New applications of Landau’s a fluctuating hydrodynamics

Jan V. Sengers
Institute for Physical Science and Technology
University of Maryland, College Park, MD 20742

Phase Transitions in Hydrocarbon Fluids:
Theory and Experiments, Moscow, 2016

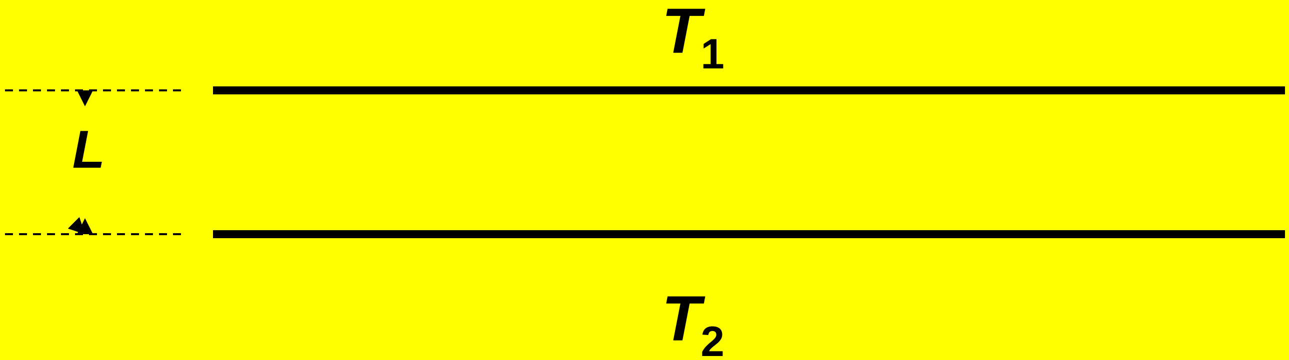
Messages

Old: critical fluctuations in fluids

New: even more dramatic fluctuations in fluids with a temperature gradient

Surprise: it was all hidden in Landau's fluctuating hydrodynamics

Thermal fluctuations in equilibrium

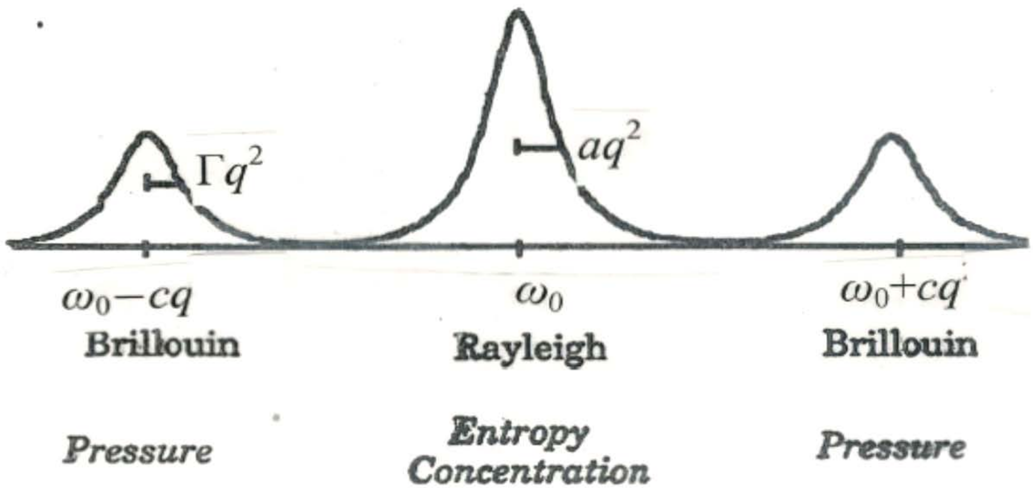


$$T_1 = T_2$$

Rayleigh scattering

Mandelstam-Brillouin scattering

Light-Scattering Spectrum in Thermal Equilibrium



at constant pressure:

$$ds = \frac{c_p}{T} dT$$

$$I(q,\omega) \propto \left(\frac{\partial\rho}{\partial s}\right)_p^2 \left\langle \delta s^*(q,\omega)\,\delta s(q,\omega)\right\rangle + \left(\frac{\partial\rho}{\partial p}\right)_s^2 \left\langle \delta p^*(q,\omega)\,\delta p(q,\omega)\right\rangle$$

Rayleigh Line + **Brillouin Lines**

Thermal Diffusion — *Sound Propagation*

Landau's fluctuating hydrodynamics

Example: stochastic temperature evolution equation
(at constant pressure)

$$\rho c_p \left[\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right] = -\nabla \cdot \mathbf{Q}$$

$$\mathbf{Q} = -\lambda \nabla T + \delta \mathbf{Q}$$

Linear phenomenological laws are valid only "on average":

$$\langle \delta \mathbf{Q} \rangle = 0$$

"Fluctuating" heat equation

$$\rho c_p \left[\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right] = \lambda \nabla^2 T - \nabla \cdot \delta \mathbf{Q}$$

Fluctuations in equilibrium

$$\rho c_p \left[\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right] = \lambda \nabla^2 T - \nabla \cdot \delta \mathbf{Q}$$

$$T = T_0 + \delta T(\mathbf{r}, t), \qquad \mathbf{v} = 0 + \delta \mathbf{v}(\mathbf{r}, t),$$

$$\boxed{\rho c_p \frac{\partial \delta T}{\partial t} = \lambda \nabla^2 \delta T - \nabla \cdot \delta \mathbf{Q}}$$

Fluctuation-dissipation theorem:

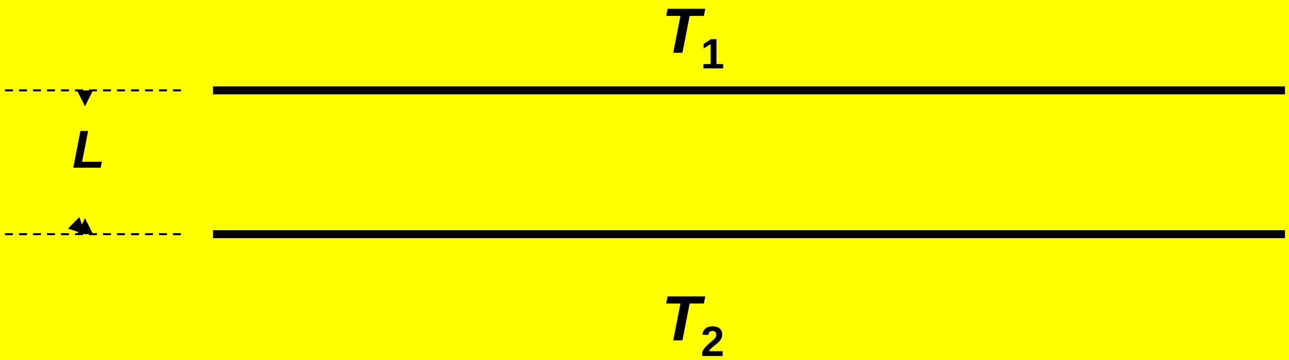
$$\left\langle \delta Q_i^*(\mathbf{r}, t) \cdot \delta Q_j(\mathbf{r}', t') \right\rangle = 2 k_\mathrm{B} \lambda T_0^2 \; \delta_{ij} \, \delta(\mathbf{r} - \mathbf{r}') \, \delta(t - t')$$

Equilibrium solution

$$\left\langle \delta T^*(q,t)\,\delta T(q,0)\right\rangle = \frac{k_\mathrm{B} T_0^2}{\rho c_p}\exp\left(-aq^2 t\right)$$

Thermal diffusivity $a = \dfrac{\lambda}{\rho c_p}$

Thermal fluctuations in a temperature gradient: Heated from above



$T_1 > T_2$

Local equilibrium?

Fluid in temperature gradient

$$\rho c_p \left[\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right] = \lambda \nabla^2 T - \nabla \cdot \delta \mathbf{Q}$$

$$T = T_0 + \delta T(\mathbf{r}, t), \qquad \mathbf{v} = 0 + \delta \mathbf{v}(\mathbf{r}, t),$$

Fluctuating heat equation:

$$\rho c_p \left[\frac{\partial \delta T}{\partial t} + \delta \mathbf{v} \cdot \nabla T_0 \right] = \lambda \nabla^2 \delta T - \nabla \cdot \delta \mathbf{Q}$$

Fluctuating Navier-Stokes equation at constant pressure:

$$\frac{\partial \delta \mathbf{v}}{\partial t} = \nu \nabla^2 \delta \mathbf{v} + \frac{1}{\rho} \nabla \cdot \delta \mathbf{S}$$

Coupling between heat mode and viscous mode through □T_0

Assumption: local equilibrium for noise correlations

$$\left\langle \delta Q_i^*(\mathbf{r},t)\cdot\delta Q_j(\mathbf{r}',t')\right\rangle = 2k_\mathrm{B}\lambda T_0^2\ \delta_{ij}\,\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t')$$

$$\left\langle \delta S_{ij}^*\left(\mathbf{r},t\right)\cdot\delta S_{kl}\left(\mathbf{r}',t'\right)\right\rangle = 2k_\mathrm{B}T_0\rho\nu\left(\delta_{ij}\delta_{kl}+\delta_{il}\delta_{jk}\right)\delta\left(\mathbf{r}-\mathbf{r}'\right)\delta\left(t-t'\right)$$

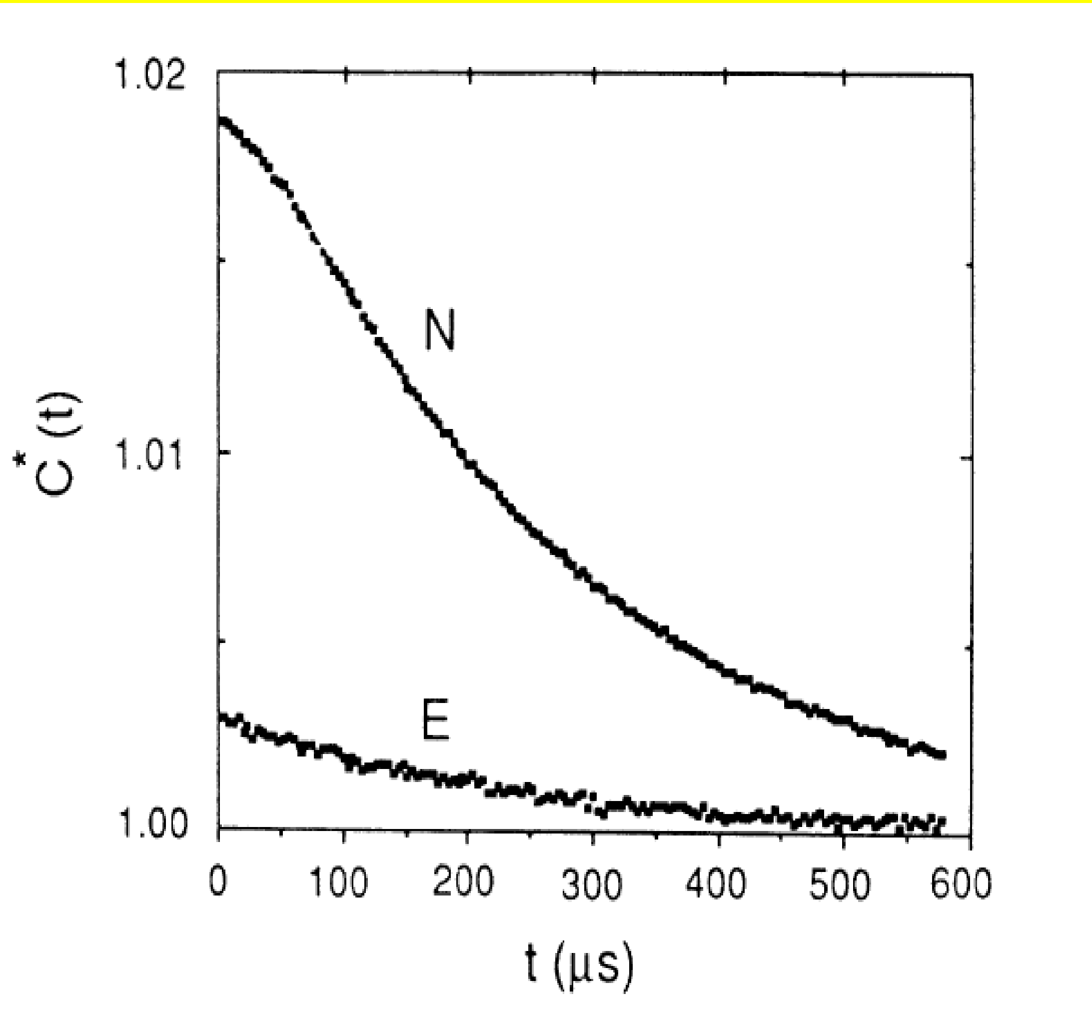
Fluids in a temperature gradient

$$C(t) = C_0\left[\left(1 + A_T\right)\exp\left(-aq^2 t\right) - A_\nu \exp\left(-\nu q^2 t\right)\right]$$

$$A_T = \frac{c_p}{T_0(\nu^2 - a^2)}\frac{\nu}{a}\frac{(\nabla T_0)^2}{q^4} \qquad A_\nu = \frac{c_p}{T_0(\nu^2 - a^2)}\frac{(\nabla T_0)^2}{q^4}$$

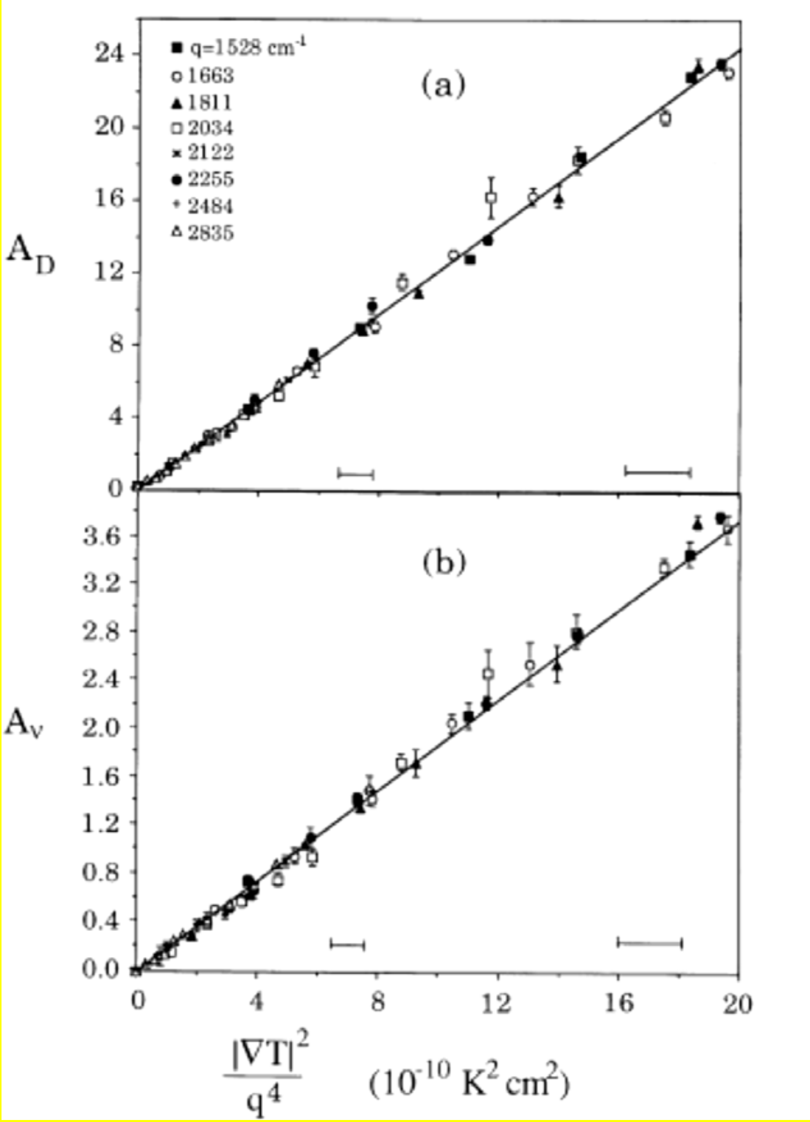
T.R. Kirkpatrick, J.R. Dorfman and E.G.D. Cohen, Phys. Rev. A 26, 995 (1982),
D. Ronis and I. Procaccia, Phys. Rev. A 26, 1812 (1982),
B.M. Law and J.V. Sengers, J. Stat. Phys. 57, 531 (1989).

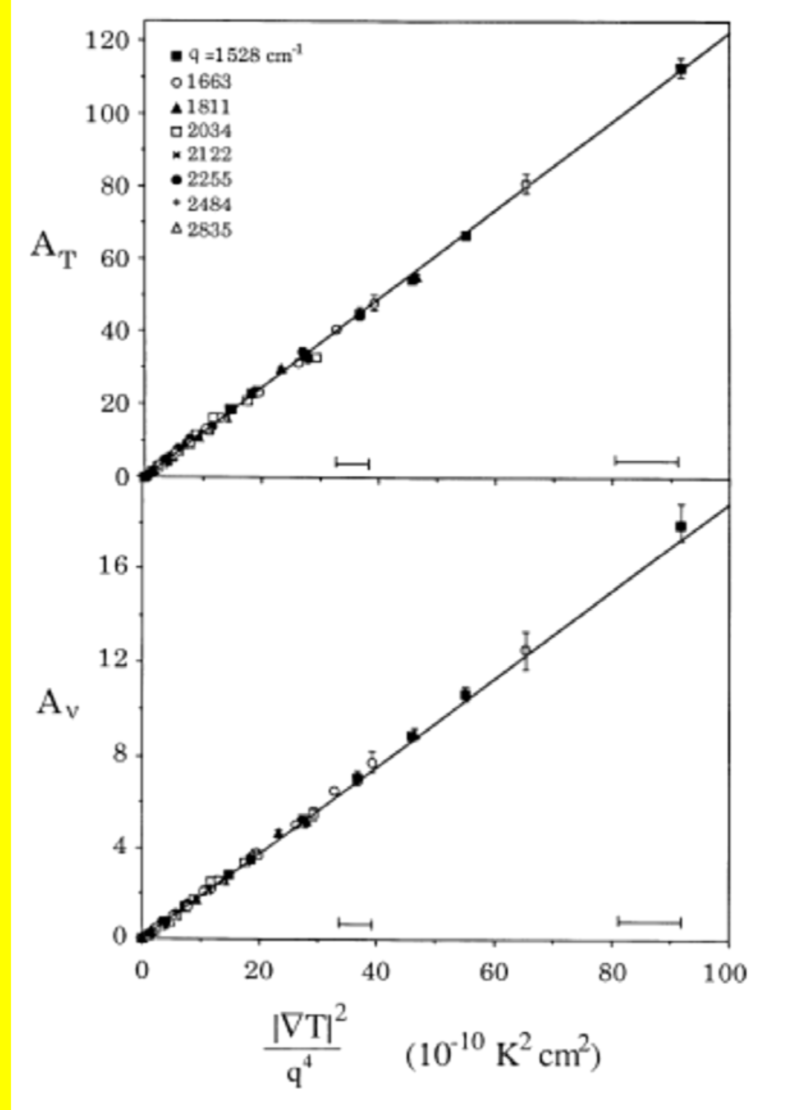
$$C(t) = C_0\left[(1+A_T)\exp\left(-aq^2t\right) - A_\nu \exp\left(-\nu q^2 t\right)\right]$$



Toluene
q=2255 cm^{-1}, □*T*=220 K/cm

Law, Segrè, Gammon, Sengers, Phys. Rev. A **41**, 816 (1990)





$$A_T = \frac{c_p}{T(\nu^2 - a^2)} \frac{\nu}{a} \frac{(\nabla T_0)^2}{q^4}$$

$$A_\nu = \frac{c_p}{T(\nu^2 - a^2)} \frac{(\nabla T_0)^2}{q^4}$$

Segrè, Gammon, Sengers, Law, Phys. Rev. A **45**, 714 (1992)

Fluid mixtures in a concentration gradient

$$\left(Le = \frac{a}{D} \gg 1\right)$$

$$\frac{\partial \delta c}{\partial t} + \delta \mathbf{v} \cdot \nabla c_0 = D \nabla^2 \delta c - \frac{1}{\rho} \nabla \cdot \delta \mathbf{J}$$

$$\frac{\partial \delta \mathbf{v}}{\partial t} = \nu \nabla^2 \delta \mathbf{v} + \frac{1}{\rho} \nabla \cdot \delta \mathbf{S}$$

$\delta \mathbf{J}$ is fluctuating mass-diffusion flux

$$\left\langle \delta J_i^*(\mathbf{r},t) \cdot \delta J_j(\mathbf{r}',t') \right\rangle = 2 k_\mathrm{B} T_0 \rho D \left(\frac{\partial c}{\partial \mu} \right)_{T,P} \delta_{ij}\, \delta(\mathbf{r} - \mathbf{r}')\, \delta(t - t')$$

Coupling between concentration mode and viscous mode through ∇c_0

$$\left\langle \delta c^{*}(q,t)\cdot\delta c(q,0)\right\rangle = C_0\left(1 + A_c\right)\exp\left(-Dq^2 t\right)$$

with

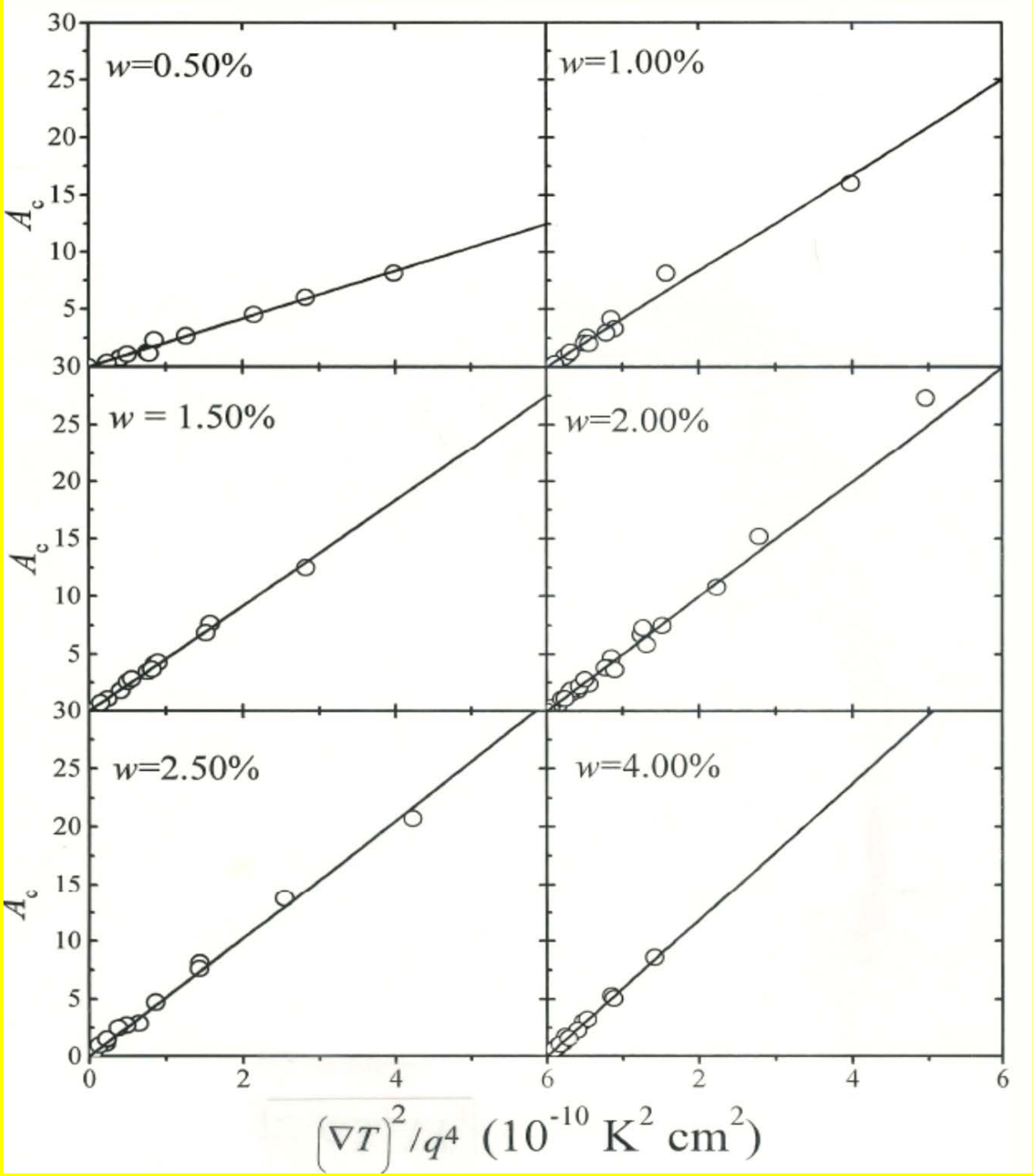
$$A_c = \left(\frac{\partial \mu}{\partial c}\right)_{p,T}\frac{1}{\nu D}\frac{\left(\nabla c_0\right)^2}{q^4}$$

$$\nabla c_0 = -c_0\left(1 - c_0\right) S_T \nabla T_0$$

S_T is Soret coefficient

Li, Zhang, Sengers, Gammon,
Ortiz de Zárate,
J. Chem. Phys. **112**, 9139 (2000)

toluene+polystyrene



CRITICAL FLUCTUATIONS:

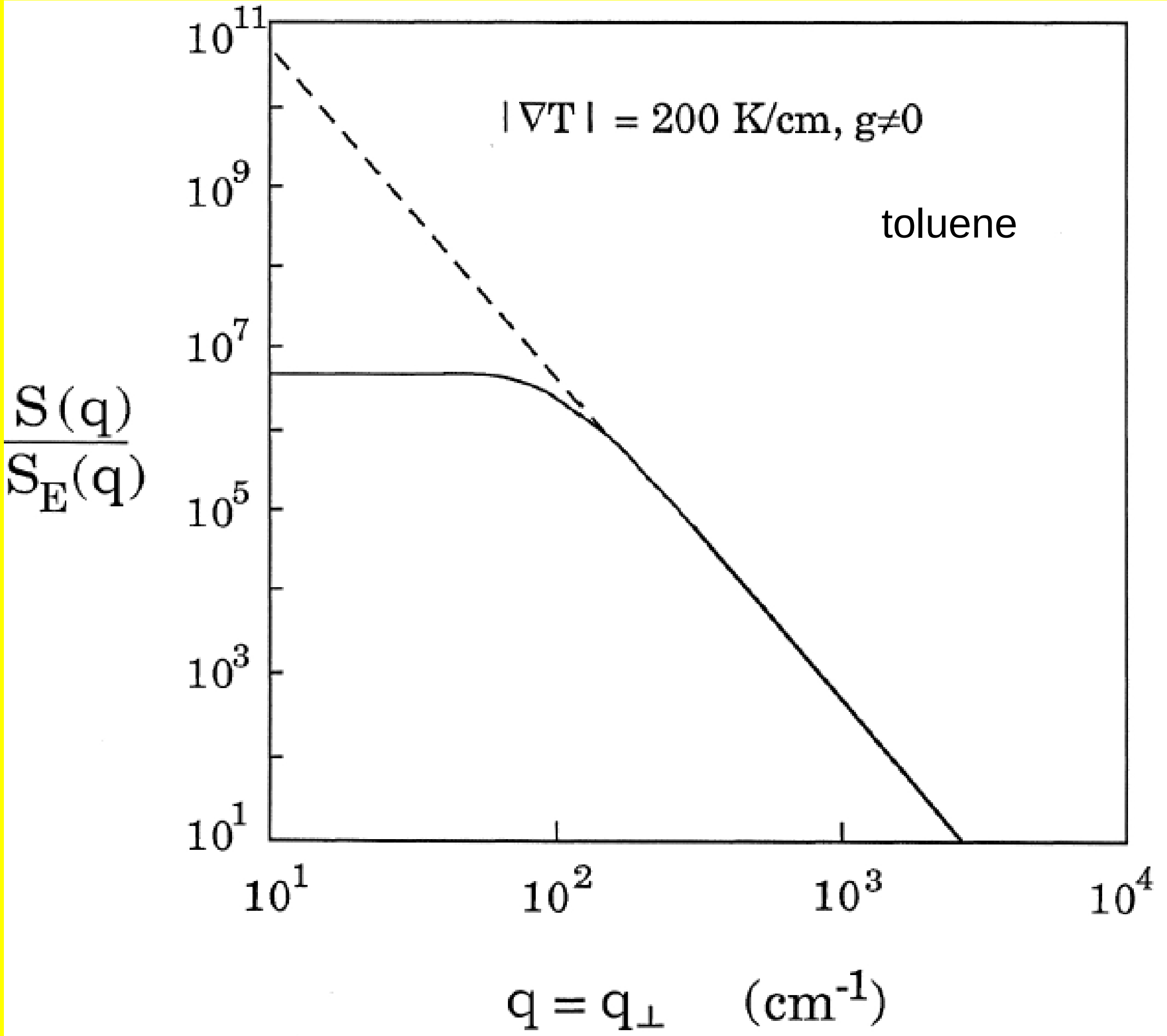
$$C_{\mathrm{cr}}(q) \propto \frac{1}{q^2} \qquad G_{\mathrm{cr}}(r) \propto \frac{1}{r}$$

NE FLUCTUATIONS

$$C_{\mathrm{NE}}(q) \propto \frac{1}{q^4} \qquad G_{\mathrm{NE}}(r) \propto O(r)$$

NE fluctuations are GIANT fluctuations:

Gravity effects
Finite-size effects



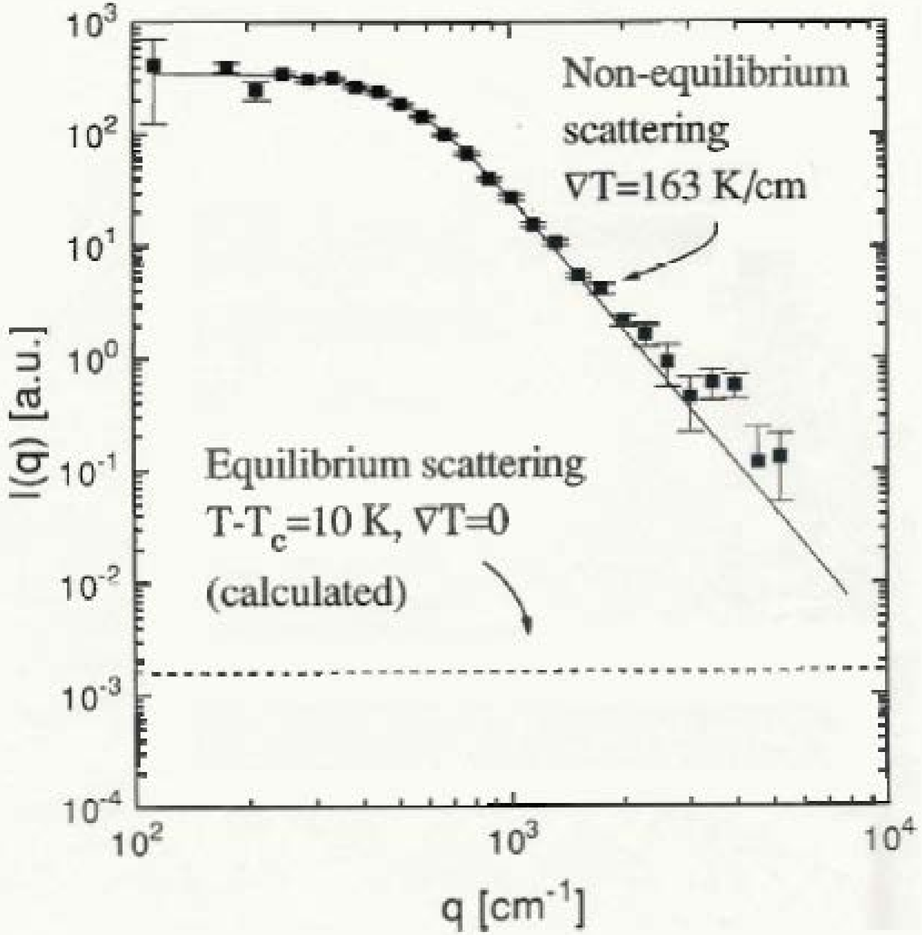
$$q_{RO}^4 = \frac{\alpha}{\nu\lambda}\left|\mathbf{g}\cdot\nabla T\right|$$

α : thermal expansion

$$q_{RO}^4 = \frac{\beta}{\nu D}\left|\mathbf{g}\cdot\nabla c\right|$$

β : solutal expansion

P.N. Segrè, R. Schmitz, J.V. Sengers, Physica A **195**, 31 (1993)



A. Vailati and M. Giglio, Phys. Rev. Lett. 77, 1484 (1996)

PRL 106, 244502 (2011) PHYSICAL REVI

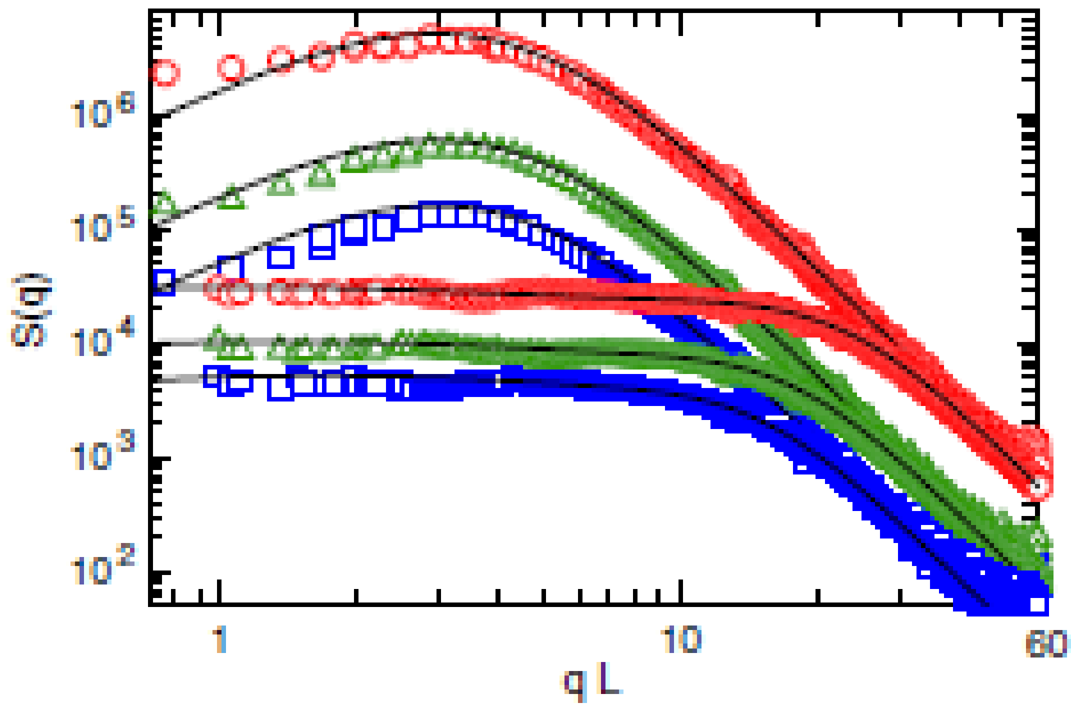


FIG. 4 (color online). Log-log plots of experimental results for $S(q)$ vs qL, with applied gradients of 17.9 (squares), 34.5 (triangles), and 101 (circles) K/cm, in microgravity (upper curves) and on Earth. The lines are the theoretical predictions.

CS_2

C.J. Takacs, A. Vailati, R. Cerbino, S. Mazzoni, M. Giglio, D.S. Cannell
Phys. Rev. Lett. **106**, 244502 (2011)

Practical Applications I

Optical techniques for measuring fluid properties:

Light scattering or imaging

Equilibrium: *a* and *D* from decay rates

Non-equilibrium: ν, $Pr = \nu/a$, C_p, S_T, α, β

Casimir pressures
(fluctuation-induced pressures)

H.B.G. Casimir, Proc. Kon. Ned. Akad. Wet. **B 51**, 793 (1948)

$$p_{\mathrm{EM}} = -\frac{\pi^2 \hbar c}{240 L^4}$$

M.E. Fisher and P.-G. de Gennes, C.R. Acad. Sci. Paris B **287**, 207 (1978)

$$p_{\mathrm{c}} = \frac{k_{\mathrm{B}} T}{L^3} \Theta\left(\frac{L}{\xi}\right)$$

What about nonequilibrium Casimir pressures?

Non-equilibrium Casimir pressure

$$\delta p = p(\rho + \delta\rho, e + \delta e) - p(\rho, e)$$

$$\delta\rho = \left(\frac{\partial\rho}{\partial T}\right)_p \delta T \qquad\qquad \delta e = \left(\frac{\partial e}{\partial T}\right)_p \delta T$$

$$\langle \delta p \rangle \equiv p_{\mathrm{NE}} = \frac{\rho c_p(\gamma - 1)}{2T_0}\left[1 - \frac{1}{\alpha c_p}\left(\frac{\partial c_p}{\partial T}\right)_p + \frac{1}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_p\right]\left\langle (\delta T)^2 \right\rangle_{\mathrm{NE}}$$

$$\left\langle (\delta T)^2 \right\rangle_{\mathrm{NE}} = \frac{k_{\mathrm{B}} T}{48\pi\rho a(\nu + a)} L(\nabla T_0)^2$$

T.R. Kirkpatrick, J.M. Ortiz de Zárate, J.V. Sengers,
Phys. Rev. E **89**, 022145 (2014)
Phys. Rev. E **93**, 012148 (2016)

Magnitudes of NE Casimir pressures ($p=p_{eq}+p_{NE}$)

TABLE I: **Estimated Casimir pressures**

	$L = 10^{-6}$ m	$L = 10^{-5}$ m	$L = 10^{-4}$ m	$L = 10^{-3}$ m
p_{EM}	-1×10^{-3} Pa	-1×10^{-7} Pa	-1×10^{-11} Pa	-1×10^{-15} Pa
p_c	$+2\times10^{-2}$ Pa	$+2\times10^{-5}$ Pa	$+2\times10^{-8}$ Pa	$+2\times10^{-11}$ Pa
p_{NE}[a]	+1 Pa	$+1\times10^{-1}$ Pa	$+1\times10^{-2}$ Pa	$+1\times10^{-3}$ Pa
p_{NE}[b]	+17 Pa	+2 Pa	$+2\times10^{-1}$ Pa	$+2\times10^{-2}$ Pa
p_{NE}[c]	−1 Pa	-1×10^{-1} Pa	-1×10^{-2} Pa	-1×10^{-3} Pa

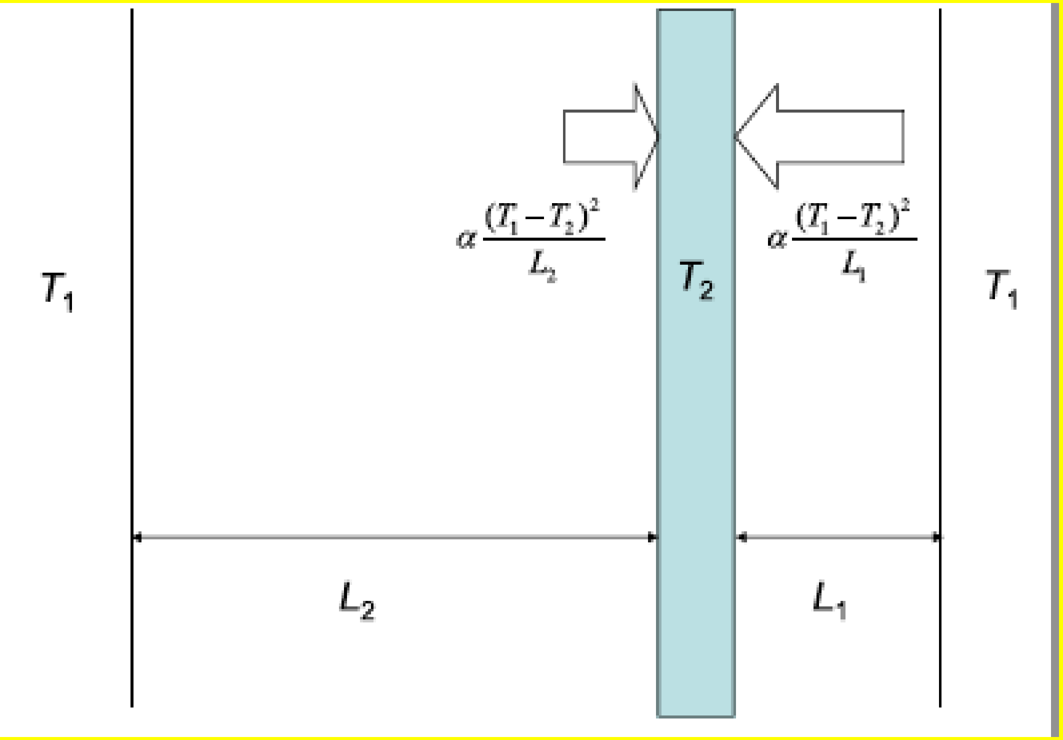
T.R. Kirkpatrick, J.M. Ortiz de Zárate, J.V. Sengers, Phys. Rev. E **93**, 012148 (2016)

Phys. Rev. E **93**, 032117 (2016)

[a] water (ΔT = 25 K)

[b] 1-methylnaphtalene + n-heptane (ΔT = 25 K)

[c] aniline + methanol (ΔT = 25 K)



$$p_{\mathrm{NE}} \propto L\left(\frac{\nabla T_0}{T_0}\right)^2 \propto \frac{1}{L}\left(\frac{\Delta T}{T_0}\right)^2$$

Kirkpatrick, Ortiz de Zárate, Sengers, Phys. Rev. Lett. **115**, 035901 (2015)

CONCLUSIONS

- **Fluctuating hydrodynamics has been confirmed experimentally, also for non-equilibrium states**
- **Thermal fluctuations exhibit always a strong NE enhancement; they never satisfy local equilibrium**
- **NE fluctuations are always long ranged covering the entire system**
- **NE fluctuations are affected by the finite size of system**
- **NE fluctuations are affected by gravity**
- **NE fluctuations enable new techniques for measuring properties**
- **NE fluctuations induce large NE Casimir forces (**NE micromechanics**)**

ACKNOWLEDGEMENTS

Current principle collaborators:

T.R. Kirkpatrick (College Park)
J.M. Ortiz de Zárate (Madrid)

Past collaborators:

B.M. Law (1988-1992)
R.W. Gammon (1988-2000)
P.N. Segrè (1992-1995)
W.B. Li (1994-1998)
K.J. Zhang (1996-2000)