Self dynamics in simple liquids: connections between the Gaussian approximation and the asymptotic impulsive regime

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Talk outline

1. Quantum self dynamics: the problem.
2. What is the Gaussian approximation?
3. What is the impulse approximation?
4. How to make them “talk” to each other?
5. Simple tests on liquid *p*-H_2.
6. Conclusions & perspectives.

1) Quantum self-dynamics: the problem

Single-particle microscopic **dynamics** in condensed disorder systems:

$$I_s(Q,t) = \frac{1}{N}\sum_{j=1}^{N}\left\langle \exp\left[-i\mathbf{Q}\cdot\mathbf{r}_j(0)\right]\exp\left[i\mathbf{Q}\cdot\mathbf{r}_j(t)\right]\right\rangle$$

$$:= \left\langle \exp\left[-i\mathbf{Q}\cdot\mathbf{r}_1(0)\right]\exp\left[i\mathbf{Q}\cdot\mathbf{r}_1(t)\right]\right\rangle,$$

where $I_s(Q,t)$ is the **self intermediate scattering function**, *i.e.* the time autocorrelation function of the spatial Fourier components (with wave-vector modulus Q) of the microscopic density fluctuations. From it one writes the **self-dynamic structure factor:**

$$S_s(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t} I_s(Q,t)\,dt,$$

which is simply related to the incoherent component of the **double differential cross sections**:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{inc} = \frac{k'}{k}\frac{\sigma_{inc}}{4\pi}S_s(Q,\omega).$$

In some cases $\sigma_{inc} >> \sigma_{coh}$ (*e.g.* H, *V etc.*), so that:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) \cong \frac{k'}{k}\frac{\sigma_{tot}}{4\pi}S_s(Q,\omega).$$

Thus the single-particle microscopic dynamics **problem** is the following: *"how to calculate, in a real disordered system, the physical quantity $I_s(Q,t)$ to be compared to experimental data?"*

2) What is the Gaussian approximation?

$$I_s(Q,t) = \exp\left(-Q^2 \frac{k_B T}{2M} t^2\right)$$ **classical ideal gas** ($Q \to \infty$, $t \to 0$);

$$I_s(Q,t) = \exp\left(-Q^2 D_s |t|\right)$$ **hydrodynamic diffusion** ($Q \to 0$, $t \to \infty$).

In general, at any Q, t, one might guess:

$$I_s(Q,t) \approx I_{GA}(Q,t) = \exp\left(-Q^2 \gamma_1(t)\right).$$

This is the **Gaussian approximation** (**GA**) !

General treatment of the self-dynamics including **quantum systems**:

$$I_s(Q,t) = \exp\left(\sum_{k=1}^{\infty} (iQ)^{2k} \gamma_k(t) \right),$$

where: $$\gamma_1(t) = -i\frac{\hbar t}{2M} + \frac{1}{3}\int_0^t d\tau\ (t-\tau)\, u(\tau),$$

and where: $$u(t) = \frac{1}{N}\sum_{i=1}^{N} \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle.$$

$\gamma(t) \equiv \gamma_1(t)$ **GA** → Related to the **velocity autocorrelation function** (VACF);

$\gamma_2(t)$ → first **non-GA** correction.

From the VACF to the spectrum

In general: $u(-t) = u^*(t) = u\left(t + \frac{i\hbar}{k_B T}\right),$

and its spectrum is a **real** (but not **even**) function of **ω**:

$$p(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} u(t),$$

that can be cast as:

$$p(\omega) = \frac{p(\omega) + p(-\omega)}{2} + \frac{p(\omega) - p(-\omega)}{2} = p_S(\omega) + p_A(\omega).$$

Defining a **phonon-like spectrum**: $f(\omega) = \frac{4M}{3\hbar} \frac{p_A(\omega)}{\omega}$, one gets:

$$\gamma_1(t) = \frac{\hbar}{2M} \int_0^{\infty} d\omega\, \frac{f(\omega)}{\omega} \left[(1 - \cos\omega t) \coth\left(\frac{\hbar\omega}{2k_B T}\right) - i \sin\omega t \right].$$

3) What is the impulse approximation?

In general, one can write:

$$S_s(Q,\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} \exp\left(-\mathrm{i}\omega t\right) \left\langle e^{-i\mathbf{Q}\cdot\mathbf{R}_1(0)} e^{i\hbar^{-1}\hat{H}t} e^{i\mathbf{Q}\cdot\mathbf{R}_1(0)} e^{-i\hbar^{-1}\hat{H}t} \right\rangle$$

$$= \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} \exp\left(-\mathrm{i}\omega t\right) \left\langle e^{i\hbar^{-1}\hat{H}(\mathbf{P}_1+\hbar\mathbf{Q})t} e^{-i\hbar^{-1}\hat{H}(\mathbf{P}_1)t} \right\rangle.$$

The rationale of the **impulse approximation** (**IA**) now, is trying to estimate $H(\mathbf{P}_1+\hbar\mathbf{Q})$:

$$\hat{H}(\mathbf{P}_1+\hbar\mathbf{Q}) = \frac{(\mathbf{P}_1+\hbar\mathbf{Q})^2}{2M_1} + \sum_{n=2}^{N} \frac{\mathbf{P}_n^{\,2}}{2M_n} + V(\mathbf{R}_1,\ldots\mathbf{R}_N) = \hat{H}(\mathbf{P}_1) + \frac{\hbar^2\mathbf{Q}^2}{2M_1} + \frac{\hbar\mathbf{Q}\cdot\mathbf{P}_1}{M_1},$$

to be plugged into the $S_s(Q,\omega)$ formula:

$$S_s(Q,\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} \exp\left(-\mathrm{i}\omega t + i\,\frac{\hbar Q^2}{2M_1} t\right)$$

$$\times \left\langle \exp\left\{ i\hbar^{-1}\left[\hat{H}(\mathbf{P}_1) + M_1^{-1}\hbar\mathbf{Q}\cdot\mathbf{P}_1\right]t\right\} \exp\left[-i\hbar^{-1}\hat{H}(\mathbf{P}_1)t\right]\right\rangle.$$

Let us calculate the mean value in **crude** way:

$$\left\langle \exp\{i\hbar^{-1}[\hat{H}(\mathbf{P}_1) + M_1^{-1}\hbar\mathbf{Q}\cdot\mathbf{P}_1]t\} \exp[-i\hbar^{-1}\hat{H}(\mathbf{P}_1)t]\right\rangle$$

$$\approx \left\langle \exp(iM_1^{-1}\mathbf{Q}\cdot\mathbf{P}_1 t)\right\rangle = \int d\,\mathbf{P}_1\, n(P_1) \exp(iM_1^{-1}\mathbf{Q}\cdot\mathbf{P}_1 t),$$

where $n(P_1)$ is the **single-particle momentum distribution**. This is rigorous only if $V(\mathbf{R}_1,\ldots\mathbf{R}_N)$=*const.*, but is realistic if $Q\to\infty$, $t\to 0$. However, in the case of a true **free-particle gas,** one has: $V(\mathbf{R}_1,\ldots\mathbf{R}_N)\equiv 0$.

The $S_s(Q,\omega)$ formula for the **IA** now reads:

$$S_s(Q,\omega) \approx \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} \exp\left(-i\omega t + i\,\frac{\hbar Q^2}{2M_1}\,t\right) \int d\mathbf{P}_1 n(P_1) \exp\left(iM_1^{-1}\mathbf{Q}\cdot\mathbf{P}_1\,t\right)$$

$$= \int d\mathbf{P}_1 n(P_1) \delta\left(\hbar\omega - \frac{\hbar^2 Q^2}{2M_1} - \frac{\hbar\mathbf{P}_1\cdot\mathbf{Q}}{M_1}\right) \equiv S_{\mathrm{IA}}(Q,\omega).$$

In the semi-classical case, one has an **equilibrium velocity distribution** given by the well-known Maxwell's law (but with an effective temperature: $T^*>T$):

$$n(P_1) = \frac{1}{\left(2\pi M_1 k_{\mathrm{B}} T^*\right)^{3/2}} \exp\left(-\frac{P_1^2}{2M_1 k_{\mathrm{B}} T^*}\right) = \frac{1}{\left(2\pi\sigma_p^2\right)^{3/2}} \exp\left(-\frac{P_1^2}{2\sigma_p^2}\right)$$

4. How to make GA and IA "talk" to each other?

What are the relationships between these two distinct, although very popular, approximations of the microscopic self-dynamics?

In general, one can always write two rather trivial, exact equations:

$$S_s(Q,\omega) = S_{\mathrm{GA}}(Q,\omega) + S_{\mathrm{non-GA}}(Q,\omega);$$
$$S_s(Q,\omega) = S_{\mathrm{IA}}(Q,\omega) + S_{\mathrm{FSI}}(Q,\omega),$$

where the well-known **"final-states effects"** (**FSE**) have been introduced.

Let us now assume that $n(P_1)$ exhibits a **Maxwellian shape** (with no constraint on its width σ_p). This is very general and, in practice, excludes only liquid ^{4}He and ^{3}He!

Under this assumption one obtains well-known result:

$$I_{\mathrm{IA}}(Q,t) = \exp\left(i\frac{\hbar Q^2 t}{2M} - \frac{Q^2\sigma_p^2 t^2}{2M^2} \right),$$

The **IA** is just a special case of the **GA**, where:

$$\gamma_{1,\,\mathrm{IA}}(t) = -i\frac{\hbar t}{2M} + \frac{\sigma_p^2 t^2}{2M^2},$$

and the following (less trivial…) formula holds:

$$S_s(Q,\omega) = \underbrace{S_{\mathrm{IA}}(Q,\omega) + S_{\text{GA-FSE}}(Q,\omega)}_{\mathrm{GA}} + S_{\text{non–GA}}(Q,\omega),$$

where split the **FSE** in two different terms:

$$S_{FSE}(Q,\omega) \equiv \underbrace{S_{\text{GA-FSE}}(Q,\omega)}_{Gaussian FSE} + \underbrace{S_{\text{non–GA}}(Q,\omega)}_{non\text{–}Gaussian FSE}.$$

What are Gaussian FSE?

This is the “easy” part of the problem! Keeping in mind that:

$$\gamma_1(t) = -i\frac{\hbar t}{2M} + \frac{1}{3}\int_0^t d\tau (t-\tau) u(t) \ ,$$

one can expand in power series and obtain:

$$\gamma_1(t) = -i\frac{\hbar t}{2M} + \frac{1}{3}\sum_{n=0}^{\infty}\left(\frac{d^n u(t)}{dt^n}\right)_{t=0}\frac{t^{n+2}}{(n+2)!} \equiv -i\frac{\hbar t}{2M} + \sum_{n=0}^{\infty}\frac{d_n\, t^{n+2}}{(n+2)!}.$$

Excluding the terms in *t* and t^2 (*i.e.* those forming the **IA**), the **GA-FSE** are simply obtained:

$$I_{\text{GA-FSI}}(Q,t) = \exp\left(i\frac{\hbar Q^2 t}{2M} - Q^2\sum_{n=0}^{\infty}\frac{d_n\, t^{n+2}}{(n+2)!}\right) - \exp\left(i\frac{\hbar Q^2 t}{2M} - Q^2\frac{d_0\, t^2}{2}\right) =$$

$$= I_{\mathrm{IA}}(Q,t)\sum_{k=1}^{\infty}\frac{(-)^k Q^{2k}}{k!}\left[\sum_{n=1}^{\infty}\frac{d_n t^{n+2}}{(n+2)!}\right]^k$$

$$= I_{\mathrm{IA}}(Q,t)\left[\underbrace{-\frac{Q^2 d_1 t^3}{3!}-\frac{Q^2 d_2 t^4}{4!}}_{\text{**Sears** corrections routinely used on **VESUVIO**...}}+\frac{Q^4}{2}\left(\frac{d_1 t^3}{3!}\right)^2+\ldots\right].$$

West scaling *(in t domain)*

$$t \to s = \frac{\hbar Q t}{M} \quad (\text{Fourier conjugate of } y)$$

$$I_s(Q,t) \to \tilde{F}(s,Q) = \exp\left(-i\frac{\hbar Q^2 t}{2M}\right) I_s(Q,t) = \exp\left(-i\frac{Qs}{2}\right) I_s\left(Q,\frac{Ms}{\hbar Q}\right)$$

$$[\text{Fourier conjugate of } F(y,Q)]$$

So, in the **West formalism**, **IA** and **GA-FSE** read, respectively, as:

$$\tilde{F}_{\mathrm{IA}}(s) = \exp\left(-\frac{d_0 M^2 s^2}{2\hbar^2}\right) = \exp\left(-\frac{\sigma_p^2 s^2}{2\hbar^2}\right);$$

$$\tilde{F}_{\mathrm{GA\text{-}FSE}}(s,Q) = \tilde{F}_{\mathrm{IA}}(s)\left[-\frac{M^3 d_1 s^3}{3!\hbar^3 Q} - \frac{M^4 d_2 s^4}{4!\hbar^4 Q^2} + \frac{1}{2}\left(\frac{M^3 d_1 s^3}{3!\hbar^3 Q}\right)^2 + \ldots\right]$$

$$= \tilde{F}_{\mathrm{IA}}(s)\left[-i\frac{M\langle\nabla^2 V\rangle s^3}{36\hbar^2 Q} + \frac{M^2\langle(\vec{\nabla}V)^2\rangle s^4}{72\hbar^4 Q^2} - \frac{1}{2}\left(\frac{M\langle\nabla^2 V\rangle s^3}{36\hbar^2 Q}\right)^2 + \ldots\right]$$

We have proved that the <u>two standard</u> **Sears corrections** to the **IA** are already fully contained in the **GA**!

Where to look for non-Gaussian FSE?

- 1st strategy, from the **RSS** formula:

$$I_{s,\text{non-GA}}(Q,t) = \exp\left(-Q^2\gamma_1(t)\right)\left[\exp\left(\sum_{k=2}^{\infty}(iQ)^{2k}\gamma_k(t)\right)-1\right]$$

$$= I_{s,\text{GA}}(Q,t)\left[\sum_{n=1}^{\infty}\frac{1}{n!}\left(\sum_{k=2}^{\infty}(iQ)^{2k}\gamma_k(t)\right)^n\right]$$

$$\approx I_{s,\text{GA}}(Q,t)\left[Q^4\gamma_4(t)-Q^6\gamma_3(t)+Q^8\left(\gamma_4(t)+\frac{1}{2}\gamma_2^2(t)\right)\right].$$

Tough, because functions $\gamma_{n>1}(t)$ are extremely complicated and difficult to be evaluated, being related to the whole hierarchy of the velocity autocorrelation functions up to the $2n$-time one:

$$\left\langle v_{1,z}(0)v_{1,z}(t_1)\ldots v_{1,z}(t_{2n-2})v_{1,z}(t_{2n-1})\right\rangle.$$

However, calculating their short-time contributions (always assuming a Maxwellian $n(P_1)$), one gets:

$$I_{\text{s,non-GA}}(Q,t\to 0)\approx \exp\left(i\frac{\hbar Q^2 t}{2M}\right)\left[i\frac{Q^4}{5!}\bar{a}_{5,4}t^5-\frac{Q^4}{6!}\bar{a}_{6,4}t^6\right]$$

$$\approx\left[i\frac{Q^4}{5!}\bar{a}_{5,4}t^5-\frac{Q^4}{6!}\bar{a}_{6,4}t^6-\frac{\hbar Q^6}{5!\,2M}\bar{a}_{5,4}t^6\right],$$

or, equivalently, moving to the West formalism:

$$\tilde{F}_{\text{s,non-GA}}(s,Q\to\infty)\approx\left[i\frac{(2M)^5}{5!\hbar^5 Q}\bar{a}_{5,4}s^5-\frac{(2M)^6}{6!\hbar^6 Q^2}\bar{a}_{6,4}s^6\right].$$

We have found the first two leading terms of the non-Gaussian **FSE**, but we do not know what $\underline{a}_{5,4}$ and $\underline{a}_{6,5}$ are….

Another strategy is needed!

The GRS theory of the FSE: a GA-independent approach

There is an alternative approach to the microscopic self dynamics which is **possible** (provided the inter-particle potential is not **hard-sphere**) and **fully GA independent**: the so-called **Gersch-Rodriguez-Smith** theory (**GRS**):

$$\tilde{F}(s,Q) = \sum_{n=0}^{\infty} \left(\frac{iM}{\hbar^2 Q} \right)^n F_n(s)$$

$$\text{where } F_0(s) = \tilde{F}_{IA}(s)$$

The various $F_{n>0}(s)$ are not easy to be evaluated, but are **equilibrium properties** of the system (related to the *n*-body density matrix hierarchy).

Let us write down the first three terms: $F_0(s)$ (**IA**), $F_1(s)$ (**exact** at all T), and $F_2(s)$ (**exact** at T=0, a good approximation at low T):

$$F_0(s) = \left\langle \exp\left(i\hbar^{-1} s p_{1,z}\right)\right\rangle;$$

$$F_1(s) = \left\langle \exp\left(i\hbar^{-1} s p_{1,z}\right)\int_0^s d\sigma_1 \delta_1 U(\sigma_1)\right\rangle;$$

$$F_2(s) \cong \left\langle \exp\left(i\hbar^{-1} s p_{1,z}\right)\int_0^s d\sigma_1 \left[\delta_1 U(\sigma_1) - \delta_1 U(s)\right]\int_0^{\sigma_1} d\sigma_2 \delta_1 U(\sigma_2)\right\rangle,$$

where the difference between two potential energy ($U(\mathbf{r}_1,\ldots,\mathbf{r}_N)$) values of the system (with the particle **"1"** shifted by σ and un-shifted, respectiveluy) are requested:

$$\delta_1 U(\sigma) = U(\vec{r}_1 - \sigma\hat{Q}, \vec{r}_2, ..., \vec{r}_N) - U(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N).$$

Now we have seen that **all** the **GA-FSE** terms $\sim Q^{-1}$ are:

$$\left(\frac{iM}{\hbar^2 Q}\right)F_{1,\mathrm{GA}}(s)=\tilde{F}_{\mathrm{IA}}(s)\left(-\frac{M^3 d_1 s^3}{3!\hbar^3 Q}\right),$$

while **all** the **GA-FSE** terms $\sim Q^{-2}$ are:

$$\left(\frac{iM}{\hbar^2 Q}\right)^2 F_{2,\mathrm{GA}}(s)=\tilde{F}_{\mathrm{IA}}(s)\left[-\frac{M^4 d_2 s^4}{4!\hbar^4 Q^2}+\frac{1}{2}\left(\frac{M^3 d_1 s^3}{3!\hbar^3 Q}\right)^2\right].$$

So we are ready to write the first two **non-GA-FSE** terms (in Q^{-1} and Q^{-2}):

$$\left(\frac{iM}{\hbar^2 Q}\right)F_{1,\mathrm{non-GA}}(s)=\left(\frac{iM}{\hbar^2 Q}\right)F_1(s)+\tilde{F}_{\mathrm{IA}}(s)\frac{M^3 d_1 s^3}{3!\hbar^3 Q};$$

$$\left(\frac{iM}{\hbar^2 Q}\right)^2 F_{2,\text{non–GA}}(s) = \left(\frac{iM}{\hbar^2 Q}\right)^2 F_2(s) + \tilde{F}_{\text{IA}}(s)\left[\frac{M^4 d_2 s^4}{4!\hbar^4 Q^2} - \frac{1}{2}\left(\frac{M^3 d_1 s^3}{3!\hbar^3 Q}\right)^2\right].$$

Using some algebra, one finally writes:

$$F_{1,\text{non–GA}}(s) = \left\langle \exp\left(i\hbar^{-1} s p_{1,z}\right) \int_0^s d\sigma_1 \delta_1 U(\sigma_1) \right\rangle + \frac{s^3}{12}\left\langle \frac{\partial^2 U}{\partial z_1^2} \right\rangle F_0(s);$$

$$F_{2,\text{non–GA}}(s) = \left\langle \exp\left(i\hbar^{-1} s p_{1,z}\right) \int_0^s d\sigma_1 [\delta_1 U(\sigma_1) - \delta_1 U(s)] \int_0^{\sigma_1} d\sigma_2 \delta_1 U(\sigma_2) \right\rangle$$

$$+ \left(\frac{s^4}{24}\left\langle \left(\frac{\partial U}{\partial z_1}\right)^2 \right\rangle - \frac{s^6}{288}\left\langle \frac{\partial^2 U}{\partial z_1^2} \right\rangle^2 \right) F_0(s).$$

Since it is possible to prove that the respective leading terms are exactly given by:

$$\left(\frac{iM}{\hbar^2 Q}\right) F_{1,\text{non-GA}}(s \to 0) = i\left[\frac{(2M)^5 \bar{a}_{5,4}}{5!\hbar^5}\right]\frac{s}{Q}^5;$$

$$-\frac{M^2}{\hbar^4 Q^2} F_{2,\text{non-GA}}(s \to 0) = -\left[\frac{(2M)^6 \bar{a}_{6,4}}{6!\hbar^6}\right]\frac{s^6}{Q^2},$$

we have also found a way to evaluate $\underline{a}_{5,4}$ and $\underline{a}_{6,5}$.

5. Simple tests on liquid *p*-H_2

We are going to calculate the magnitude of the **non-GA FSE** on liquid para-H_2, because is a **semi-quantum liquid** (with an anharmonic dynamics even at low T), but still exhibits a Maxwellian $n(P_1)$.

Why hydrogen is a "semi-quantum" fluid?

- Liquid **H_2** exhibit strong **quantum effects**: still liquid (13.8 K < T < 33.1 K) at $T<\Theta_D$ (with $\Theta_D \approx 100$ K).

- It is a prototypical "***quantum Boltzmann fluid***": particle delocalization, but negligible exchange.

$$\Lambda_{DB} = \frac{h}{\sqrt{2\pi\, M\, k_B T}}$$

σ : L.J. potential range

l : mean inter-particle distance

System	$(\Lambda_{DB}/\sigma)_{CP}$	$(\Lambda_{DB}/\sigma)_{TP}$	$(\Lambda_{DB}/l)_{CP}$	$(\Lambda_{DB}/l)_{TP}$
He	1.50	2.31	0.84	1.66
H_2	0.72	1.11	0.44	0.94
D_2	0.47	0.68	0.31	0.60
Ne	0.21	0.29	0.14	0.26

[from **M. Zoppi** *et al.* (1998)]

Simulating the *p*-H_2 equilibrium properties by *Path Integral Monte Carlo* (PIMC)

Rigid cubic box V, T=20 K, ρ=22.53 nm^{-3}, N=256 "point-like" molecules interacting through the Silvera-Goldman isotropic pair potential $v_2(r)$, P=8, 16, 32, 64 (extrapolated to ∞).

$\Downarrow$

$g(r)$: pair distribution function $\Longrightarrow$ $\langle \partial^2 U/\partial z^2 \rangle$, $\langle (\partial U/\partial z)^2 \rangle$.

$\langle E_k \rangle$: mean kinetic energy $\Longrightarrow$ σ_p.

But how to calculate $F_1(s)$ and $F_2(s)$?

We have seen that $F_1(s)$ and $F_2(s)$ can be expressed using the ***n*-body density matrixes**, ρ_n. $F_1(s)$ involves ρ_2, while $F_2(s)$ needs both ρ_2 and ρ_3. Namely:

$$F_1(s) = \frac{1}{\rho}\int d\vec{x}\rho_2\left(\vec{x},0;\vec{x}+s\hat{Q},0\right)\int_0^s d\sigma\left(v_2(|\vec{x}+\sigma\hat{Q}|)-v_2(|\vec{x}+s\hat{Q}|)\right),$$

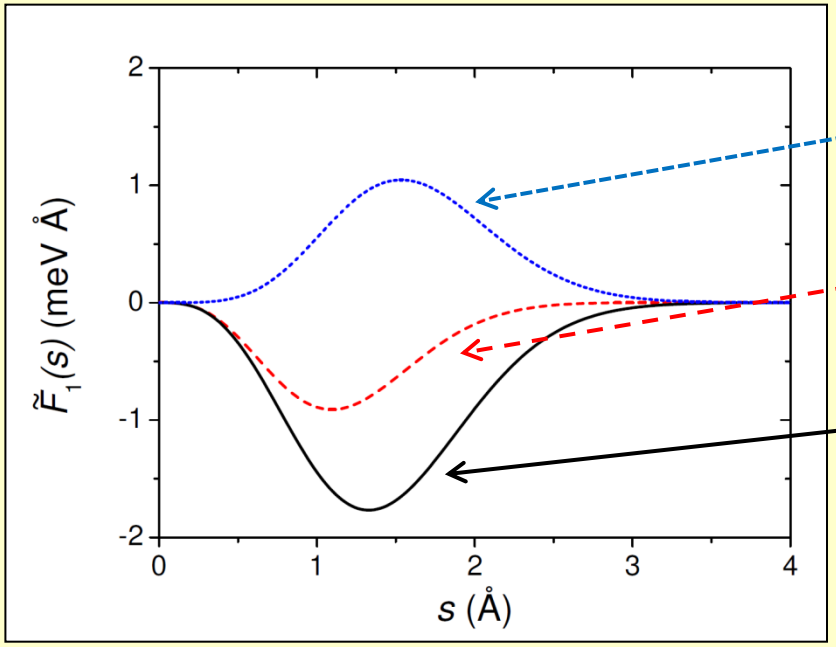
where $\rho_2(\mathbf{x},0;\mathbf{y},0)$ can be approximated by:

$$\rho_2\left(\vec{x},0;\vec{y},0\right) \approx \rho^2 \widetilde{F}_{\mathrm{IA}}(|\vec{x}-\vec{y}|)\sqrt{g(x)g(y)}.$$

$F_2(s)$ is slightly more complicate involving also the **3-body density matrix**. However, if only **binary collisions** are retained [*i.e.* $F_{2,\mathrm{bin}}(s)$], a simpler expression can be given:

$$F_{2,\mathrm{bin}}(s) \approx \rho F_{\mathrm{IA}}(s) \int d\vec{x} \sqrt{g(x) g(|\vec{x} - s\hat{Q}|)} \left\{ \left(v_2(x) - v_2(|\vec{x} - s\hat{Q}|) \right) \right.$$

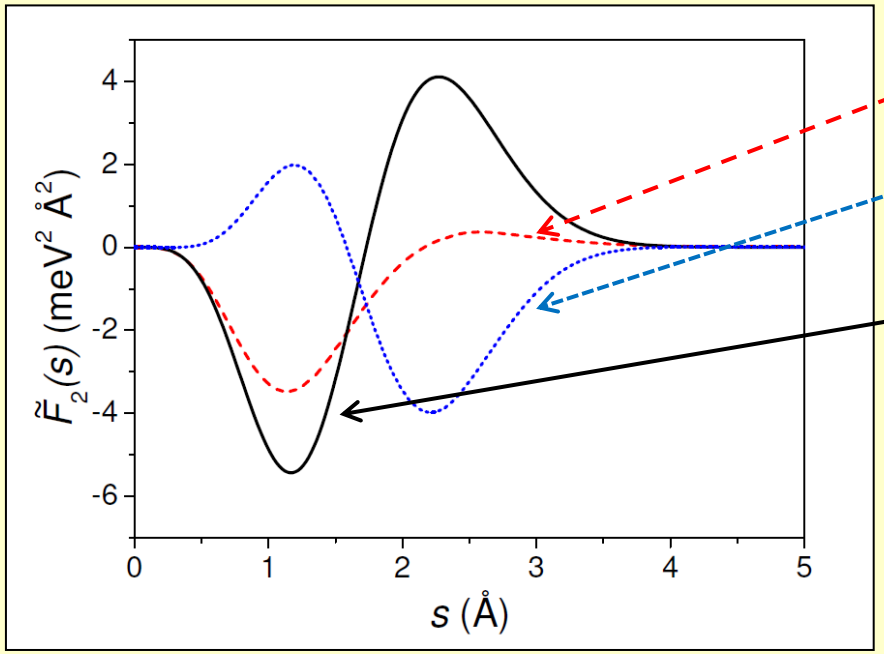
$$\left. \times \int_0^s d\sigma \int_0^\sigma d\sigma' \left(v_2(|\vec{x} - \sigma'\hat{Q}|) - v_2(x) \right) + \frac{1}{2} \left[\int_0^s d\sigma \left(v_2(|\vec{x} - \sigma\hat{Q}|) - v_2(x) \right) \right]^2 \right\}.$$



$F_{1,non-GA}(s)$ [diff.]

$F_1(s)$

$$-\frac{s^3}{12} \left\langle \frac{\partial^2 U}{\partial z_1^2} \right\rangle \tilde{F}_{\mathrm{IA}}(s)$$

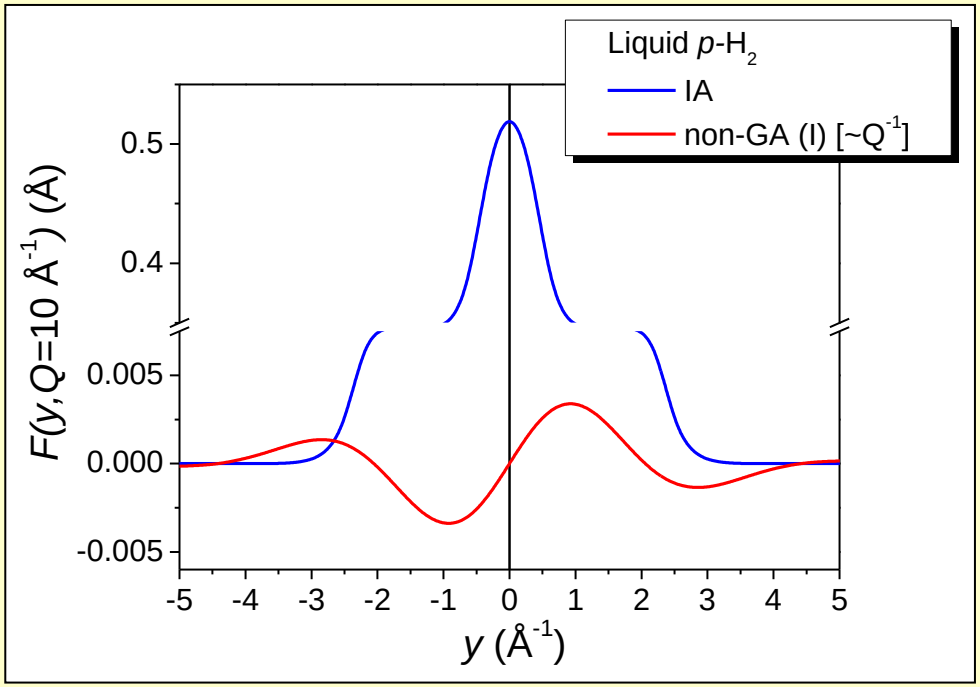


$$F_2(s)$$

$$F_{2,non-GA}(s)\,[\text{diff.}]$$

$$\left(-\frac{s^4}{24}\left\langle\left(\frac{\partial U}{\partial z_1}\right)^2\right\rangle+\frac{s^6}{288}\left\langle\frac{\partial^2 U}{\partial z_1^2}\right\rangle^2\right)\tilde{F}_{IA}(s)$$

Taking the Fourier transform of $F_{1,non\text{-}GA}(s)$ and $F_{2,non\text{-}GA}(s)$, one can easily evaluate the first two **non-GA corrections** to $F_{IA}(y)$.



Calculation for Q=10 Å^{-1} (*e.g.* **MARI** experiments on liquid H_2 explored 5 Å^{-1}<Q<15 Å^{-1}): $F_{1,\text{non-GA}}(y,Q)$ is small, but still visible, while $F_{2,\text{non-GA}}(y,Q)$ is not detectable.

6. Conclusions & perspectives

- We have clarified the general relationship between the **IA** and the **GA**. If $n(P_1)$ has a Maxwellian shape then: **IA** $\subset$ **GA**. If not, they are independent approximations.

- We have shown the two widely-used Sears corrections ($\propto Q^{-1}$ and Q^{-2}, respectively) come directly from **GA**. So **non-GA** effects cannot be included.

- **Non-GA** effects are difficult to be estimated, due to the presence of $u_{2n}(t_{2n},\ldots,t_1)$. However, for Maxwellian $n(P_1)$, one can see that the their leading terms are $\propto is^5/Q$ and s^6/Q^2, respectively.

- There exists an alternative route to the **non-GA** terms, via the well-known **GRS** theory, which uses equilibrium quantities like the ρ_n.

- The fully quantum ρ_n are not simple to be evaluated, but acceptable approximations exist, at least for ρ_2 and ρ_3.

- A test on liquid *p*-H_2 has been presented, proving that **non-GA** effects $F_1(s)$ are small but not totally negligible for 5 Å^{-1}<Q<15 Å^{-1}. In addition, they seem to weaken the well-known Sears corrections.

- Calculations on other model systems might reveal interesting results as far as **FSE** are concerned.

Many thanks to all the audience members

for their kind attention to this talk!

Wanting to know more?

D. Colognesi *et al.*, *On the non-Gaussian corrections in the self dynamics of semi-quantum fluids*, *Chem. Phys.* **446**, 57 (2015).

D. Colognesi, *Microscopic self dynamics in liquids: Connections between the Gaussian approximation and the asymptotic impulsive regime*, *Physica B* **515**, 56 (2017).

Additional slides for discussion

Four-time velocity autocorrelation functions

General

$$2\text{T - VACF}: \frac{1}{3N}\sum_{i=1}^{N}\left\langle \mathbf{v}_i(t_2)\cdot\mathbf{v}_i(t_1)\right\rangle = \left\langle v_{1,z}(t_2)\cdot v_{1,z}(t_1)\right\rangle$$

$$= \left\langle v_{1,z}(t_2-t_1)\cdot v_{1,z}(0)\right\rangle = u_2(t_2-t_1,0).$$

$$4\text{T - VACF}: \left\langle v_{1,z}(t_4)v_{1,z}(t_3)v_{1,z}(t_2)v_{1,z}(t_1)\right\rangle = \left\langle v_{1,z}(t_4-t_1)v_{1,z}(t_3-t_1)v_{1,z}(t_2-t_1)v_{1,z}(0)\right\rangle$$

$$= u_4(t_4-t_1,t_3-t_1,t_2-t_1,0)$$

Irreducible components

$$\text{IRR. 4T - VACF}:$$

$$u_{4,\text{irr}}(t_4,t_3,t_2,t_1) = u_4(t_4,t_3,t_2,t_1) - u_2(t_4,t_3)u_2(t_2,t_1)$$

$$- u_2(t_4,t_2)u_2(t_3,t_1) - u_2(t_4,t_1)u_2(t_3,t_2)$$

Non-Gaussian components

$$\gamma_1(t) \equiv \int_0^t dt_1 \int_0^{t_1} dt_2 \left\langle v_{z,1}(t_2) v_{z,1}(t_1) \right\rangle;$$

$$\gamma_2(t) \equiv \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \left\langle v_{z,1}(t_4) v_{z,1}(t_3) v_{z,1}(t_2) v_{z,1}(t_1) \right\rangle - \frac{1}{2}\gamma_1^2(t);$$

$$\gamma_3(t) \equiv \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_4} dt_5 \int_0^{t_5} dt_6 \left\langle v_{z,1}(t_6) v_{z,1}(t_5) \ldots v_{z,1}(t_2) v_{z,1}(t_1) \right\rangle - \gamma_1(t)\gamma_2(t)$$

$$- \frac{1}{6}\gamma_1^3(t)$$

The two-body density matrix: definitions

General

$$\rho_2(\mathbf{x},\mathbf{y};\boldsymbol{\xi},\boldsymbol{\upsilon}) \equiv N(N-1)\sum_i p_i \int d\mathbf{r}_3 \ldots \int d\mathbf{r}_N \Psi_i^*(\mathbf{x},\mathbf{y},\mathbf{r}_3,\ldots,\mathbf{r}_N)\Psi_i(\boldsymbol{\xi},\boldsymbol{\upsilon},\mathbf{r}_3,\ldots,\mathbf{r}_N)$$

$$= N(N-1)\sum_i p_i \int d\mathbf{r}_3 \ldots \int d\mathbf{r}_N \Psi_i^*(\mathbf{x}-\boldsymbol{\upsilon},\mathbf{y}-\boldsymbol{\upsilon},\mathbf{r}_3,\ldots,\mathbf{r}_N)\Psi_i(\boldsymbol{\xi}-\boldsymbol{\upsilon},0,\mathbf{r}_3,\ldots,\mathbf{r}_N);$$

$$= \rho_2(\mathbf{x}-\boldsymbol{\upsilon},\mathbf{y}-\boldsymbol{\upsilon};\boldsymbol{\xi}-\boldsymbol{\upsilon},0).$$

Semi-diagonal

$$\rho_2(\mathbf{x},\mathbf{y};\boldsymbol{\xi},\mathbf{y}) \equiv N(N-1)\sum_i p_i \int d\mathbf{r}_3 \ldots \int d\mathbf{r}_N \Psi_i^*(\mathbf{x},\mathbf{y},\mathbf{r}_3,\ldots,\mathbf{r}_N)\Psi_i(\boldsymbol{\xi},\mathbf{y},\mathbf{r}_3,\ldots,\mathbf{r}_N)$$

$$= N(N-1)\sum_i p_i \int d\mathbf{r}_3 \ldots \int d\mathbf{r}_N \Psi_i^*(\mathbf{x}-\mathbf{y},0,\mathbf{r}_3,\ldots,\mathbf{r}_N)\Psi_i(\boldsymbol{\xi}-\mathbf{y},0,\mathbf{r}_3,\ldots,\mathbf{r}_N);$$

$$= \rho_2(\mathbf{x}-\mathbf{y},0;\boldsymbol{\xi}-\mathbf{y},0).$$

Diagonal

$$\rho_2(\mathbf{x},\mathbf{y};\mathbf{x},\mathbf{y}) \equiv N(N-1)\sum_i p_i \int d\mathbf{r}_3 \ldots \int d\mathbf{r}_N \Psi_i^*(\mathbf{x},\mathbf{y},\mathbf{r}_3,\ldots,\mathbf{r}_N)\Psi_i(\mathbf{x},\mathbf{y},\mathbf{r}_3,\ldots,\mathbf{r}_N)$$

$$= N(N-1)\sum_i p_i \int d\mathbf{r}_3 \ldots \int d\mathbf{r}_N \Psi_i^*(\mathbf{x}-\mathbf{y},0,\mathbf{r}_3,\ldots,\mathbf{r}_N)\Psi_i(\mathbf{x}-\mathbf{y},0,\mathbf{r}_3,\ldots,\mathbf{r}_N)$$

$$= \rho_2(\mathbf{x}-\mathbf{y},0;\mathbf{x}-\mathbf{y},0) = \rho^2 g(\mathbf{x}-\mathbf{y}) = \rho^2 g(|\mathbf{x}-\mathbf{y}|).$$

Relationship with ρ_1

$$\rho_1(\mathbf{x};\xi) \equiv N\sum_i p_i \int d\mathbf{r}_2 \ldots \int d\mathbf{r}_N \Psi_i^*(\mathbf{x},\mathbf{r}_2,\ldots,\mathbf{r}_N)\Psi_i(\xi,\mathbf{r}_2,\ldots,\mathbf{r}_N)$$

$$= N\sum_i p_i \int d\mathbf{r}_2 \ldots \int d\mathbf{r}_N \Psi_i^*(\mathbf{x}-\xi,\mathbf{r}_2,\ldots,\mathbf{r}_N)\Psi_i(0,\mathbf{r}_2,\ldots,\mathbf{r}_N)$$

$$= \rho_1(\mathbf{x}-\xi;0) = \rho\,\tilde{F}_{\mathrm{IA}}(|\mathbf{x}-\xi|).$$

$$\int d\mathbf{y}\,\rho_2(\mathbf{x},\mathbf{y};\boldsymbol{\xi},\mathbf{y}) = (N-1)\rho_1(\mathbf{x};\boldsymbol{\xi}) = (N-1)\rho_1(|\,\mathbf{x}-\boldsymbol{\xi}\,|)$$