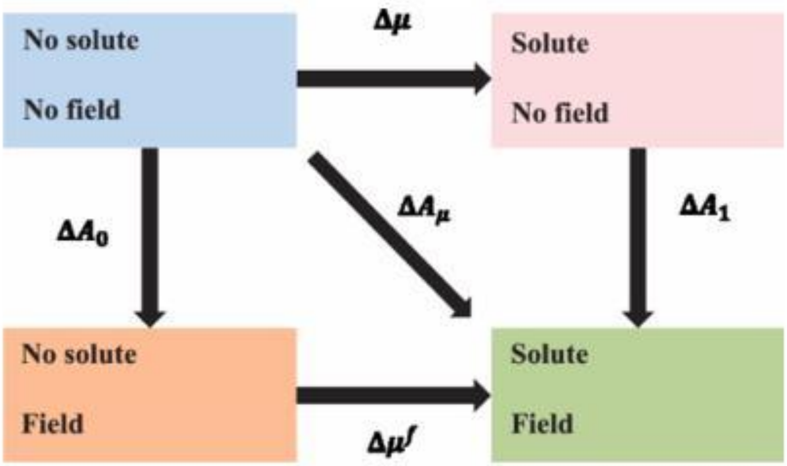
Interfacial fluctuations - solvation at liquid/vapor interface

Hamiltonian

$$H(R_i, \lambda) = V_\psi(R_1, R_2; \lambda) + V_F(R; f)$$

Potential function

$$\Omega(\lambda; R_1) = -k_B T \ln Z(R1; \lambda)$$
$$\Omega(\lambda_{ref}; R_1) = -k_B T \ln Z(R1; \lambda_{ref})$$
$$\Delta\mu(\lambda; R_1) = \Omega(\lambda; R_1) - \Omega(\lambda_{ref}; R_1)$$
$$= -k_B T \ln \frac{Z(R1; \lambda)}{Z(R1; \lambda_{ref})}$$
$$= -k_B T \ln Z(\lambda)$$



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Understanding Hydration

$$\Delta\mu(\lambda; R_1) = \int_{\lambda_{ref}}^{\lambda} \frac{d\mu(\lambda)}{d\lambda} d\lambda$$

$$= \int_{\lambda_{ref}}^{\lambda} \frac{d(-k_B T \ln Z(\lambda))}{d\lambda} d\lambda$$

$$= -k_B T \int_{\lambda_{ref}}^{\lambda} \frac{1}{Z} \cdot \frac{dZ(\lambda)}{d\lambda} d\lambda$$

$$= -k_B T \int_{\lambda_{ref}}^{\lambda} \frac{1}{Z}(-\beta \int \ldots \int e^{(-\beta V_\psi(R_1, R_2; \lambda))} \frac{dV_\psi(R_1, R_2; \lambda)}{d\lambda} d\lambda$$

$$= \int_{\lambda_{ref}}^{\lambda} \frac{\int \ldots \int e^{(-\beta V_\psi(R_1, R_2; \lambda)}}{Z} \cdot \frac{dV_\psi(R_1, R_2; \lambda)}{d\lambda} d\lambda$$

$$= \int_{\lambda_{ref}}^{\lambda} d\lambda \int dR_2 \rho(R_2; R_1, \lambda) \frac{dV_\psi(R_1, R_2; \lambda)}{d\lambda}$$

Function

First derivative

$$\frac{\delta\Delta\mu(\lambda; R_1}{\delta V_F(R; f)} = \int_{\lambda_{ref}}^{\lambda} d\lambda \int \boxed{dR_2 \frac{\rho(R_2; R_1, \lambda)}{\delta V_F(R; f)}} \frac{dV_\psi(R_1, R_2; \lambda)}{d\lambda}$$

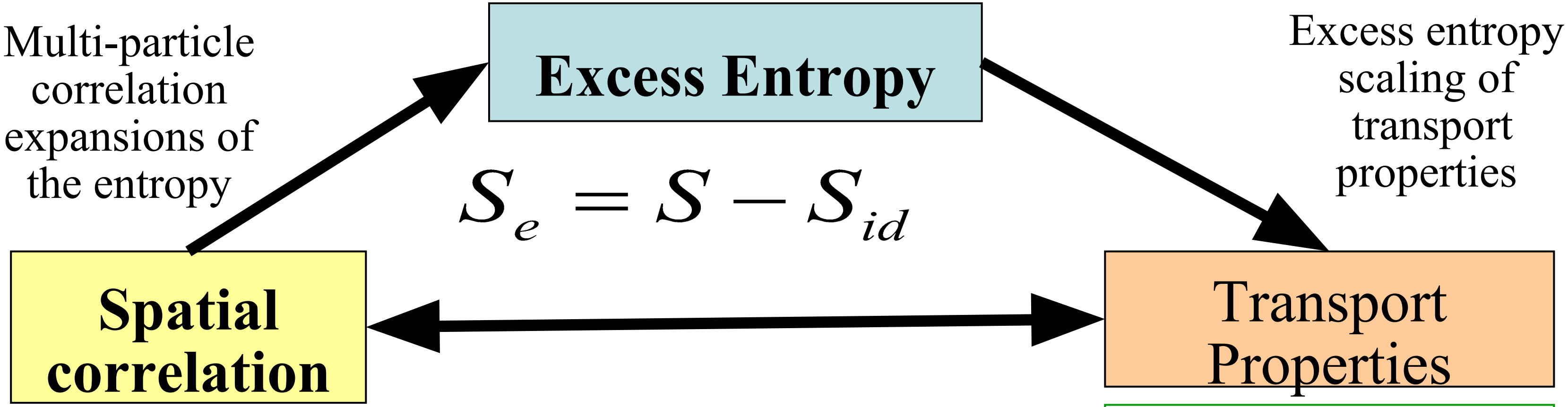
Functional

$\mathscr{X}$ - local compressibility

Excess Entropy Connections

between Structure, Mobility and Thermodynamics

Excess entropy is defined as the difference in entropy between liquid and ideal gas under identical temperature and density conditions



Viscosity

Diffusivity

Conductivity

Studied for Systems like H_2O, Mol. Phys. 106, 2008, 1925.
SiO_2, J. Chem. Phys. 125, 2006, 204501
BeF_2, J. Phys. Chem. B 111, 2007, 13294

Multiparticle correlation expansion of the entropy

$S_e = S_2 + S_3 + \ldots + S_n$;

$S_e \approx S_2$ 80-90% contribution for simple liquids

Pair correlation entropy:

$$S_2 / Nk_B = -2\pi\rho \sum_{\alpha,\beta} \chi_\alpha \chi_\beta \int_0^\infty \left\{ g_{\alpha\beta}(r) \ln g_{\alpha\beta}(r) - \left[g_{\alpha\beta}(r) - 1 \right] \right\} r^2 dr$$

$g_{\alpha\beta}(r)$ is the pair correlation function between particles of type α and β and χ_α is the mole fraction of particle of type α.

S_2 can be **calculated experimentally** from the atom-atom pair distribution function or from simulations.

Excess Entropy Scaling of Transport Properties

Based on corresponding states argument by Rosenfeld (1977) for simple liquids

$$X^* = A\exp(\alpha S_e)$$

- X is scaled using macroscopic system variables. e.g.:

$$D^* = D\frac{\rho^{1/3}}{\sqrt{k_B T / m}}$$

$$\eta^* = \eta\frac{\rho^{-2/3}}{\sqrt{mk_B T}}$$

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Spatial correlations to experimental static structure factor

Direct correlation function

$$F^{id}[\rho_1] = \Omega[u] + \int dr u(r)\rho_1(r)$$
$$= -k_B T \frac{1}{\lambda^3}\int dr e^{\beta u(r)} + \int dr u(r)\rho_1(r)$$
$$= -k_B T \int dr \rho_1(r)(\ln(\rho_1(r)\lambda^3) - 1)$$

$$F^{total}[\rho_1] = \Omega[u] + \int dr u(r)\rho_1(r)$$
$$F^{total}[\rho_1] = F^{id}[\rho_1] + F^{ex}[\rho_1]$$
$$= -k_B T \int dr \rho_1(r)(\ln(\rho_1(r)\lambda^3) - 1) + \boxed{F^{ex}[\rho_1]}$$

derivatives	interacting
$\frac{\delta F^{ex}[\rho_1]}{\delta \rho_1(r)}$	$c_1(r)$
$\frac{\delta^2 F^{ex}[\rho_1]}{\delta \rho_1(r)\delta \rho_1(r')}$	$\boxed{c_2(r, r')}$
$\frac{\delta F^{total}[\rho_1]}{\delta \rho_1(r)}$	$u(r)$
$\frac{\delta^2 F^{total}[\rho_1]}{\delta \rho_1(r)\delta \rho_1(r')}$	$\rho_2(r, r')$

$$h(r, r') = c(r, r') + \int dr'' c(r, r'')\rho_1(r'')h(r'', r')$$

$$h(k) = c(k) + c(k)\rho h(k)$$
$$= \int dr e^{ik.r} h(r)$$

Static structure factor

Thank you for listening!

Spatial correlations

Density - density correlation function

$$
\begin{aligned}
H(r,r') &= \langle(\rho(r)-\langle\rho(r)\rangle)(\rho(r')-\langle\rho(r')\rangle)\rangle \\
&= \langle\rho(r)\rho(r')\rangle - \langle\rho(r')\langle\rho(r)\rangle\rangle - \langle\rho(r)\langle\rho(r')\rangle\rangle + \langle\rho(r')\rangle\langle\rho(r)\rangle \\
&= \langle\rho(r)\rho(r')\rangle - \langle\rho(r')\rangle\langle\rho(r)\rangle \\
&= \langle\sum_{i=1}^{N}\sum_{j=1}^{N}\delta(r-r_i)\delta(r'-r_j)\rangle - \langle\rho(r')\rangle\langle\rho(r)\rangle \\
&= \langle\sum_{i\neq j}^{N}\sum\delta(r-r_i)\delta(r'-r_j)\rangle + \langle\sum_{j=1}^{N}\delta(r-r_i)\delta(r'-r_i)\rangle - \langle\rho(r')\rangle\langle\rho(r)\rangle \\
&= \langle\sum_{i\neq j}^{N}\sum\delta(r-r_i)\delta(r'-r_j)\rangle + \langle\sum_{j=1}^{N}\delta(r-r')\delta(r'-r_i)\rangle - \langle\rho(r')\rangle\langle\rho(r)\rangle \\
&= \langle\sum_{i\neq j}^{N}\sum\delta(r-r_i)\delta(r'-r_j)\rangle + \delta(r-r')\langle\sum_{j=1}^{N}\delta(r'-r_i)\rangle - \langle\rho(r')\rangle\langle\rho(r)\rangle \\
&= \rho^2(r,r') - \rho^1(r)\rho^1(r') + \rho^1(r)\delta(r-r')
\end{aligned}
$$