

Capillary Waves Dynamics at the Nanoscale

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Fundamental questions on simple liquids

Hydrodynamics at the nanoscale

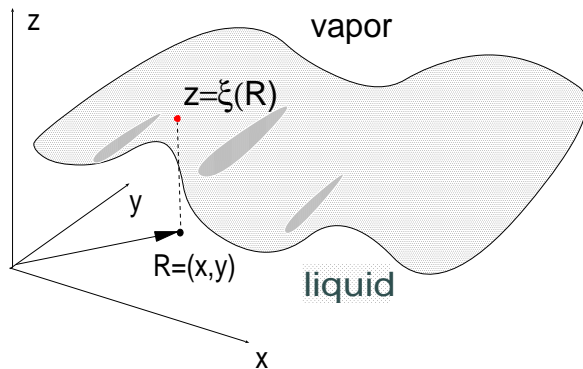
- What is the limit of validity of surface-tension driven hydrodynamics?
- How does the surface modes behave beyond that limit?

Surface tension and liquid surface at molecular scales

- How does the surface tension depends on the wavenumber $\gamma(q)$?
- It is possible to define the rightful **intrinsic surface** of a liquid at the molecular level?

Definition of the intrinsic surface and surface modes

- Capillary wave theory (CWT) **assumes** the existence of the *intrinsic surface* of a liquid, $z = \xi(\mathbf{R})$.



- Intrinsic surface (IS): $z = \xi(\mathbf{R})$
- Fourier modes: $\hat{\xi}_{\mathbf{q}}$
- The intrinsic surface described through $\hat{\xi}_{\mathbf{q}}$,

$$\xi(\mathbf{R}) = \sum_{|\mathbf{q}|=q_l}^{q_u} \hat{\xi}_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}}$$

- The intrinsic surface is an intuitive concept in the macroscopic world.
- However, **at the nanoscale, it is not clear** how to define it, from **the individual molecular positions**.

The **structural** approach to surface tension

- Effective surface Hamiltonian

$$H(q) = \frac{A}{2} \sum_q \gamma(q) |\hat{\xi}_q|^2 q^2$$

- Using the equipartition theorem one gets a **structural** measure of the surface tension (A is the nominal area of the surface)

$$\gamma_s(q) = \frac{k_B T}{q^2 \langle |\hat{\xi}_q|^2 \rangle A}$$

- Correct macroscopic limit $\gamma_s(0) = \gamma_o$
- **But** for $q\sigma > 0.5$ there is a strong dependence of $\gamma_s(q)$ on the specific proposal to get $\hat{\xi}_q$ from the molecular positions
[Chacon et al. PRL **91** 166103 (2003)]

Methods to construct the intrinsic surface

$$\langle |\hat{\xi}_q|^2 \rangle \implies \gamma_s(q) = \frac{k_B T}{\langle |\hat{\xi}_q|^2 \rangle A}$$

- **Gibbs method**

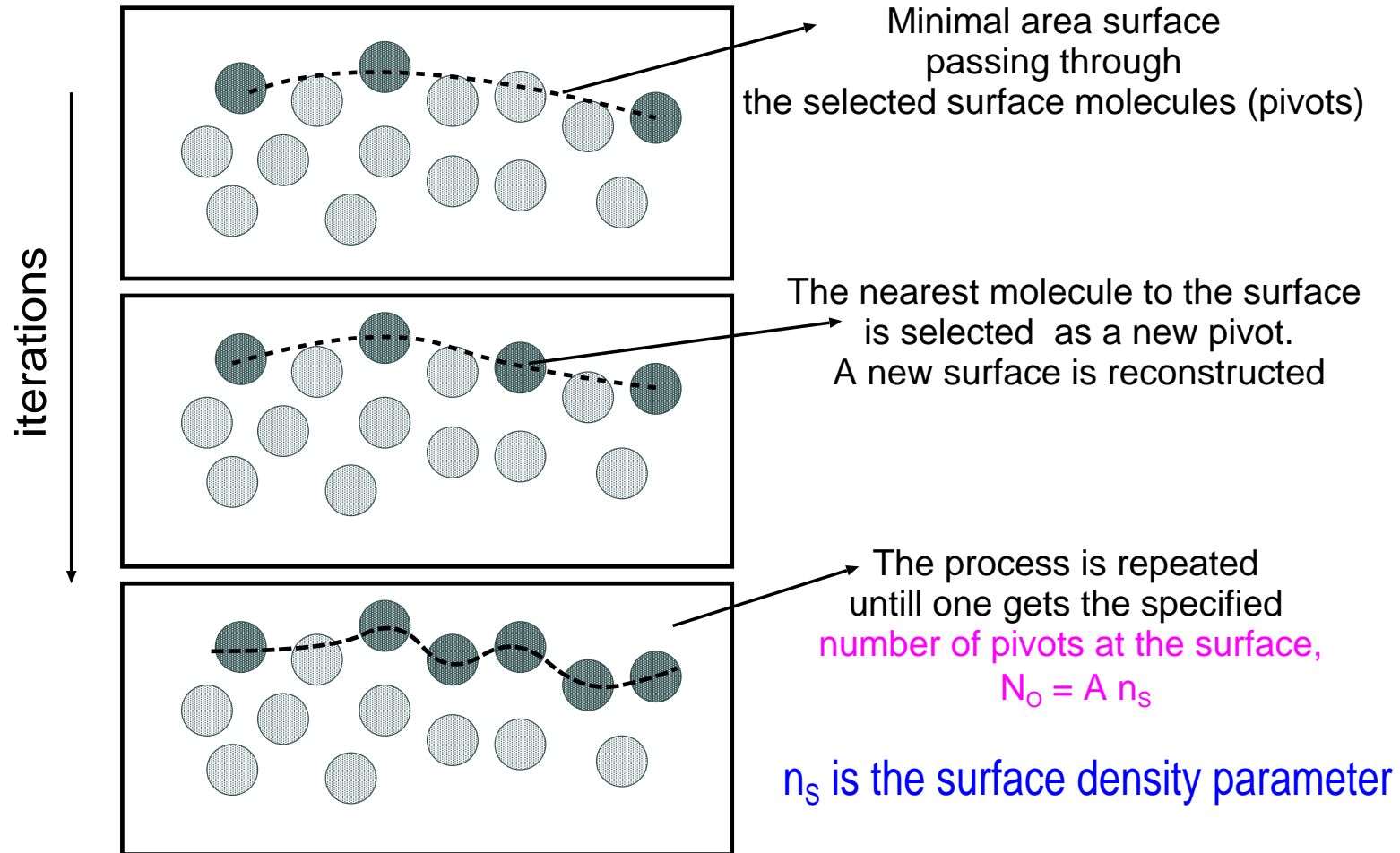
- Based on thermodynamic arguments.
- Gives correct macroscopic surface tension, γ_o .
- But it is not able to resolve bulk fluctuations from surface undulations.
- At finite q , it gives unphysical results $\gamma(q) \sim 1/q^2$. (e.g. fails to predict the finite width of the surface $\Delta = \sum_q |\hat{\xi}_q|^2$)

- **Percolation methods**

- The intrinsic surface keeps information on the positional correlations between the molecules *at* the surface.
- This information is required to resolve surface undulations from bulk mass fluctuations.

The Intrinsic Sampling Method (ISM)

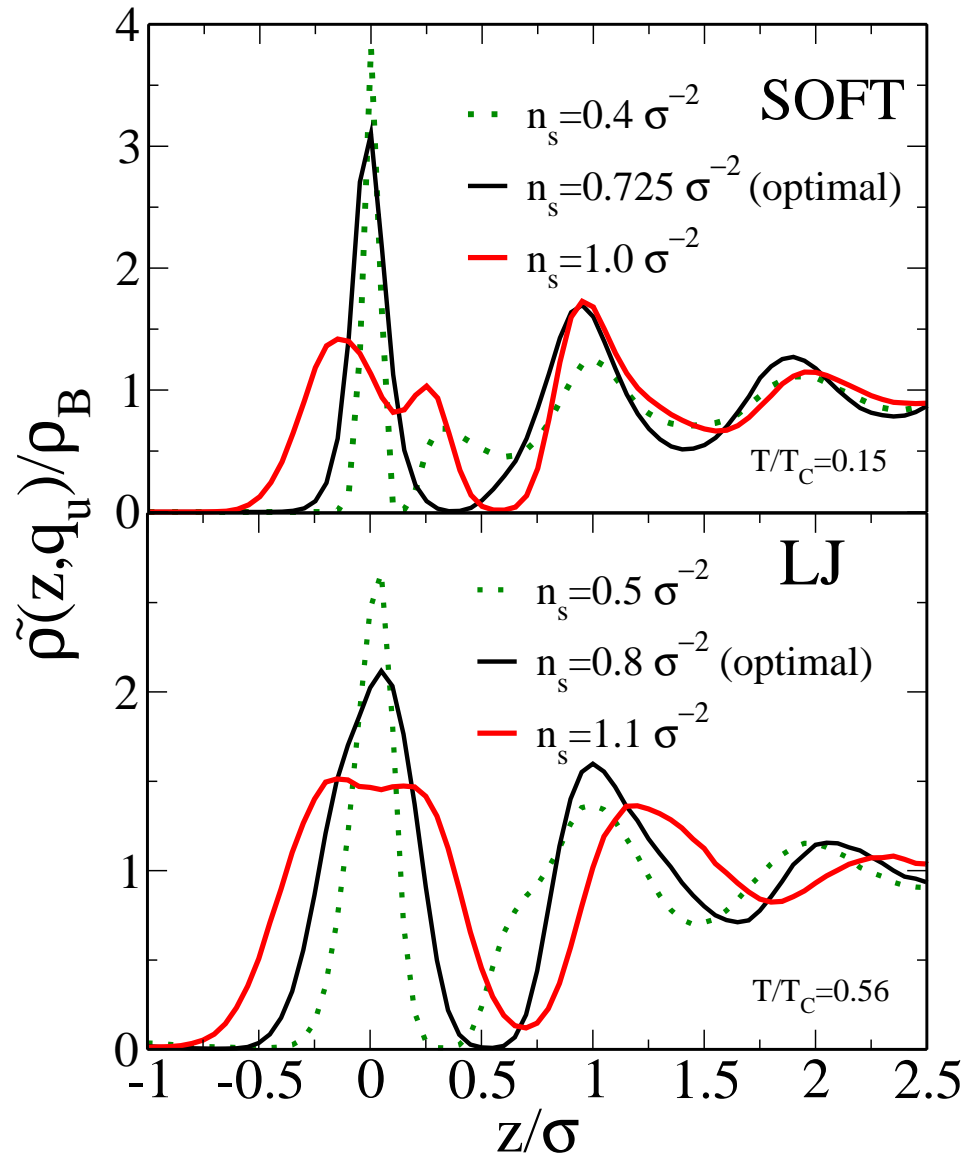
Chacón and Tarazona, Phys. Rev. Lett. **91** 166103 (2003); J. Phys.:Cond. Matter, **17**, S3493 (2005)



The parameter n_s needs to be optimized to get the sharpest molecular structure below the surface

Structural criterium for the **optimal surface density**, n_s

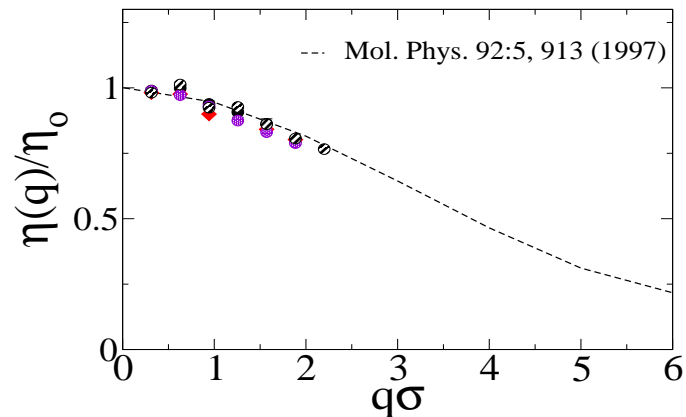
The intrinsic density profile: $\tilde{\rho}(z) = \frac{1}{A} \langle \sum_i \delta(z - z_i + \xi(\mathbf{R}_i)) \rangle$



The hydrodynamic route.

- Molecular dynamics (MD) simulations of simple liquid slabs
- Intrinsic Sampling Method \implies Fourier modes time behaviour $\hat{\xi}_{\mathbf{q}}(t)$
- Analyze ACF, $\langle \hat{\xi}_{\mathbf{q}}(t) \hat{\xi}_{\mathbf{q}}(0) \rangle \implies$ modes frequency and damping rate.
- Compare MD with **Hydrodynamic theory** + *structural* $\gamma_s(q)$ predictions
- Obtain a **dynamic** measure of the surface tension $\gamma_d(q)$.
- Physically coherent definition of the intrinsic surface? $\boxed{\gamma_d(q) = \gamma_s(q)}$

⊕ **Note:** Viscosity, Lennard-Jones liquid



The wavenumber dependence of viscosity $\eta(q)$ has to be taken into account at the nanoscale.

The hydrodynamic theory

Dispersion relation for the surface modes

- **Linearized Navier-Stokes.** J. Chem. Phys. **94**, 5208 (1991)
J. Phys.: Condens. Matter, **10**, 4955 (1998).
- **Linear response theory.** J. Phys.: Condens. Matter, **7** 4341, (1995).

$$D(q, \tilde{\omega}) = \frac{\gamma q^3}{\rho} - (\tilde{\omega} + 2i\nu q^2)^2 - 2\nu^2 q^4 \left[1 - \frac{i\tilde{\omega}}{\nu q^2} \right]^{1/2}$$

liquid density ρ , kinematic viscosity $\nu = \eta/\rho$.

- $D(q, \tilde{\omega}) = 0 \implies$ surface modes complex frequencies $\tilde{\omega}(q) = \omega(q) + i\Gamma(q)$.

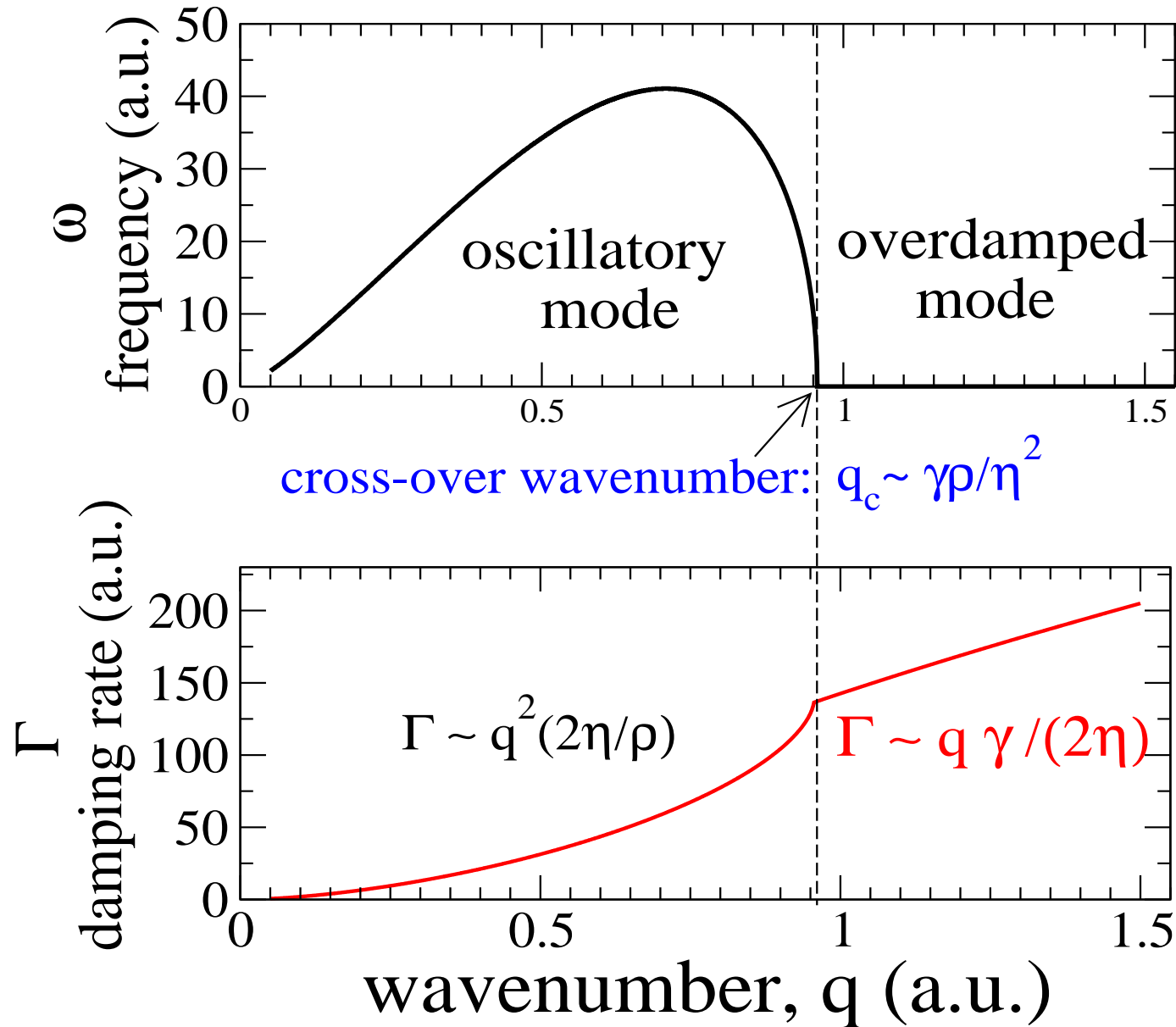
– Frequency, $\omega = \omega(q; \gamma, \eta)$

– Damping rate, $\Gamma = \Gamma(q; \gamma, \eta)$

The hydrodynamic theory

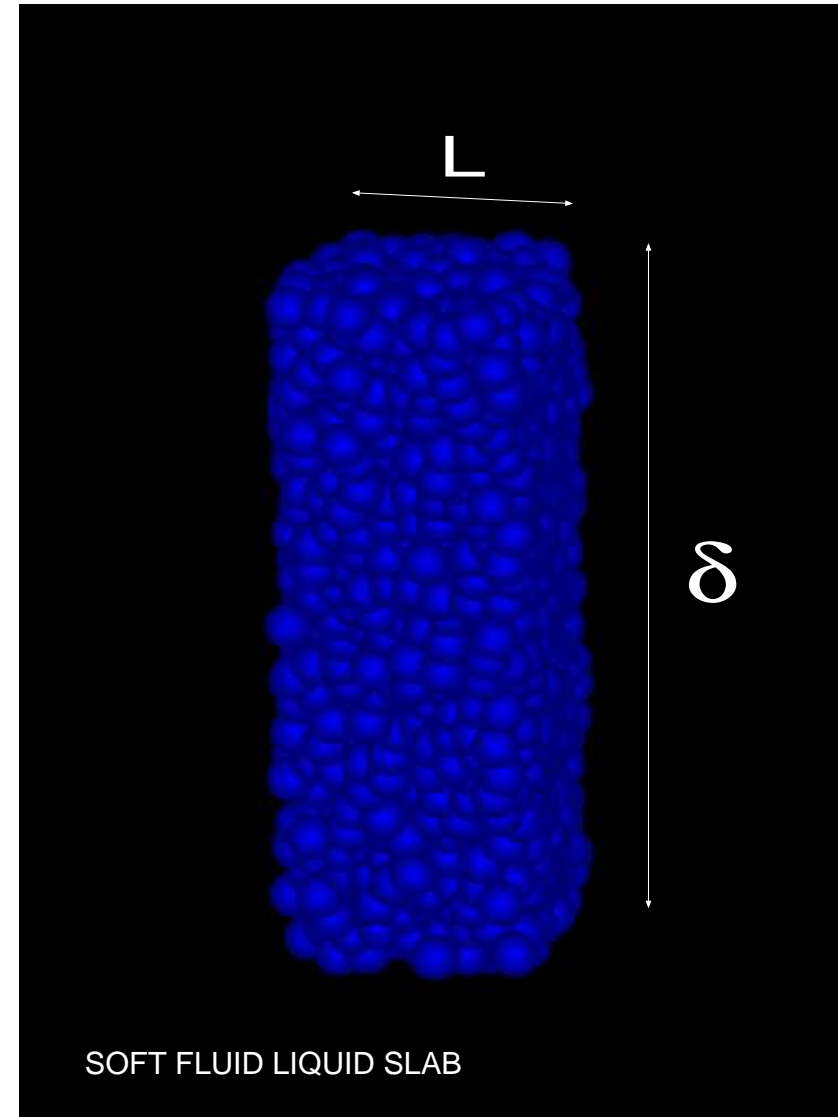
Oscillatory and overdamped regimes

Capillary waves; dispersion relation



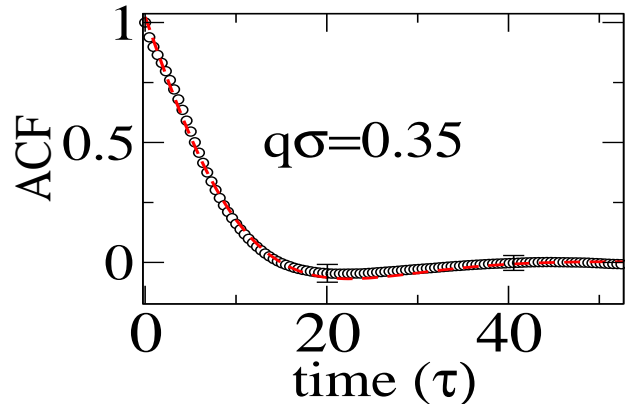
MD simulations: time dependent analysis

- Simulations are done along the **liquid-vapor coexistence line**
- NVE ensemble (also NVT with soft thermostat)
- Time step: $\Delta t = 0.005\tau$
- Transverse length, $L = \{10, 20\} \sigma$
- Slab thickness, $\delta \simeq 3L$
- Instantaneous surface modes $\hat{\xi}_q(t)$, sampled each $10\Delta t$ or $100\Delta t$.
- Working fluids
 - Lennard-Jones
 - Soft alkali (SA) liquid model
[Chacon et al., PRL, **87**, 166101, (2000)]

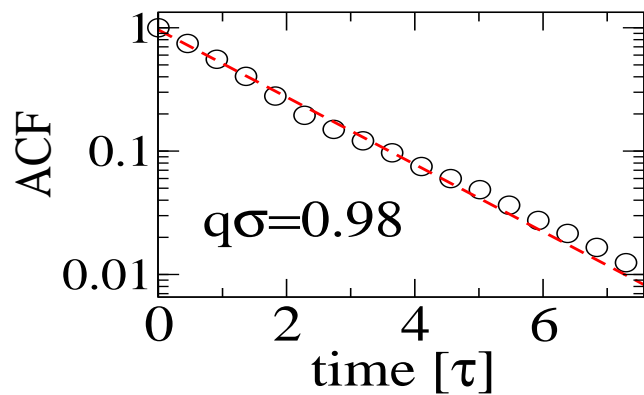


MD results

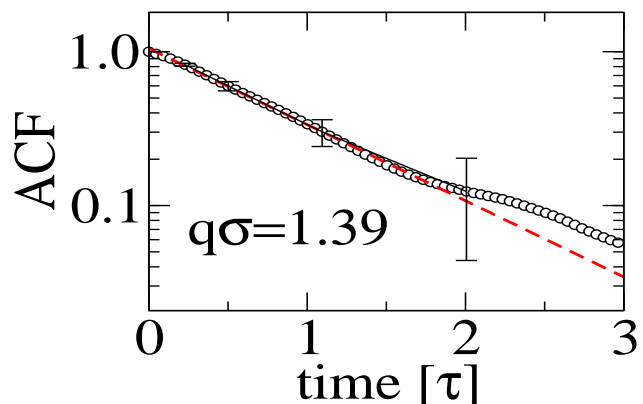
The surface mode's autocorrelation function (ACF)



oscillatory regime



overdamped regime



overdamped regime

- MD+ISM $\implies \langle \hat{\xi}_q(t) \hat{\xi}_q^*(0) \rangle$

- Fits $\langle |\hat{\xi}_q|^2 \rangle \exp(-\Gamma_d t) \cos(\omega_d t)$

\Downarrow

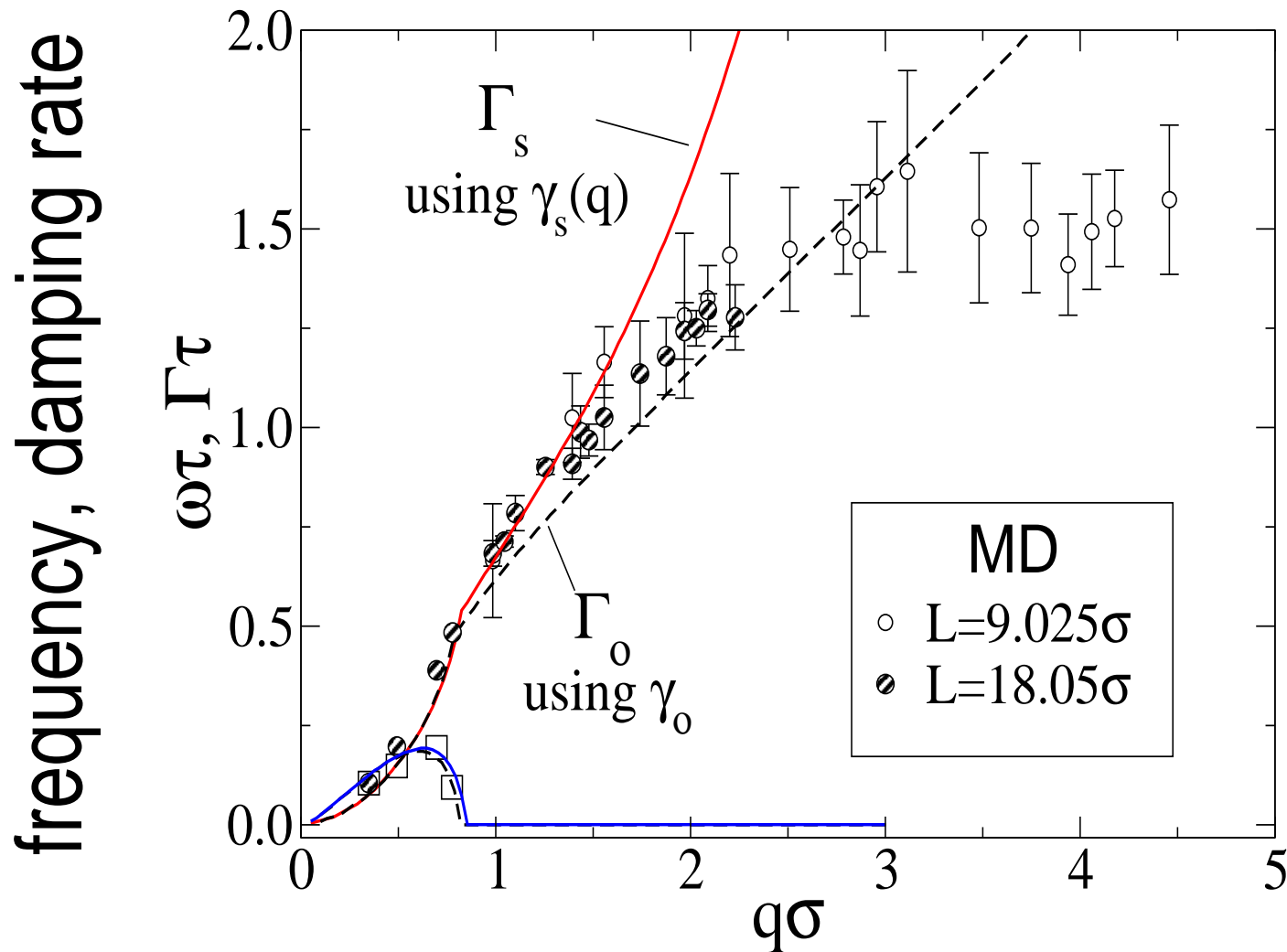
- frequency $\omega_d(q)$
 - damping rate $\Gamma_d(q)$

\leftarrow Results from the **soft alkali** liquid model

Hydrodynamics and MD results

The soft alkali liquid model

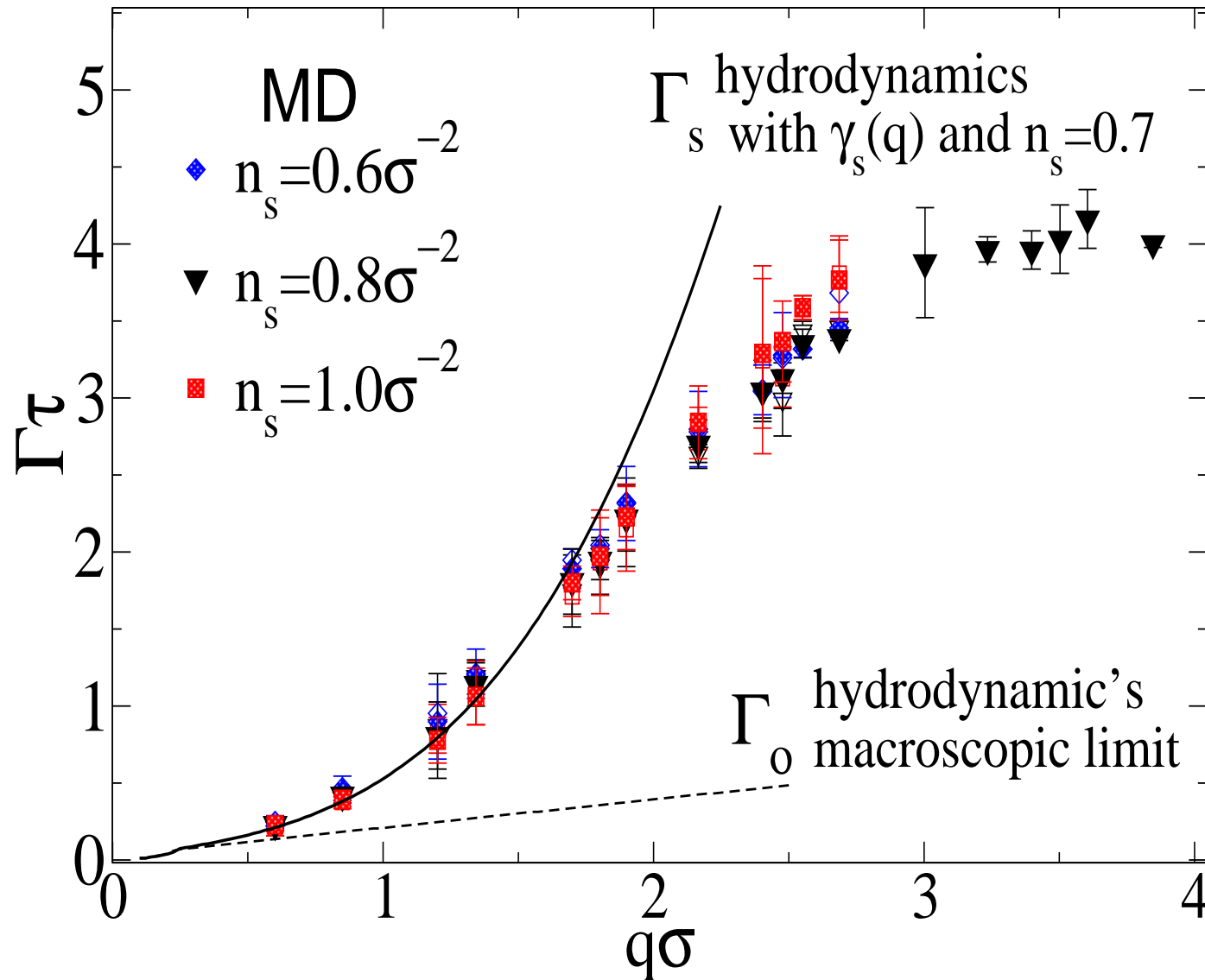
cross-over wavenumber at $q_{cr}\sigma \sim 0.8$



The damping rate at the overdamped regime

Lennard-Jones liquid @ $kT = 0.848\epsilon$

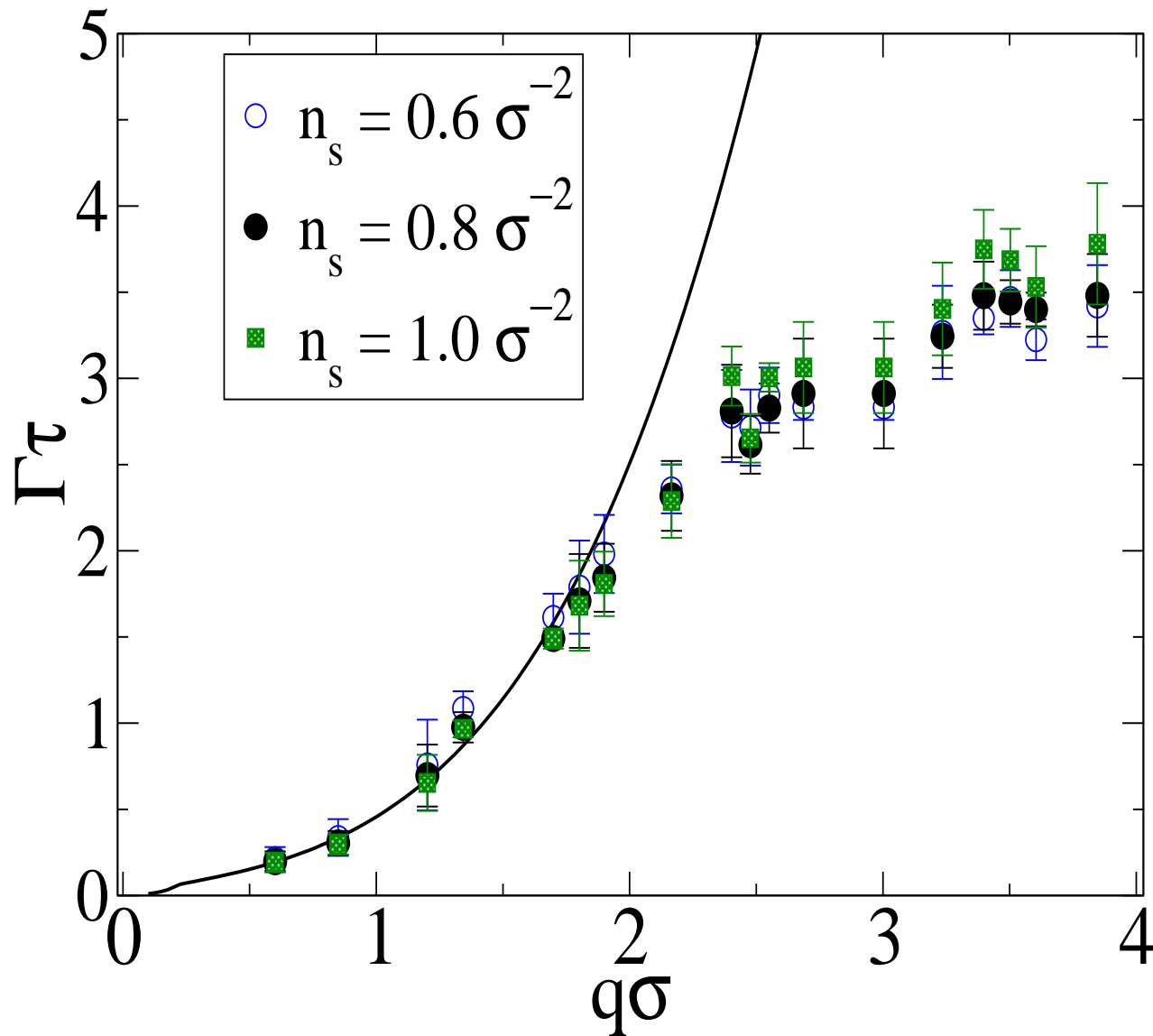
Full line: hydrodynamic result using the **optimal surface density** $n_s = 0.7\sigma^{-2}$



The damping rate at the overdamped regime

Lennard-Jones liquid @ $kT = 0.763\epsilon$

Hydrodynamic result (full line) using optimal surface density $n_s = 0.75\sigma^{-2}$

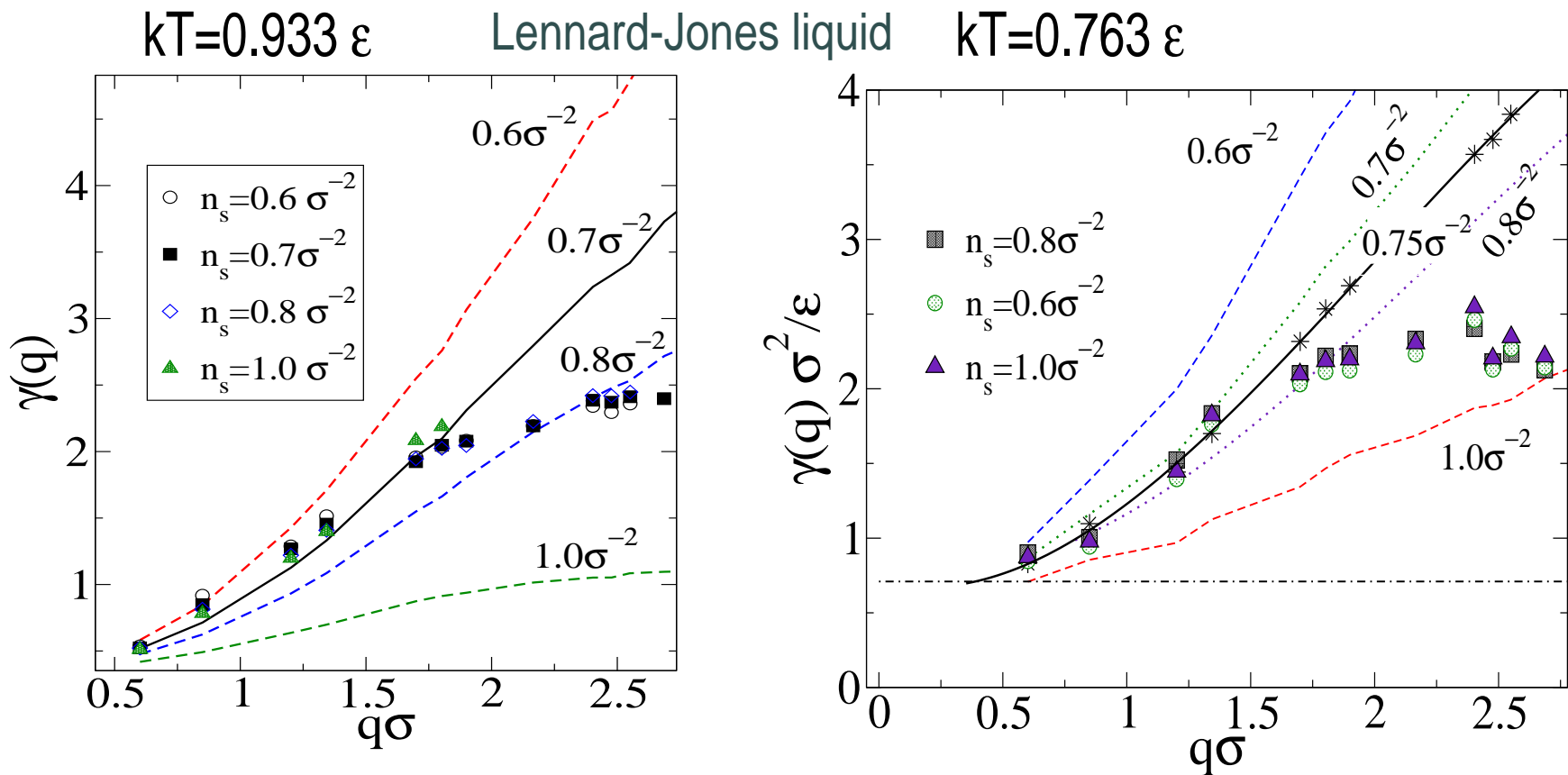


The *dynamic* surface tension, $\gamma_d(q)$

- Dispersion relation, $D(\Gamma, q) = 0 \rightarrow \Gamma(q; \gamma) = \Gamma_d(q)$

- Numerical inversion provides, $\gamma_d(q) = \gamma(q; \Gamma_d)$

- Only for **optimal surface density** $\gamma_d(q) = \gamma_s(q)$



Critics to enhanced capillary waves

several claims of experimental observation

letters to nature

Reduction in the surface energy of liquid interfaces at short length scales

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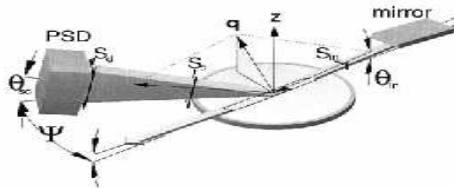
Liquid-vapour interfaces, particularly those involving water, are common in both natural and artificial environments. They were

critics to experimental accuracy

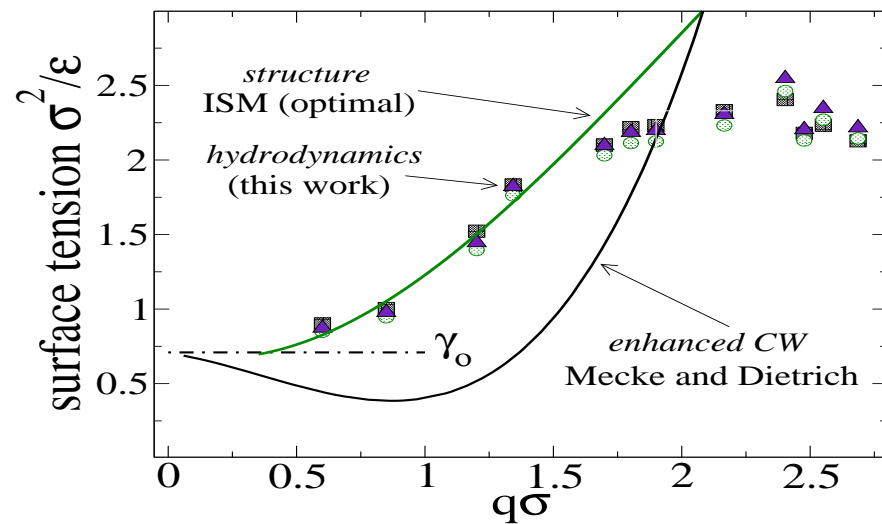
Pershan et al. Colloids Surf. A, 171 (2000)

Shpyrko et al. PRB, 69 (2004)

energy of submicrometre waves that cannot be explained by capillary theory, but is in accord with the effects arising from the non-locality of attractive intermolecule interactions as predicted by a recent density functional theory¹. Our data, and the results of comparable measurements on liquid solutions, metallic alloys, surfactants, lipids and wetting films should thus provide a stringent test for any new theories that attempt to describe the structure of liquid interfaces with nanometre-scale resolution.



Theoretical prediction:
Mecke and Dietrich. Phys. Rev. E **59**, 6766 (1999)



Contradictions in the theoretical prediction of enhanced CW
PRL, 99, 196101 (2007)

PRL 99, 196101 (2007)

PHYSICAL REVIEW LETTERS

week ending
9 NOVEMBER 2007

Critical Analysis of the Density Functional Theory Prediction of Enhanced Capillary Waves

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E. Chacón

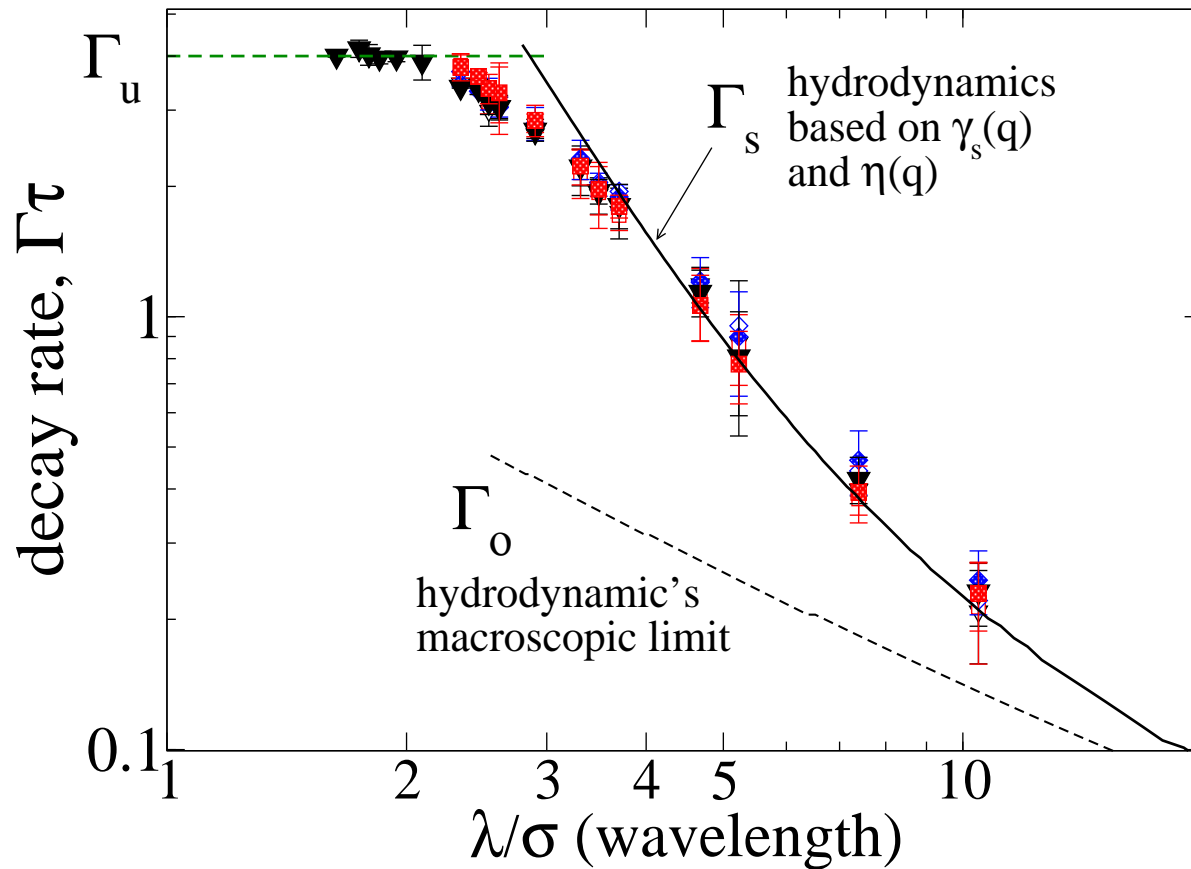
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(Received 18 July 2007; published 5 November 2007)

We present a critical analysis of the density functional description for capillary wave fluctuations on free liquid surfaces. The proposal made by Mecke and Dietrich, [Phys. Rev. E **59**, 6766 (1999)], to obtain

The limit of surface-tension hydrodynamics

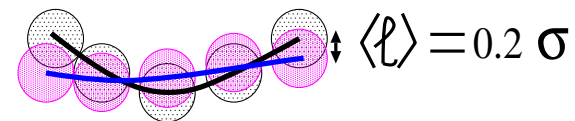
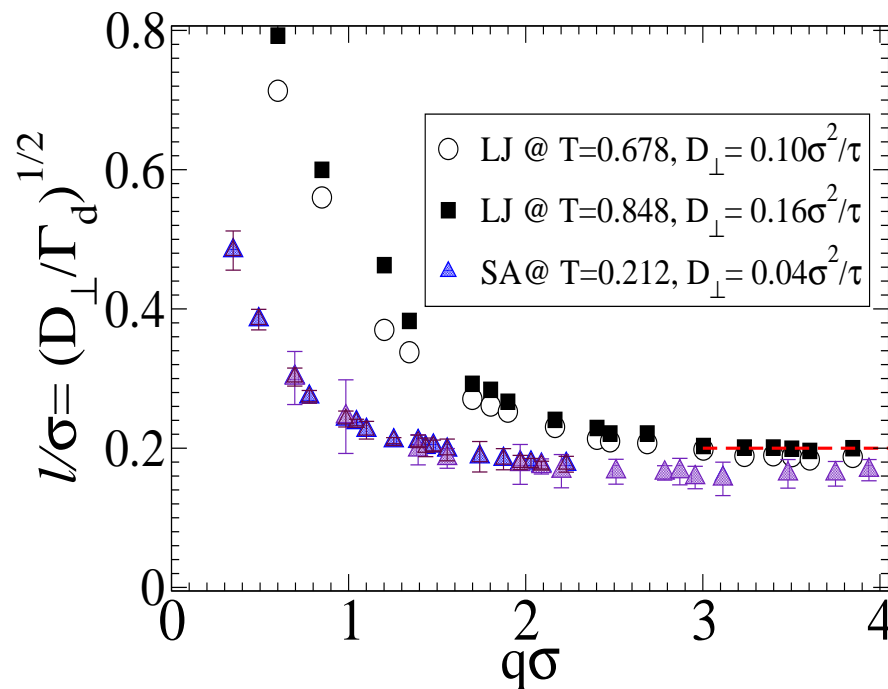
...extends up to surprisingly small wavelengths of **about 4 molecule diameters**.



What is the origin of the limiting decorrelation time Γ_u^{-1} observed at molecular scales?

Molecular diffusion decorrelation length

- Distance covered by surface molecular diffusion in out-of-plane direction, upon the decorrelation time: $\ell = \left(\frac{D_{\perp}}{\Gamma_d}\right)^{1/2}$
- The diffusion coefficient for out-of-plane displacements D_{\perp} calculated by Duque et al. J. Chem. Phys **128**, 134704, (2008).

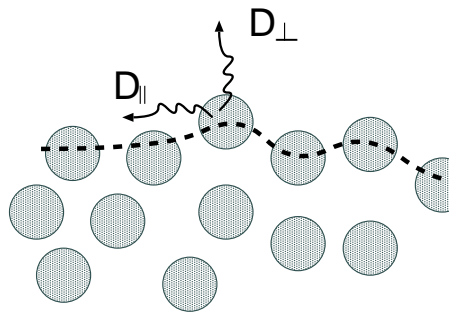


For $q\sigma > 2$
 $\ell \simeq 0.2\sigma$

Anisotropic diffusion at the interface.

Decorrelation distance and split length

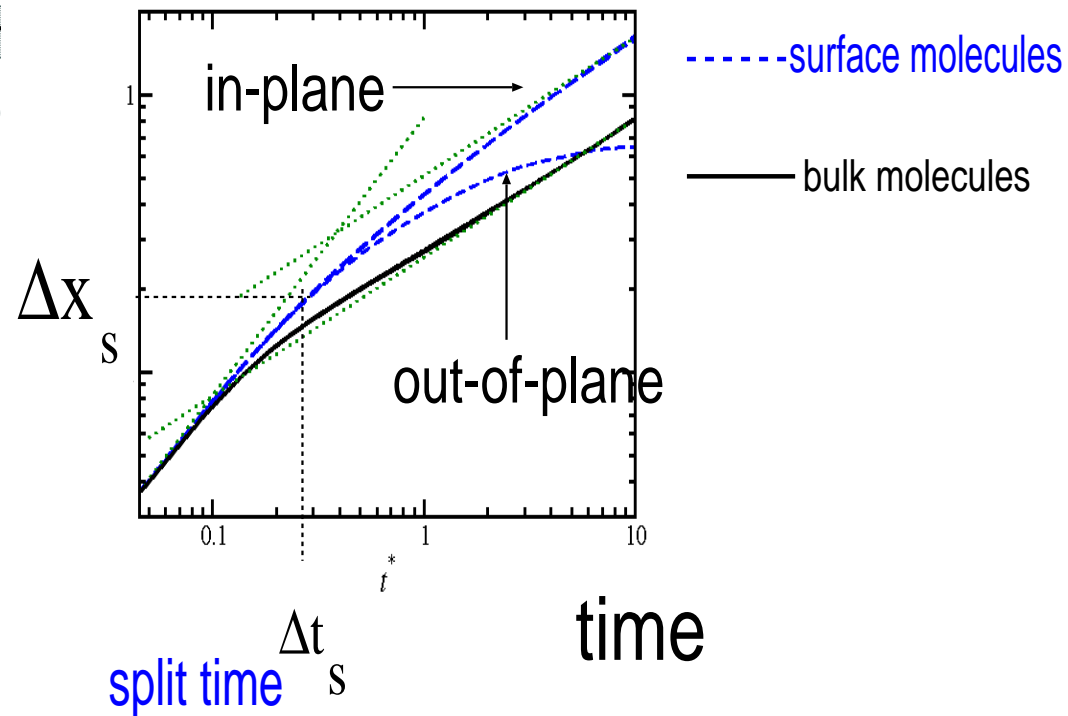
$$l \simeq \Delta x_s$$



Split distance

$$\Delta x_s = 0.2\sigma$$

sqrt. mean squared displacement



Conclusions

- **Hydrodynamics** provides an estimation of the surface tension $\gamma_d(q)$ which is **much more robust** than the structural one $\gamma_s(q)$.
- The **optimal** ISM surface provides a **physically consistent liquid surface** with respect to **structure and hydrodynamics**: $\gamma_d(q) = \gamma_s(q)$.
- The **surface tension increases monotonically with the wavenumber**. This result contradicts the existence of an enhanced capillary wave regime, that would imply a decrease of $\gamma(q)$ below the macroscopic value [Nature **403**, (2000); PRL, **90** (2003)]; PRL, **94** (2004), PRE, **59** (1999)]
- **Hydrodynamics remain valid up to nanometric scales** (wavelengths of about 4 molecule diameters)
- **At smaller scales**, surface modes are governed by **molecular diffusion**
- Diffusive mode dynamics are controlled by the **anisotropy of molecular diffusion at the surface**

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