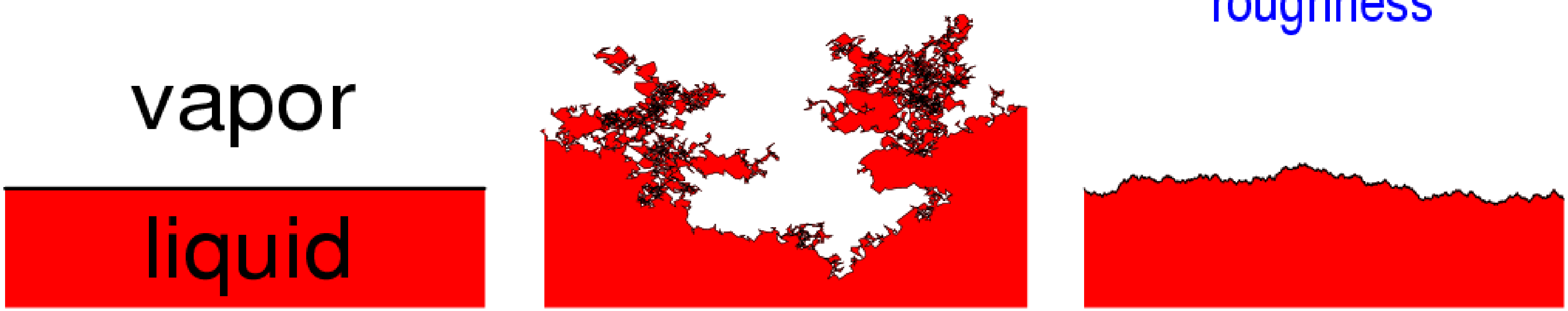
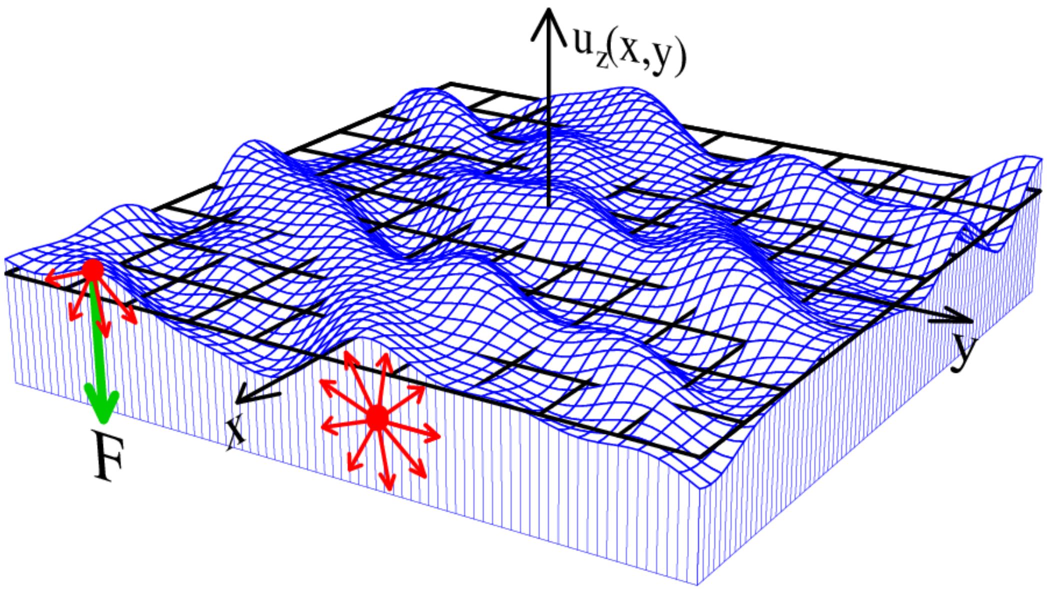
Example : Capillary waves
(thermally induced surface fluctuations of liquid surfaces)

Enthalpy	Entropy	Both Terms
completely smooth	completely disordered	finite surface roughness



Even liquids do not have a perfectly smooth surface!

Theoretical description by the equilibium of forces at the surface.



Break of symmetry
at the surface =>

Resulting force directed
to the bulk =>

surface tension

Equilibrium in the liquid: balance of forces => Navier Stokes Eq.

$$\rho \frac{\partial}{\partial t} \boldsymbol{v} = -\nabla p + \eta \Delta \boldsymbol{v}$$

with boundary conditions:

$$\sigma_{zz} = \gamma \frac{\partial^2}{\partial^2 z} u_z + g \rho \% u_z$$

ρ : density, v : velocity
p : pressure, η : viscosity
σ_{zz} : from stress tensor
γ : surface tension
g : gravitational constant
u_z : displacement at surface

With this knowledge the **dynamical susceptibility** $\chi_{zz}(q,\omega) = u_z / p_z$ can be calculated.

χ_{zz} describes the response of the surface on extranal forces and depends on the frequency ω and the wave vector q.

The **equipartition theorem** states that each thermally excited surface wave (mode) has in average the energy $k_B T$.

The PSD of the modes can be calculated by:

$$\tilde{C}(\boldsymbol{q},\omega) = 2 k_B T \frac{\Im\{\chi_{zz}(\boldsymbol{q},\omega)\}}{\omega}$$

In the static case for a bulk liquid (average in time)

$$\tilde{C}(\boldsymbol{q}) = \frac{k_B T}{4\pi^2 \gamma}\left[q^2 + \frac{g\rho}{\gamma}\right]^{-1}$$

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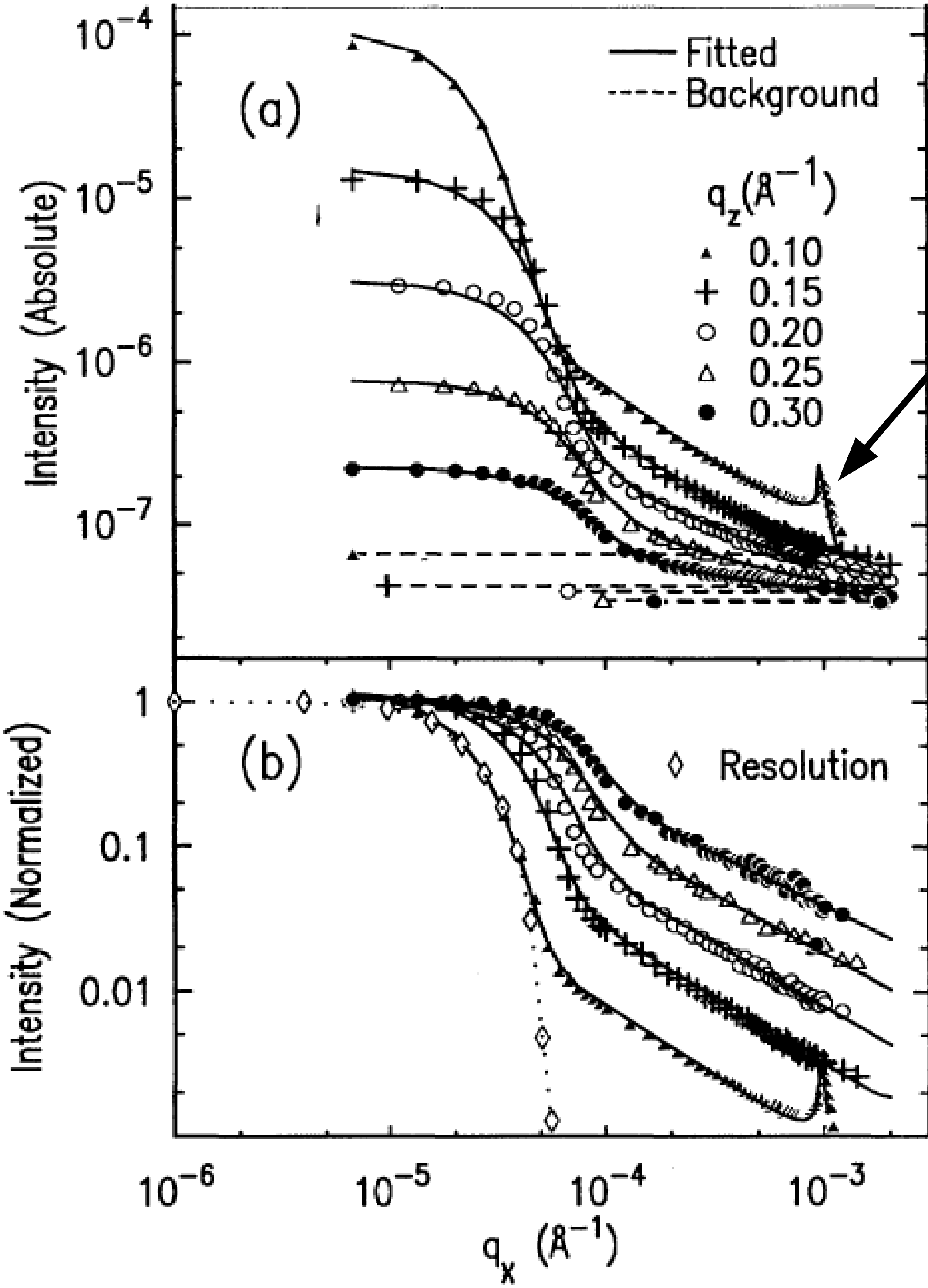
after 2-dim Fourier-backtrans-formation leads to a logarithmic auto-correlation function C(r)

$$C(\boldsymbol{r}) = -\frac{k_B T}{2\pi^2 \gamma} \left[\ln\left(\frac{g\rho}{\gamma} r \right) + 0.5772 \right]$$

With logarithmic auto-correlation function C(r) the diffuse scattering in Born approximation is for $q^2 > g\rho/\gamma$ in good approximation given by

$$I^{BA}_{diff,\,liquid}(\boldsymbol{q}) \sim q_x^{\frac{k_B T}{2\pi\gamma} q_z^2 - 1}$$

q_z -dependent power low: slope contains the surface tension



Yoneda peak

Picture taken from Sanyal et al. Phys.Rev.Lett 66, 628 (1991)

X-ray diffuse scattering at a liquid ethanol surface

From the data extracted parameters:
Roughness = 0.69nm
surface tension = 0.022N/m
(exactly the known value)

Summary

- Rough surfaces and interfaces can be described via their power spectral density (PSD) or their auto-correlation function.
- The PSD is measure of the number of modes in a wave vector interval.
- Rough interfaces will cause diffuse x-ray scattering.
- Diffuse x-ray scattering can be calculated in Born approximation and in DWBA (better). The formular contains the PSD of the interface.
- The PSD of liquids contain macroscopic material parameters such as temperature, surface tension and density.
  These parameters show up in the diffuse scattering.