Fluctuating Hydrodynamics of Non-Ideal Fluids Via Stochastic Hard-Sphere Molecular Dynamics (SHSD)

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[1]This work performed in part under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

DSMC09, Santa Fe, NM
September 9, 2009

Stochastic Molecular Dynamics

- In real fluids particles (atoms) interact continuously via interaction forces: **Molecular Dynamics** (MD).
- A notable exception are **hard-sphere fluids**.
- At low densities, particles travel almost freely in-between brief but intense **collisions**.
- Momentum and energy transport in a collisional fluid have two components:
  - **Kinetic**: advective motion made diffusive by the randomizing collisions
  - **Collisional**: momentum and energy exhange during the collisions
- *Stress tensor* is an average over collisions,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_k + \boldsymbol{\sigma}_{\mathbf{c}} = m \left\langle \mathbf{v}_i \otimes \mathbf{v}_i \right\rangle + m \frac{\left\langle \mathbf{r}_{ij} \otimes \Delta \mathbf{v}_{ij} \right\rangle_c}{\Delta t}$$

Traditional DSMC

- Traditional DSMC assumes a low-density gas, meaning that the *kinetic transport dominates*: the collisional terms do not really matter!
- In particular, the typical collisional distance $\langle r_{ij} \rangle$ does not matter as long as $\langle r_{ij} \rangle \ll \lambda$.
- Traditional DSMC algorithm:
  - Propagate particles *advectively*, $\mathbf{r}_i^{'} = \mathbf{r}_i + \mathbf{v}_i \Delta t$, and sort them into a grid of **collision cells**.
  - For each cell c a certain number $N_{tc} \sim \Gamma_{tc} N_c (N_c - 1) \Delta t$ of random **trial collisions** are executed.
  - The collision rate $\Gamma_{tc} \sim \sigma$ is chosen based on kinetic theory and a prescribed **collisional cross-section** σ.
  - The trial collision is accepted with some probability $p_{ij}^{(acc)}$ dependent on $v_{rel} = |\mathbf{v}_{ij}|$, e.g., $p_{ij}^{(acc)} = v_{rel} / v_{rel}^{(max)}$ for hard-sphere gases.
  - Momentum and energy is exchanged conservatively, choosing $\Delta \mathbf{v}_{ij}$ randomly, independently of $\mathbf{r}_{ij}$.

DSMC for Dense Flows

- As the density is *increased*, i.e., when $\langle r_{ij} \rangle \gtrsim \lambda$, the collisional contributions to the transport begin to become important...
- *Grid artifacts* in traditional DSMC:
  - It is **not** *Galilean invariant*: the grid of cells must be shifted randomly before each collision step.
  - It is **not** *microscopically isotropic* and does not strictly conserve angular momentum.
- The collisional stress tensor in traditional DSMC is **anisotropic** and the particle interactions are not frame invariant: this is *not acceptable* for liquids or dense gases!

Isotropic DSMC

- **Isotropic DSMC**: All pairs of particles closer than distance D are collision candidates, even if in **neighboring cells**!
- In the limit of small time steps, the I-DSMC method simulates the following *stochastic particle system*:
  - *Particles move ballistically in-between collisions.*
  - *While two particles i and j are less than a diameter D apart, $r_{ij} \leq D$, there is a probability rate $\chi D^{-1} K_c(\mathbf{v}_{ij}, \mathbf{r}_{ij})$ for them to collide and change velocities without changing their positions.*
  - *The pair center-of-mass velocity does not change, while the relative velocity is drawn from a probability density $P_c(\mathbf{v}'_{ij}; \mathbf{v}_{ij}, \mathbf{r}_{ij})$,* $\left\| \mathbf{v}'_{ij} \right\| = \| \mathbf{v}_{ij} \|$.

I-DSMC Collision Kernels

- The I-DSMC fluid is specified through: the *pre- and post-***collision kernels** K_c and P_c, the **cross-section factor** χ and the **density** (hard-sphere volume fraction) $\phi = \pi N D^3/(6V)$.
- Normalization is such that for $\chi = 1$ and $\phi \ll 1$, the *effective* collisional cross-section is the same as traditional DSMC:

1. **Traditional** DSMC collisions:
   - $K_c = 3v_{rel}/4$, requiring costly rejection to implement.
   - The relative velocity is rotated uniformly independent of $\mathbf{r}_{ij}$ [1].
2. **Maxwell** collisions:
   - $K_c = 3\overline{v}_{rel}/4 = 3\sqrt{k_B T_0/\pi m}$, no rejection necessary!
   - This is *unphysical* if the temperature dependence matters, but otherwise preferred.

I-DSMC Algorithm

1. Visit the cells one by one in *random order.*
2. For each cell c perform $N_{tc}^{(c)} = \Gamma_{tc}^{(c)} N_c N_p \Delta t$ trial collisions between one of the N_c particles in that cell and one of the N_p particles in the 3^d neighboring cells, rejecting self-collisions. The **local collisional rate** $\Gamma_{tc}^{(c)} = \chi D^{-1} K_c^{(max)}/2$.
3. Perform an actual collision for the trial pair ij with probability

$$p_{ij}^c = K_c(\mathbf{v}_{ij}, \mathbf{r}_{ij})/K_c^{(max)}.$$

4. For the Maxwell kernel $K_c^{(max)} = 3\overline{v}_{rel}/4 = \text{const}$.
5. For the traditional pre-collision kernel $K_c^{(max)} = 3v_{rel}^{(max)}/4$.

Practicalities

- Guidelines for **parameter selection**:
  - Cell length $L_c \gtrapprox D$.
  - Choose ϕ such that there are a couple of particles per cell.
  - Trial collision frequency χ should be adjusted to tune viscosity.
  - Choose dimensionless time step $\delta t \lessapprox 0.10 - 0.25$ s.t.

$$l_{\Delta t} \approx \Delta t \sqrt{k_B T_0 / m} \sim D \delta t.$$

  - Time steps should be such that there are *no more* than $0.25 - 0.5$ collisions per particle per time step.

Comparison with Traditional DSMC

- I-DSMC is **not** meant to replace traditional DSMC at low densities! For one, it is several times **less efficient**.
- The molecular properties enter in traditional DSMC only in the form of collisional **cross-sections** $\sigma \sim D_m^2$.
- For rarified gas flows, the collision diameter D is like the cell length L_c, *not* D_m!
- *I-DSMC for a low-density gas* of hard-sphere of diameter D_m: Choose the collision diameter $D \approx \lambda/4 \gg D_m$, and set $\chi_B \sim (D_m/\lambda)^2 \ll 1$.

Non-Ideal Fluids

- Recall stress tensor

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_k + \boldsymbol{\sigma}_{\mathbf{c}} = m \left\langle \mathbf{v}_i \otimes \mathbf{v}_i \right\rangle + m \frac{\left\langle \mathbf{r}_{ij} \otimes \Delta \mathbf{v}_{ij} \right\rangle_c}{\Delta t}$$

- For randomized collision kernels, at equilibrium $\boldsymbol{\sigma}_{\mathbf{c}} = \mathbf{0}$ and the fluid has an **ideal equation of state** (EOS),

$$p = PV/Nk_B T = 1$$

- The (I-)DSMC fluid is thus very **compressible** and has large density fluctuations.
- Idea: *Mimic repulsion* by biasing the momentum exchange $\Delta \mathbf{p}_{ij} = m \Delta \mathbf{v}_{ij}$ to be (statistically) aligned to $\mathbf{r}_{ij}$.

Hard-Sphere Collision Kernels

- Maximal repulsion when $\Delta \mathbf{p}_{ij} \parallel \mathbf{r}_{ij}$, i.e., the hard-sphere collision rule,

$$\begin{aligned} \mathbf{v}_i' &= \mathbf{v}_i + v_n \hat{\mathbf{r}}_{ij} \\ \mathbf{v}_j' &= \mathbf{v}_j - v_n \hat{\mathbf{r}}_{ij}, \end{aligned}$$

  where $v_n = -\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}$ is the **normal** *(relative)* **speed**.
- Only accept collisions of approaching particles, $v_n > 0$.
- Thermodynamics requires that $p_c \sim T_c$ for a fluid with no internal energy.
- Locally, $p_c \sim \langle \Delta \mathbf{v}_{ij} \cdot \mathbf{r}_{ij} \rangle_c \sim \Gamma_l \sqrt{T_l}$, where Γ_l is the *local* collisional frequency, and thus we require $\Gamma_l \sim \sqrt{T_l}$.
- This requires a pre-collision kernel that is **linear** in the *relative speed*!

Collision Kernels contd.

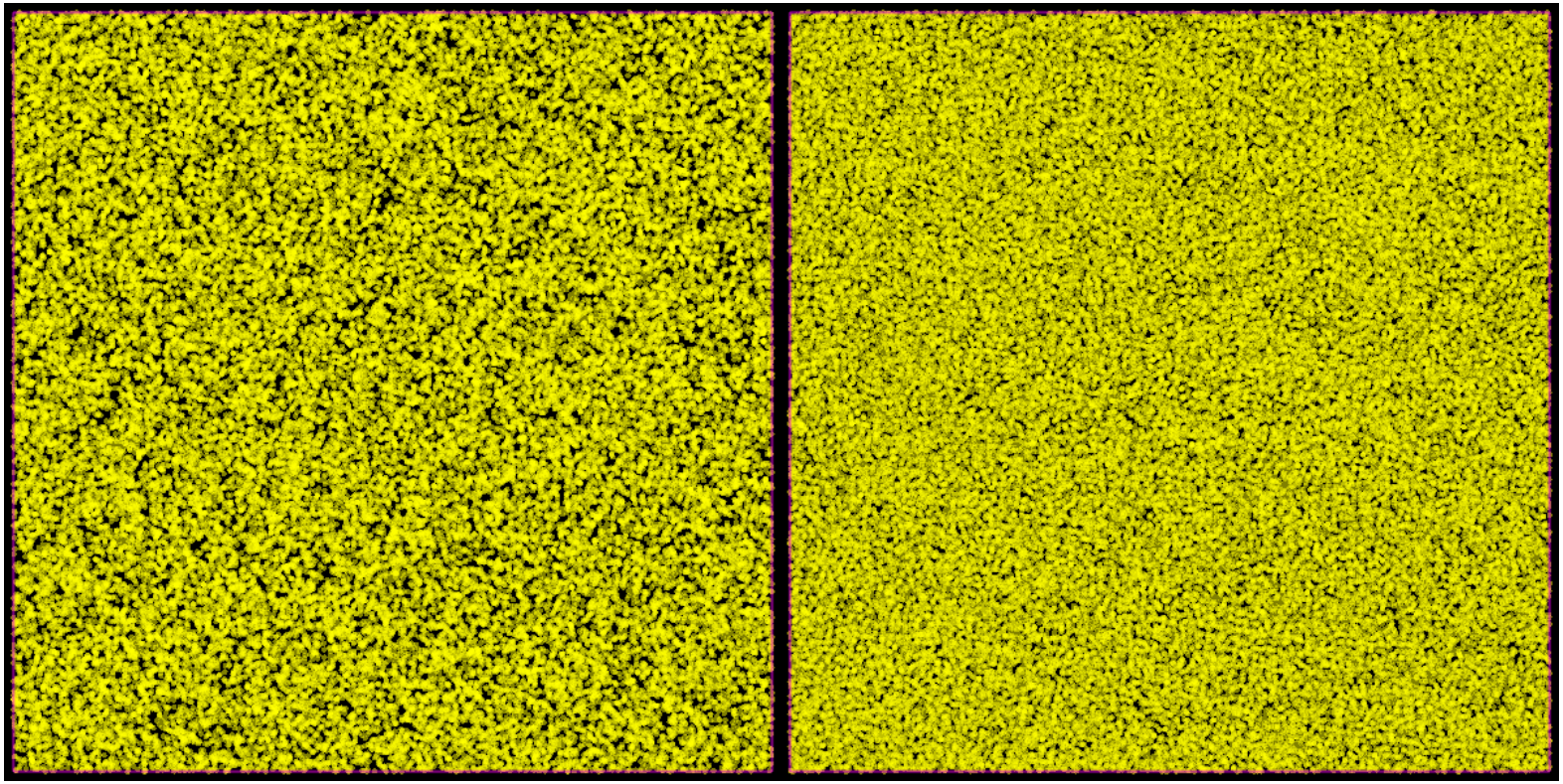
- **Stochastic Hard-Sphere Dynamics** (**SHSD**) collision kernels [2]:

$$P_c(\mathbf{v}'_{ij}; \mathbf{v}_{ij}, \mathbf{r}_{ij}) = \delta(\mathbf{v}_{ij} + 2v_n\hat{\mathbf{r}}_{ij}).$$
$$K_c(\mathbf{v}_{ij}, \mathbf{r}_{ij}) = 3v_n\Theta(v_n)$$

- SHSD is a specific version of I-DSMC and is implemented with the I-DSMC algorithm.
- **Rejection** of collision trial pairs slows things down significantly but is necessary (we use $K_c^{(max)} = 3v_{max}^{(rel)}$).
- A. Donev, A. L. Garcia and B. J. Alder [3, 4]
  "*Stochastic Hard-Sphere Dynamics for Hydrodynamics of Non-Ideal Fluids*", Phys. Rev. Lett. 101:075902 (2008) [**arXiv:0803.0359**]
  "*A Thermodynamically-Consistent Non-Ideal Stochastic Hard Sphere Fluid*", submitted [**arXiv:0908.0510**].

The SHSD Fluid

- The SHSD fluid has **non-trivial structure**



- But is the structure thermodynamically-consistent with the EOS, $p(\phi) = PV/Nk_BT$, i.e.,
  Are the ***density fluctuations*** *consistent with the* ***compressibility***?!?

SHSD as a Penetrable Sphere Fluid

- The SHSD fluid is *not* a classical Hamiltonian fluid, so classical statistical mechanics is not directly applicable.
- We find numerically that the SHSD system is **thermodynamically equivalent** to a system of penetrable spheres interacting with a **linear core** pairwise effective potential

$$U(r)/kT = 3\chi(1-x)\Theta(1-x)$$

- This potential is similar to the Dissipative Particle Dynamics (DPS) quadratic core potential.
- This equivalence **guarantees** *thermodynamic consistency* for SHSD, i.e.,

$$S(\omega = 0, k = 0) = \frac{k_B T}{m} c_T^{-2} = (p + \phi dp/d\phi)^{-1}$$

Pair Correlation Function

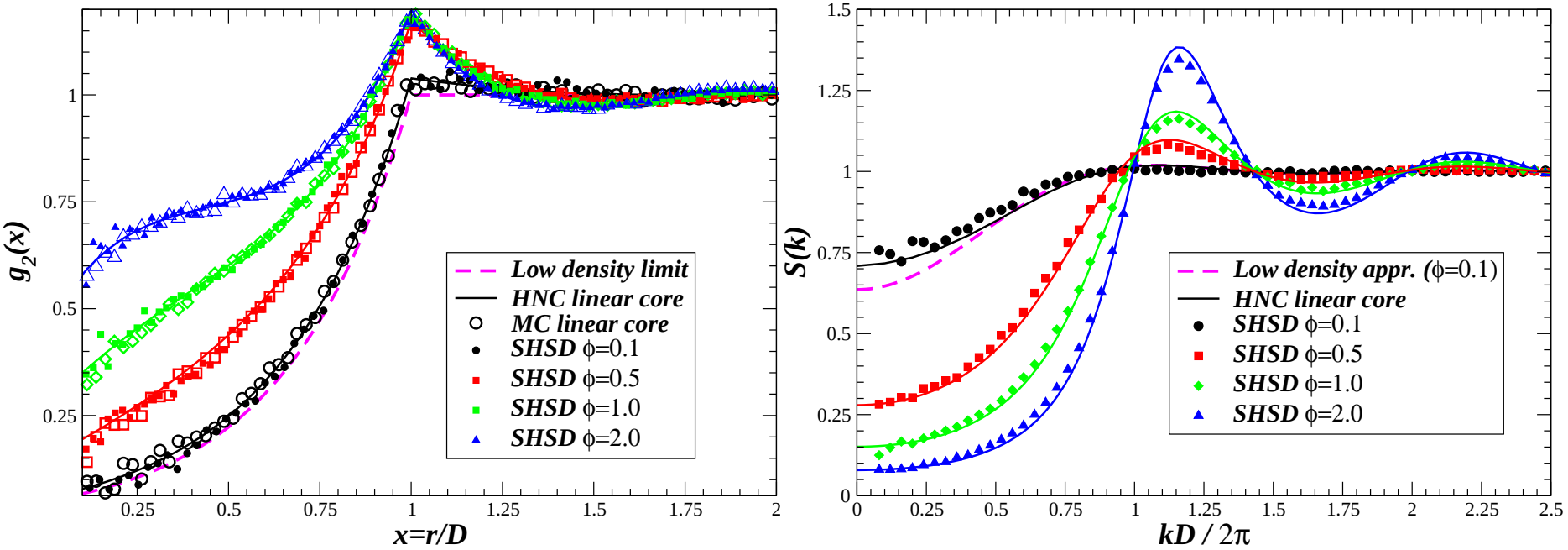


Figure: $g_2(x)$ and $S(k)$ for SHSD with $\chi = 1$

Transport Coefficients

- The hydrodynamics of SHSD is described by a *stochastic revised Enskog equation* [5],

$$\frac{\partial f(t,\mathbf{r},\mathbf{v})}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla}_{\mathbf{r}} f(t,\mathbf{r},\mathbf{v}) = 3\chi D^2 \int_0^1 dx \int_{\mathcal{R}^3} d\mathbf{w} \int_{S_+^2} d\mathbf{e} \quad x^2 v_n$$
$$\left[g_2(\mathbf{r},\mathbf{r}+x\mathbf{e};n) f(t,\mathbf{r},\mathbf{v}') f(t,\mathbf{r}+x\mathbf{e},\mathbf{w}')\right.$$
$$\left. - g_2(\mathbf{r},\mathbf{r}-x\mathbf{e};n) f(t,\mathbf{r},\mathbf{v}) f(t,\mathbf{r}-x\mathbf{e},\mathbf{w})\right]$$

  where $v_n = -\mathbf{e}\cdot(\mathbf{v}-\mathbf{w}) \geq 0$, $\mathbf{v}' = \mathbf{v} + \mathbf{e}v_n$ and $\mathbf{w}' = \mathbf{w} - \mathbf{e}v_n$.

- A standard second-order **Chapman-Enskog expansion** [5] gives theoretical estimates for transport coefficients in terms of the moments of pair correlation function $g_2(x = r/D)$, $x_k = \int_0^1 x^k g_2(x) dx$.

Pressure

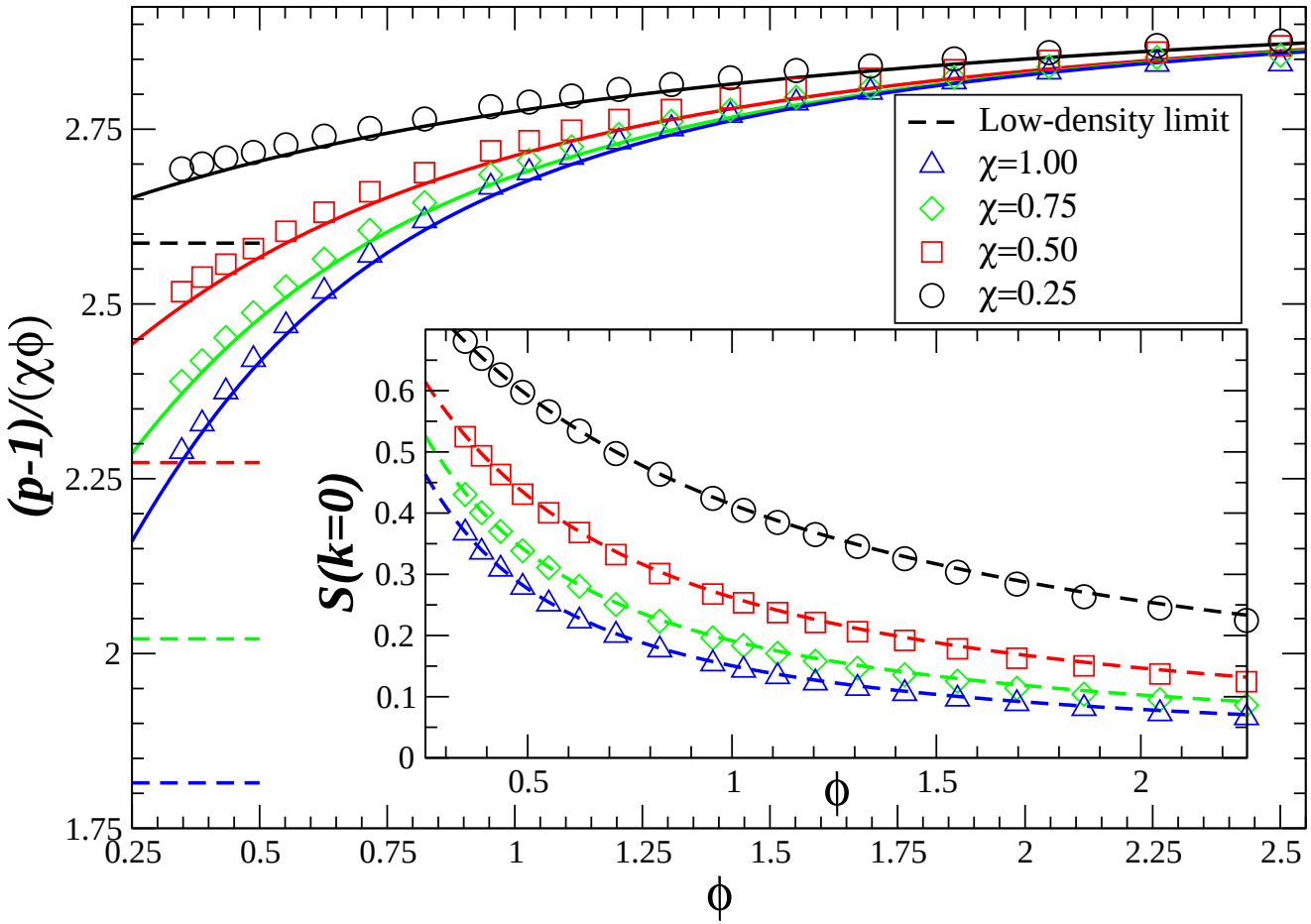


Figure: $p(\phi;\chi) = PV/Nk_BT = 1 + 12\phi\chi x_3$

Viscosity

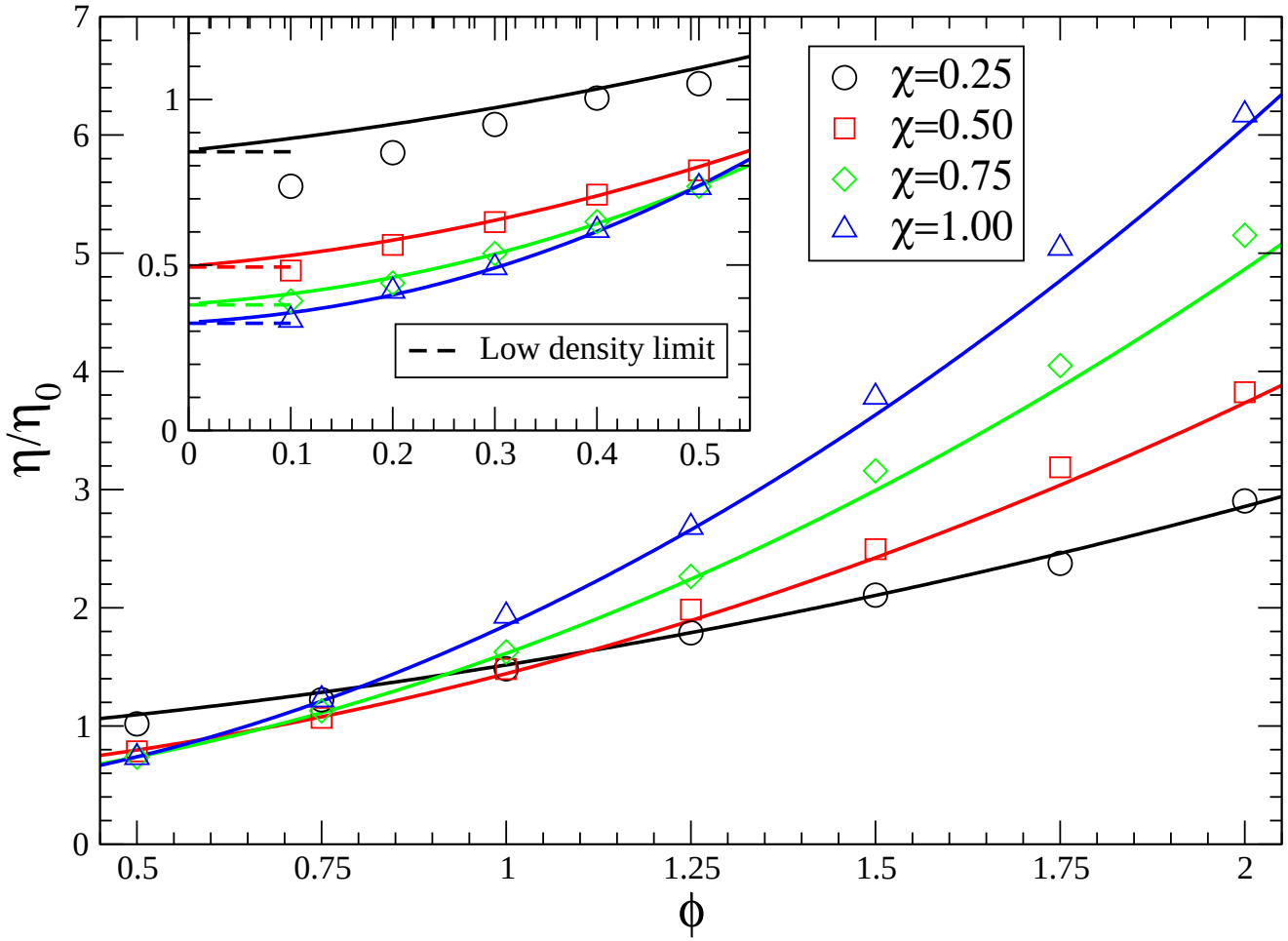


Figure: $\eta(\phi;\chi)D^2/\sqrt{mk_BT} = \frac{5}{48\sqrt{\pi}\chi x_2}(1+\frac{24\phi\chi x_3}{5})^2 + \frac{144\phi^2\chi x_4}{5\pi^{3/2}}$

SHSD as a Stochastic Fluid

- The SHSD algorithm gives a fluctuating hydrodynamic medium with **tunable compressibility and viscosity** that is significantly more efficient than classical Molecular Dynamics!
- We have verified that the spatio-temporal correlations of the fluctuating hydrodynamic field $\mathbf{U} = (\rho_0 + \delta\rho, \delta v, T_0 + \delta T)$ are consistent with the (linearized) **Landau-Lifshitz Navier Stokes (LLNS)** equations.
- The speed of sound increases with ϕ and χ, and the density fluctuations are correspondingly reduced.
- For reasonable parameters the SHSD fluid is still relatively compressible compared to a dense liquid, Schmidt number $S_c = \eta(\rho\zeta)^{-1} \sim 10$ instead of $S_c \sim 1000$ for water.

Dynamic Structure Factor

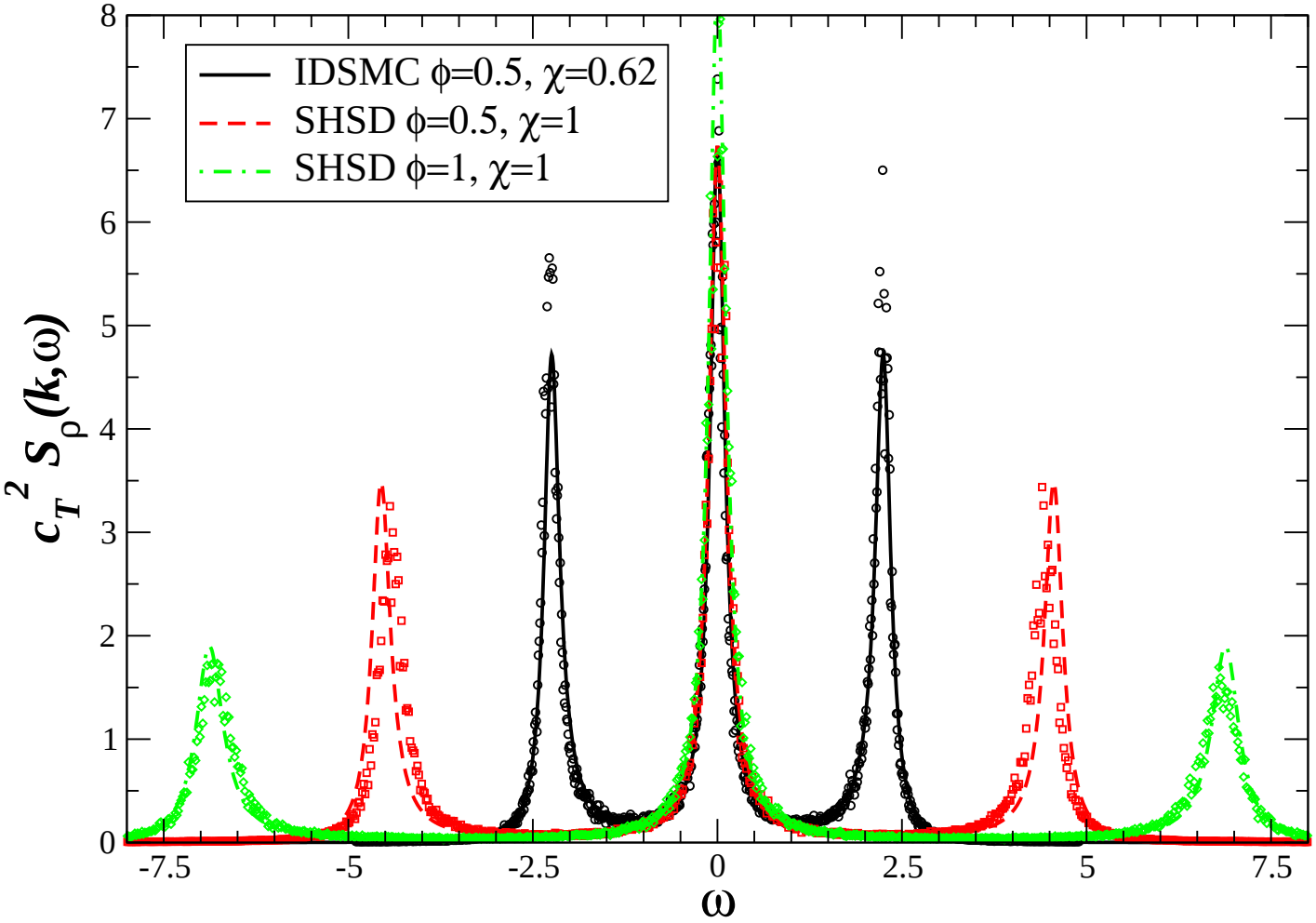


Figure: Shifting of the two symmetric Brillouin peaks at $\omega \approx c_s k$ toward higher frequencies as compressibility is reduced.

Conclusions

- Collisional contribution to the stress tensor can be made Gallilean invariant and isotropic by making DSMC grid-free: **Isotropic DSMC** (I-DSMC).
- Eliminating grid artifacts is expensive but becomes important for **dense** and **non-ideal** fluids.
- A non-ideal equation of state can be introduced in I-DSMC by using the hard-sphere pre- and post-collision kernels: **Stochastic Hard-Sphere Dynamics** (SHSD).
- We have coupled I-DSMC to a continuum fluctuating hydrodynamics solver in a **hybrid method** [6]
  "*A hybrid particle-continuum method for hydrodynamics of complex fluids*", by A. Donev and A. L. Garcia and J. B. Bell and B. J. Alder, under preparation, 2009.

Future Work

- Develop **kinetic theory** for I-DSMC for the traditional and Maxwell collision kernels.
- Deeper **theoretical understanding** of the connection between stochastic and deterministic fluids.
- I-DSMC and SHSD can and should be **parallelized**.
- Our hybrid method works only for ideal DSMC fluids: Can we **couple** SHSD to a continuum solver?
- Ultimately we require an **Adaptive Mesh and Algorithm Refinement** (AMAR) framework that couples deterministic MD for the polymer chains (**micro**), a stochastic solvent (**micro-meso**), with compressible fluctuating Navier-Stokes (**meso**), and incompressible CFD (**macro**).

References/Questions?

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