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# Non-local fluctuation phenomena in liquids[*]

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**Abstract.** Fluids in non-equilibrium steady states exhibit long-range fluctuations which extend over the entire system. They can be described by non-equilibrium thermodynamics and fluctuating hydrodynamics that assume local equilibrium for the thermophysical properties as a function of space and time. The experimental evidence for the consistency between this assumption of local equilibrium in the equations and the non-local fluctuation phenomena observed is reviewed.

## 1 Introduction

Non-equilibrium thermodynamics (NET) is a powerful tool to describe and understand the physics of systems that are not in global equilibrium, but in which the thermodynamic properties depend on space and on time [1]. NET is essential for dealing with a wide range of applications and systems such as fluid physics, soft matter physics, astrophysics, statistical physics, biology, metallurgy and engineering [2]. NET is much more general than equilibrium thermodynamics (ET) which describes systems in equilibrium conditions; conditions that do not apply to many relevant "real" cases [3].

The history of NET has recently been reviewed by Bedeaux *et al.* [4]. The beginning of the formal development of NET is commonly attributed to the work of Onsager in 1931 in which he put the earlier research on the subject into a systematic framework [5]. A survey of the various books and monographs on NET can also be found in [4].

The well-established equations of ET apply to systems that are in global equilibrium. A fundamental assumption in NET is that the equilibrium thermodynamic relations remain valid at the local level, *i.e.*, at any given volume element at any time. The purpose of the present paper is to discuss the consistency between the assumption of local equilibrium of the NET equations and various non-local phenomena appearing in non-equilibrium. A variety of non-equilibrium steady states have been considered in the literature [6]. In this paper we shall consider fluctuations in a quiescent fluid layer between two horizontal boundaries in the presence of either a temperature gradient or a concentration gradient. A review of fluctuations in fluid layers in the presence of a velocity gradient can be found elsewhere [7].

This paper is organized as follows. In sect. 2 we introduce the concept of fluctuating hydrodynamics for dealing with thermal fluctuation in fluids in global equilibrium. In sect. 3 we consider the extension to thermal fluctuations in non-equilibrium states. These fluctuations are non-local and extend over the entire system [8]. As a consequence, the non-equilibrium fluctuations are affected by gravity, considered in sect. 4, and by the finite size of the fluid layer, considered in sect. 5. Most recently, it has been predicted that the long-range non-equilibrium fluctuations will induce non-equilibrium Casimir-like forces [9–13], reviewed in sect. 6. We summarize our conclusions in sect. 7.

## 2 Fluctuations in equilibrium

### 2.1 Fluctuating hydrodynamics

A complete description of a thermodynamic system must include fluctuations. Fluctuations in fluids in thermodynamic equilibrium can be described by the method of fluctuating hydrodynamics originally developed by Landau and Lifshitz [14,15] with subsequent contributions from Fox and Uhlenbeck [16,17]. The idea is that the fluctuations of the thermodynamic properties satisfy the NET equations provided that the thermodynamic fluxes are

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supplemented with stochastic contributions accounting for the noise resulting from molecular motions [18].

In a one-component fluid one encounters a heat mode causing temperature fluctuations, two sound modes associated with pressure fluctuations and a viscous mode causing velocity fluctuations [6]. In normal fluids, sound modes are fast propagating modes while the heat mode is a slow diffusive one. Hence, to deal with the slow diffusive temperature fluctuations we may neglect any pressure fluctuations. In linear approximation the resulting hydrodynamic equation for the temperature $T$ reads

$$\rho c_p \left[\frac{\partial T}{\partial t} + \mathbf{v}\cdot\nabla T\right] = -\nabla\cdot\mathbf{Q}, \tag{1}$$

where $\rho$ is the mass density, $c_p$ the specific heat capacity at constant pressure, $\mathbf{v}$ the fluid velocity, and $\mathbf{Q}$ the heat flux. In fluctuating hydrodynamics, the heat flux $\mathbf{Q}$ is related to the temperature gradient $\nabla T$ as

$$\mathbf{Q} = -\lambda\nabla T + \delta\mathbf{Q}, \tag{2}$$

where $\lambda$ is the thermal conductivity according to Fourier's law and $\delta\mathbf{Q}$ a fluctuating heat flux which is zero on average: $\langle\delta\mathbf{Q}\rangle = 0$ [6]. Equation (2) thus becomes

$$\rho c_p \left[\frac{\partial T}{\partial t} + \mathbf{v}\cdot\nabla T\right] = \lambda\nabla^2 T - \nabla\cdot\delta\mathbf{Q}. \tag{3}$$

We write the temperature $T$ and the fluid velocity $\mathbf{v}$ as sums of an average temperature $T_0$ and an average velocity $\mathbf{v}_0$ and the fluctuating parts $\delta T(\mathbf{r},t)$ and $\delta\mathbf{v}(\mathbf{r},t)$ depending on position $\mathbf{r}$ and time $t$: $T = T_0 + \delta T(\mathbf{r},t)$ and $\mathbf{v} = \mathbf{v}_0 + \delta\mathbf{v}(\mathbf{r},t)$. In equilibrium $\nabla T_0 = 0$ and $\mathbf{v}_0 = 0$, and the equation for the temperature fluctuation becomes

$$\rho c_p \frac{\partial \delta T}{\partial t} = \lambda\nabla^2 \delta T - \nabla\cdot\delta\mathbf{Q}. \tag{4}$$

In a fluid mixture there is an additional concentration mode. An important parameter in (binary) fluid mixtures is the Lewis number $Le = a/D$, where $a = \lambda/\rho c_p$ is the thermal diffusivity and $D$ the mass diffusion coefficient. In many liquid mixtures the Lewis number is substantially larger than unity. For $Le \gg 1$ the concentration mode and the heat mode decouple [19] and for large $Le$ the relevant equation for the concentration $c$ becomes [18]

$$\frac{\partial c}{\partial t} + \mathbf{v}\cdot\nabla c = D\nabla^2 c - \frac{1}{\rho}\nabla\cdot\delta\mathbf{J}, \tag{5}$$

where $c$ is the mass fraction of one of the two components and $\mathbf{J}$ a fluctuating mass flux [6]. Again we write the concentration $c$ as the sum of an average value and a fluctuating part: $c = c_0 + \delta c(\mathbf{r},t)$. Again in equilibrium $\nabla c_0 = 0$ and $\mathbf{v}_0 = 0$, so that

$$\frac{\partial \delta c}{\partial t} = D\nabla^2 \delta c - \frac{1}{\rho}\nabla\cdot\delta\mathbf{J}. \tag{6}$$

## 2.2 Equilibrium correlation functions

To solve eqs. (4) and (6) for the temperature and concentration fluctuations, we need the correlation functions for the fluctuating heat flux and the fluctuating mass flux, which are given by the fluctuation-dissipation theorem [6, 18, 20]:

$$\langle\delta Q_i^*(\mathbf{r}',t')\cdot\delta Q_j(\mathbf{r},t)\rangle = 2k_\mathrm{B}\lambda T_0^2\delta_{ij}\delta(\mathbf{r}'-\mathbf{r})\delta(t'-t), \tag{7}$$

$$\langle\delta J_i^*(\mathbf{r}',t')\cdot\delta J_j(\mathbf{r},t)\rangle = 2k_\mathrm{B}DT_0\rho\chi_{p,T}\delta_{ij}\delta(\mathbf{r}'-\mathbf{r})\delta(t'-t), \tag{8}$$

where $k_\mathrm{B}$ is Boltzmann's constant. In eq. (8) for the binary mixture $\chi_{p,T} = (\partial c/\partial\mu)_{p,T}$, where $\mu$ is the difference between the chemical potentials of the two components, so that $\chi_{p,T}$ can be identified with the osmotic compressibility. For fluids of molecules with short-range forces, the noise correlations are short ranged so that they are represented by delta functions at hydrodynamic length and time scales. Fluctuations are commonly studied experimentally by various optical techniques as a function of the wave number $q$ of the fluctuations [6]. Using eq. (7) and taking a spatial Fourier transform, one can readily solve eq. (4) for the temperature correlation function:

$$\langle\delta T^*(q',t)\delta T(q,0)\rangle = \frac{k_\mathrm{B}T_0^2}{\rho c_p}\exp\left(-aq^2t\right)(2\pi)^3\delta(q'-q). \tag{9}$$

The temperature fluctuations are related to the fluctuations $\delta s$ of the entropy density as $\delta s = (\rho c_p/T)\delta T$, so that

$$\langle\delta s^*(q',t)\delta s(q,0)\rangle = k_\mathrm{B}\rho c_p T_0\exp\left(-aq^2t\right)(2\pi)^3\delta(q'-q). \tag{10}$$

As a reminder, we are only considering here the fluctuations resulting from the slow heat mode which can be probed by Rayleigh scattering. Similarly, one obtains from eqs. (6) and (8) for the concentration fluctuations in a binary mixture in the large $Le$ approximation [18]:

$$\langle\delta c^*(q',t)\delta c(q,0)\rangle = \frac{k_\mathrm{B}T_0}{\rho}\chi_{p,T}\exp\left(-Dq^2t\right)(2\pi)^3\delta(q'-q). \tag{11}$$

We see that the equilibrium fluctuations are short ranged. Hence, the intensity of equal-time fluctuations, obtained by taking $t = 0$ in eqs. (10) and (11), is independent of the wave number $q$. The time-correlation functions of fluctuations decay exponentially with a relaxation time $\tau(q) = 1/aq^2$ for the temperature fluctuations and $\tau(q) = 1/Dq^2$ for the concentration fluctuations. Traditionally, these results for the equilibrium fluctuations are obtained by solving deterministic hydrodynamic equations with arbitrary initial conditions [21–24]. We prefer to use the stochastic fluctuating hydrodynamics equations, since this method can be extended to non-equilibrium states as further discussed in sect. 3.

## 2.3 Critical fluctuations

At a vapour-liquid critical point in a one-component fluid the isobaric heat capacity $c_p$ diverges. Thus the intensity of the fluctuations of the entropy density becomes very large, while the intensity of the fluctuations of the temperature becomes vanishingly small. Similarly, the osmotic compressibility $\chi_{p,T}$ diverges at a critical consolute point of a binary fluid mixture. Near a critical point the fluctuations become long ranged with a correlation length $\xi$ that diverges at the critical point. As a consequence, the correlation function, eq. (10), of the entropy density fluctuations near a vapour-liquid critical point and of the correlation function, eq. (11), for the concentration fluctuations near a critical consolute point, need to be multiplied by a scaling function $g(q\xi)$. In the so-called Ornstein-Zernike approximation [25]

$$g(q\xi) \simeq \frac{1}{1+q^2\xi^2}\,. \tag{12}$$

Thus in states near a critical point, the intensity of the fluctuations diverges at small wave numbers proportional to $q^{-2}$, leading to finite-size effects [26,27] and Casimir pressures in confined fluid layers [28–30] near a critical point.

While the critical fluctuations generally still decay exponentially, a hydrodynamic coupling between the fluctuations of the order parameter and the viscous fluctuations causes the transport coefficient determining the relaxation time $\tau$ of the critical fluctuations to become dependent on the wave number. Asymptotically close to the critical point one finds

$$\tau(q) = \frac{6\pi\eta\xi}{k_\mathrm{B}T}\frac{1}{q^2\Omega(q\xi)}\,, \tag{13}$$

where $\eta$ is the shear viscosity and $\Omega(q\xi)$ a dynamical scaling function [31–33]. At the critical point both $\xi$ and $\eta$, and, hence, the relaxation time $\tau$ diverge. This phenomenon is known as critical slowing-down of the fluctuations. Theory also predicts deviations from exponential decay of the fluctuations extremely close the critical point [34]. Such deviations have been observed experimentally [35], but they turn out to be very small and negligible in practice.

## 3 Fluctuations in non-equilibrium steady states

### 3.1 Fluctuations in a temperature gradient

We consider a fluid layer bounded between two horizontal plates located at $z = \pm L/2$ in the presence of a temperature gradient $\nabla T_0 \neq 0$. Thus the temperature to be substituted into eq. (3) now is a function of $z$: $T = \overline{T_0} + z\nabla T_0 + \delta T(\mathbf{r},t)$. When the temperature gradient is in the $z$-direction opposite to the direction of gravity, convection can be avoided so that the fluid velocity continues to be $\mathbf{v} = \delta\mathbf{v}(\mathbf{r},t)$ with $\mathbf{v}_0 = 0$. It thus follows from eq. (3) that the equation for the temperature, at linear order in the fluctuations, now becomes

$$\rho c_p\left[\frac{\partial\delta T}{\partial t} + \delta\mathbf{v}\cdot\nabla T_0\right] = \lambda\nabla^2\delta T - \nabla\cdot\delta\mathbf{Q}. \tag{14}$$

In contrast to equilibrium, the temperature gradient causes a coupling between the temperature fluctuations and the velocity fluctuations, the latter satisfying a linearized fluctuating Navier-Stokes equation of the form [6, 36]

$$\frac{\partial\delta\mathbf{v}}{\partial t} = \nu\nabla^2\delta\mathbf{v} + \frac{1}{\rho}\nabla\cdot\delta\Pi, \tag{15}$$

In eq. (15) $\nu = \mu/\rho$ is the kinematic viscosity and $\delta\Pi$ a fluctuating stress tensor whose correlation function in accordance with the fluctuation-dissipation theorem is given by [15,18,20]

$$\begin{aligned}&\left\langle\delta\Pi^*_{ij}(\mathbf{r}',t')\cdot\delta\Pi_{kl}(\mathbf{r},t)\right\rangle = \\ &2k_\mathrm{B}T_0\eta(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\delta(\mathbf{r}'-\mathbf{r})\delta(t'-t).\end{aligned} \tag{16}$$

Now in accordance with a basic postulate of local equilibrium in NET [1,3,37], we assume that all thermophysical properties, like the isobaric specific heat capacity, the thermal conductivity in eqs. (7) and (14), and the viscosities in eqs. (15) and (16), are taken as their equilibrium values corresponding to the average local temperature $T_0$ and average local density $\rho = \rho_0$. Since the average local temperature $T_0$ depends on $z$, it follows that also all thermophysical properties in principle will depend on $z$. While such a dependence of the thermophysical properties on the location in the fluid layer can be taken into account in solving the fluctuating hydrodynamics equations [38,39], the effect appears to be small [40,41]. Hence, in practice we use a stronger local equilibrium assumption by identifying all thermophysical properties with their local equilibrium values corresponding to the average temperature $\overline{T_0} = T_0(0)$ and the average density $\overline{\rho_0} = \rho_0(0)$.

Solving the two coupled fluctuating hydrodynamics equations, eqs. (14) and (15), one obtains for the special case that the wave vector $\mathbf{q}$ of the fluctuations is perpendicular to the temperature gradient

$$\begin{aligned}\langle\delta T^*(q',t)\delta T(q,0)\rangle &= \frac{k_\mathrm{B}\overline{T_0}^2}{\rho c_p}\left[(1+A_T)\exp\left(-aq^2t\right)\right.\\ &\left.- A_\upsilon\exp\left(-\nu q^2 t\right)\right](2\pi)^3\delta(q'-q),\end{aligned} \tag{17}$$

with

$$\begin{aligned}A_T &= \frac{c_p}{\overline{T_0}(\nu^2-a^2)}\frac{\nu}{a}\frac{(\nabla T_0)^2}{q^4}\,,\\ A_\nu &= \frac{c_p}{\overline{T_0}(\nu^2-a^2)}\frac{(\nabla T_0)^2}{q^4}\,.\end{aligned} \tag{18}$$

It follows that the total intensity of the non-equilibrium fluctuations is given by

$$\begin{aligned}&\langle\delta T^*(q',0)\,\delta T(q,0)\rangle = \\ &\frac{k_\mathrm{B}\overline{T_0}^2}{\rho c_p}\left[1+\frac{c_p}{\overline{T_0}(\nu+a)a}\frac{(\nabla T_0)^2}{q^4}\right](2\pi)^3\delta(q'-q).\end{aligned} \tag{19}$$

These expressions were first obtained by Kirkpatrick *et al.* from basic non-equilibrium statistical mechanics [42]. Shortly thereafter, Ronis and Procaccia [43] pointed out that this result can also be obtained by extending fluctuating hydrodynamics to non-equilibrium, a method subsequently implemented by Law and Sengers [44]. The existence of these non-equilibrium temperature and viscosity fluctuations, proportional to $(\nabla T_0)^2$ and proportional to $q^{-4}$, with amplitudes $A_T$ and $A_\nu$ exactly as given by eq. (18) without any adjustable parameters, was first demonstrated experimentally by Sengers and coworkers [40,45].

This result has a number of important implications:

1) The presence of a temperature gradient induces a coupling between heat mode and viscous mode that is absent in equilibrium except when close to a critical point.

2) The amplitudes of the non-equilibrium temperature and viscous fluctuations differ by a factor equal to the Prandtl number $Pr = \nu/a$, which is typically of the order of 10 in liquids and liquid mixtures.

3) The intensity of the non-equilibrium fluctuations is proportional to the square of the temperature gradient. This is a rigorous result and not the result of a perturbation expansion in terms of $\nabla T_0$ [46].

4) For small wave numbers the intensity of the non-equilibrium fluctuations diverges as $q^{-4}$. First, it means that the intensities of the non-equilibrium fluctuations become much larger than those corresponding to local equilibrium. Second, the non-equilibrium fluctuations are long range, and not local but extending over the entire size of the system [47].

5) While the intensity of critical fluctuations diverges at small wave numbers $q$ as $q^{-2}$ in accordance with eq. (12), the intensity of the non-equilibrium fluctuations diverges as $q^{-4}$. Hence, the non-equilibrium fluctuations are much more dramatic than critical fluctuations. Moreover, the presence of such pronounced non-local long-ranged fluctuations will be ubiquitous whenever a gradient is present in fluids, and not restricted to the close vicinity of a critical point.

6) The agreement with theory and experiment without adjustable parameters [40,45] confirms the validity of non-equilibrium fluctuating hydrodynamics with coefficients that satisfy local equilibrium even though in reality dramatic non-local fluctuations appear.

### 3.2 Fluctuations in a concentration gradient

Next we consider binary fluid mixtures bounded between two horizontal plates located at $z = \pm L/2$ in the presence of a concentration gradient $\nabla c_0 \neq 0$. Thus the concentration to be substituted into eq. (5) now is a function of $z$: $c = \overline{c_0} + z\nabla c_0 + \delta c(\mathbf{r}, t)$. Again we assume that the system is far away from any convective instability, so that the fluid velocity is again $\mathbf{v} = \delta\mathbf{v}(\mathbf{r}, t)$ with $\mathbf{v}_0 = 0$. It thus follows from eq. (5) that the fluctuating equation for the concentration becomes

$$\frac{\partial \delta c}{\partial t} + \delta\mathbf{v} \cdot \nabla c_0 = D\nabla^2 \delta c - \frac{1}{\rho}\nabla \cdot \delta\mathbf{J}. \qquad (20)$$

We see that the concentration gradient induces a coupling between concentration fluctuations and velocity fluctuations, the latter being given again by eq. (15). Again we use the assumption that the thermophysical properties in eqs. (8), (15) and (20) are given by their local equilibrium values. Solving the two coupled fluctuating hydrodynamics equations, eqs. (15) and (20), one obtains again for the case that the wave vector $\mathbf{q}$ of the fluctuations is perpendicular to the concentration gradient

$$\langle \delta c^*(q', t)\delta c(q, 0)\rangle = \frac{k_\mathrm{B}T_0}{\rho}\chi_{p,T}\,(1 + A_c)\exp\left(-Dq^2 t\right)(2\pi)^3\delta(q' - q) \qquad (21)$$

with

$$A_c = \frac{1}{\nu D}\chi_{p,T}^{-1}\frac{(\nabla c_0)^2}{q^4}\,. \qquad (22)$$

The complete expression for the non-equilibrium concentration fluctuation in a binary fluid mixture was first derived by Law and Nieuwoudt [48], who considered non-equilibrium concentration fluctuations, non-equilibrium temperature fluctuations, and non-equilibrium velocity fluctuations which, in general, will be present in a mixture [48–50]. Equations (21) and (22) represent a simplification for $Le \gg 1$, verified experimentally by Li *et al.* [51].

A convenient experimental procedure for establishing a concentration gradient $\nabla c_0$ is applying a temperature gradient $\nabla T_0$ to the mixture, thus inducing a concentration gradient through the Soret effect:

$$\nabla c_0 = -c_0\,(1 - c_0)\,S_T \nabla T_0, \qquad (23)$$

where $S_T$ is the appropriate Soret coefficient [49–52]. Just as for one-component fluids, we consider here only steady non-equilibrium states in which convection is absent. The conditions for which both the concentration gradient and the temperature gradient are stabilizing have been specified in the literature [53–55].

Strictly speaking, eq. (21) is valid for a liquid mixture in a steady non-equilibrium state. Several investigators have also studied concentration fluctuations in the presence of transient concentration gradients in isothermal liquid mixtures induced by free diffusion. These experiments have also confirmed that the intensity of the non-equilibrium concentration fluctuations at any given time vary as $q^{-4}$ [56–58].

The implications of this result are similar to those mentioned earlier for the non-equilibrium concentration fluctuations:

1) The presence of a concentration gradient induces a coupling between mass diffusion mode and viscous mode that is absent in equilibrium except when close to a critical consolute point.

2) In general non-equilibrium concentration, temperature, and velocity fluctuations will be present in a mixture. But for $Le \gg 1$ the non-equilibrium concentration fluctuations will be dominant.

3) The intensity of the non-equilibrium fluctuations is proportional to $(\nabla c_0)^2$ and, hence, to $(\nabla T_0)^2$ when the concentration gradient is caused by the Soret effect.

4) For small wave numbers the intensity of the non-equilibrium concentration fluctuations also diverges

as $q^{-4}$. As a consequence, also the intensities of the non-equilibrium concentration fluctuations become much larger than those corresponding to local equilibrium. The non-equilibrium concentration fluctuations are long range, and not local but extending over the entire size of the system.

5) The divergence of the intensity of the non-equilibrium concentration fluctuations as $q^{-4}$ is much stronger than the divergence of critical concentration fluctuations as $q^{-2}$ near a consolute point.

6) The agreement with theory and experiment without adjustable parameters confirms again the validity of non-equilibrium fluctuating hydrodynamics for mixtures with coefficients that satisfy local equilibrium even though non-local fluctuations are present.

## 4 Gravity effects

### 4.1 Gravity effects on the intensity of non-equilibrium fluctuations

The rapid increase of the intensity of the non-equilibrium (NE) fluctuations as $q^{-4}$ cannot go on indefinitely. The first physical effects affecting NE fluctuations at very small wave numbers discussed in the literature are those resulting from gravity (buoyancy). The effect of bouyancy can be incorporated by adding in the linearized fluctuating Navier-Stokes equation, eq. (15), a coupling $-g\alpha\delta T$ with the temperature fluctuations; while for binary mixtures a second coupling $g\beta\delta c$ with concentration fluctuations must also be considered. In these expressions, $g$ is the magnitude of the gravitational force $\mathbf{g}$, $\alpha = -\rho^{-1}(\partial\rho/\partial T)_p$ the thermal expansion coefficient, and $\beta = \rho^{-1}(\partial\rho/\partial c)_{p,T}$ the solutal expansion coefficient [6,59,60].

The evaluation of gravity effects on the NE fluctuations in single-component fluids is more easily performed in the $Pr \gg 1$ limit, in which case the contribution from the viscous mode in eq. (17) can be neglected. One then finds that eq. (19) for the intensity of the non-equilibrium temperature fluctuations needs to be replaced by

$$\langle \delta T^*(q',0)\,\delta T(q,0)\rangle = \frac{k_\mathrm{B}\overline{T}_0^{\,2}}{\rho c_p}\left[1+\frac{c_p}{\overline{T}_0\nu a}\frac{(\nabla T_0)^2}{(q^4+q^4_{\mathrm{RO},T})}\right](2\pi)^3\delta(q'-q), \qquad (24)$$

where $q_{\mathrm{RO},T}$ is a "rollover" wave number such that

$$q^4_{\mathrm{RO},T} = \frac{\alpha|\mathbf{g}\cdot\nabla T_0|}{\nu a}\,. \qquad (25)$$

When $g = 0$ (so that $q^4_{\mathrm{RO},T} = 0$), eq. (24) reduces for $\nu/a \gg 1$ to eq. (19) earlier obtained in the absence of buoyancy. We further mention that, for consistency with the Boussinesq approximation, we have also neglected in eq. (24) the adiabatic temperature gradient $(\alpha\overline{T}_0/c_p)g$ as compared to the imposed temperature gradient $\nabla T_0$ [6, 60]. For later use we also note that eq. (24) is only valid for temperature gradients antiparallel to gravity (heating from above, or negative Rayleigh number). When the RHS of eq. (25) is negative there appears an unphysical divergence at finite $q$ for the intensity of NE temperature fluctuations that can only be removed by including confinement effects [61,62].

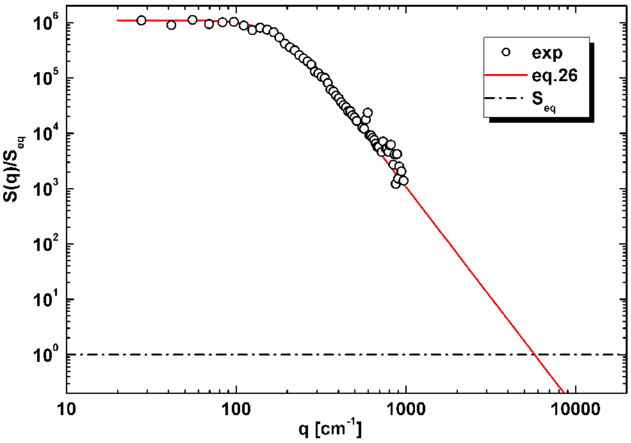

**Fig. 1.** Intensity $S(q)$ of the non-equilibrium concentration fluctuations during free diffusion in an aqueous solution of urea, relative to the intensity $S_\mathrm{eq}$ of the local equilibrium concentration fluctuations, from a reanalysis of data earlier reported in [63].

In a similar way, adopting large values for both the Prandtl and the Lewis number, one obtains for the intensity of the non-equilibrium concentration fluctuations in a binary mixture [6,60]:

$$\langle \delta c^*(q',0)\,\delta c(q,0)\rangle = \frac{k_\mathrm{B}\overline{T}_0}{\rho}\chi_{p,T}\left[1+\frac{1}{\nu D}\frac{\chi^{-1}_{p,T}(\nabla c_0)^2}{(q^4+q^4_{\mathrm{RO},c})}\right](2\pi)^3\delta(q'-q), \qquad (26)$$

with

$$q^4_{\mathrm{RO},c} = \frac{\beta|\mathbf{g}\cdot\nabla c_0|}{\nu D}\,. \qquad (27)$$

Hence, both for temperature or concentration fluctuations, if $q \gg q_\mathrm{RO}$ the intensity of the non-equilibrium fluctuations continues to vary as $q^{-4}$, but if $q \ll q_\mathrm{RO}$ the intensity will approximate a constant value, independent of $q$.

The fact that buoyancy saturates the increase of the intensity of the non-equilibrium fluctuations was originally predicted by Segrè *et al.* [59] and first demonstrated experimentally by Vailati and Giglio [52,56]. As an example we show in fig. 1 the non-equilibrium enhancement of the intensity of the NE concentration fluctuations observed during free diffusion of an aqueous solution of urea [63]. At large wave numbers the intensity $S(q)$ of the concentration fluctuations varies as $q^{-4}$, but at smaller wave numbers the enhancement saturates at a finite but very large value, $10^6$ times the intensity $S_\mathrm{eq}$ of equilibrium fluctuations at the average temperature, just as originally predicted by Segrè *et al.* [59] and earlier observed by Vailati and Giglio [52,56].

The effect of gravity on the non-equilibrium fluctuations has been dramatically illustrated by comparing

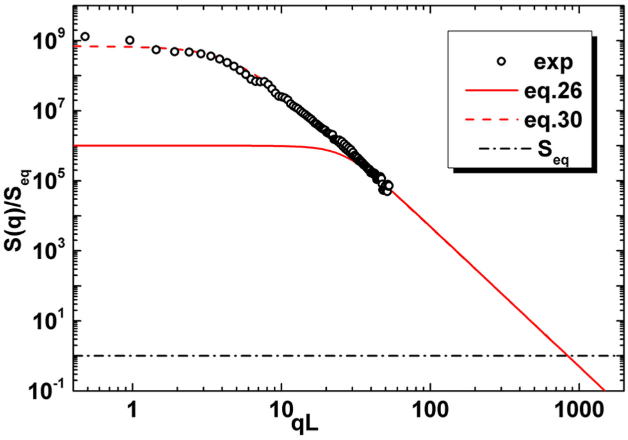

**Fig. 2.** Intensity $S(q)$ of the non-equilibrium concentration fluctuations in a solution of polystyrene in toluene as a function of $qL$ induced by a temperature gradient $\nabla T_0 = 13.25\,\mathrm{K}\cdot\mathrm{mm}^{-1}$, relative to the intensity $S_{\mathrm{eq}}$ of the local equilibrium concentration fluctuations, from an analysis of data obtained at microgravity [64–66]. The solid red curve represents the magnitude of the structure factor to be expected on earth at the same value of the temperature gradient. For $g = 0$ the intensity of fluctuations is only affected by confinement, see sect. 5.1, in particular eq. (30).

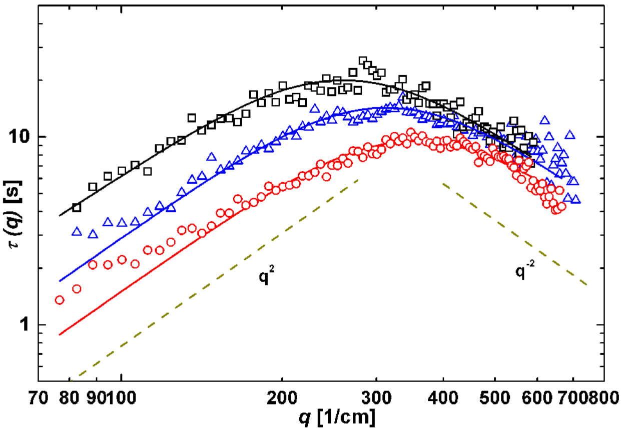

**Fig. 3.** Decay times $\tau(q)$ of non-equilibrium concentration fluctuations in an isothermal solution of colloidal particles and water diffusing against pure water as a function of $q$. Different symbols are for different times from the beginning of the experiment when a concentration gradient is created; time increases from bottom to top of the graph. The experiments confirm the crossover from a $q^{-2}$ behaviour for large $q$ to a $q^2$ behavior for small $q$ in agreement with eq. (29). Figure reproducing data already published in [69].

the intensity of the non-equilibrium fluctuations on earth with measurements of the same fluctuations at low gravity [64–66], as shown in fig. 2 for a solution of polystyrene in toluene. For large wave numbers the intensity of the non-equilibrium concentration fluctuations again varies as $q^{-4}$ [51]. For small wave numbers the intensity saturates at even much higher values in microgravity than on earth, again as predicted by theory [59]. This huge enhancement evidences the importance of performing crucial experiments in micro-gravity conditions as is the case of the future project NEUF-DIX [67]. As we shall discuss in sect. 5, the intensity of the NE fluctuations is also restricted at smaller wave numbers by finite-size effects. This is the reason that even at microgravity the intensity of the NE fluctuations cannot diverge at any wave number.

### 4.2 Gravity effects on the dynamics of non-equilibrium fluctuations

The effects of buoyancy on the dynamics of NE fluctuations have been studied in detail only for concentration fluctuations in binary mixtures. The autocorrelation function of these NE concentration fluctuations, again in the same approximations, $Pr \gg 1$ and $Le \gg 1$, adopted in the previous section, can be written as [68]

$$\langle \delta c^*(q',t)\delta c(q,0)\rangle = \frac{k_{\mathrm{B}}\overline{T_0}}{\rho}\chi_{p,T}\left(1+\frac{\chi_{p,T}^{-1}}{\nu D}\frac{(\nabla c_0)^2}{(q^4+q_{\mathrm{RO},c}^4)}\right) \times \exp\left(-t/\tau_c\right)(2\pi)^3\delta(q'-q) \qquad (28)$$

with

$$\tau_c = \frac{1}{Dq^2(1+\frac{q_{\mathrm{RO},c}^4}{q^4})}\,. \qquad (29)$$

Equation (26) for the intensity of the fluctuations is recovered from eq. (28) by setting $t = 0$. We also note that in the absence of gravity ($q_{\mathrm{RO},c}^4 = 0$), eqs. (28) and (29) reduce to eqs. (21) and (22). The effect of gravity on the dynamics is contained in eq. (29) for the decay time. Fluctuations with wave numbers larger than $q_{\mathrm{RO},c}$ behave diffusively with a time constant $\tau_c = 1/Dq^2$, while fluctuations with wave numbers smaller than $q_{\mathrm{RO},c}$ decay faster with a time constant $\tau_c = q^2/Dq_{\mathrm{RO},c}^4$. It is interesting to note that gravity also affects the dynamics of "equilibrium" fluctuations (the term associated with unity inside the brackets in eq. (28)), when a concentration gradient is present [59].

The first direct measurements of the effect of gravity on the dynamics of NE fluctuations were obtained by Croccolo *et al.*, who developed an algorithm enabling them to obtain dynamic measurements with a Shadowgraph or Schlieren optical setup [57,63,69]. Figure 3 shows the measured time decays for concentration fluctuations during free diffusion of a mixture of colloidal particles and water diffusing against pure water [69]. The typical "bell" shape can be noticed with the presence of a clear maximum for the time decay corresponding to the position of the $q_{\mathrm{RO},c}$, a quantity that decreases with time as the concentration gradient slowly decreases.

## 5 Finite-size effects in confined fluid layers

### 5.1 Finite-size effects on the intensity of non-equilibrium fluctuations

All equations for the NE fluctuations presented thus far are only valid in the bulk of the fluid, *i.e.*, far away from the boundaries. Because of the very long-range nature of the NE fluctuations, boundary conditions actually affect both the statics and the dynamics of non-equilibrium fluctuations. For this purpose one needs to obtain a solution of the fluctuating hydrodynamics subject to appropriate boundary conditions for the temperature or concentration fluctuations and for the transverse velocity fluctuations [61,62,70–72]. For a fluid layer between two impermeable thermal conducting plates, the temperature fluctuations must vanish at the bounding plates, while the vertical derivative of the concentration fluctuations must vanish at the plates. For the velocity fluctuations two types of boundary conditions are commonly considered: stress-free or no-slip boundary conditions [73]. Stress-free boundary conditions are unrealistic but they are mathematically convenient and allow for exact analytical solutions [61]. No-slip boundary conditions are realistic but exact results are generally not possible and often one then obtains solutions in terms of Galerkin approximations [6,62,70].

As a summary of the results we mention first that, as expected, typically the impact of the confinement is limited to wave numbers in the range $qL \leq 1$. Due to the perfectly thermal conducting walls boundary condition, the intensity of the NE temperature fluctuations crosses over from the non-zero $q$-independent saturated NE enhancement corresponding to the small-$q$ limit of eq. (24) to a $q^2$ dependence for even smaller $q$, thus, approaching zero in the $q \to 0$ limit. The boundary conditions cause the non-equilibrium fluctuations to depend on the Rayleigh number $Ra = -\alpha L^4 \mathbf{g} \cdot \nabla T_0 / \nu a$. In liquid layers heated from above (corresponding to negative Rayleigh numbers), the intensity of the NE temperature fluctuations as a function of $q$ presents three different regimes. At large $q$, the $q^{-4}$ dependence of eq. (19). At intermediate $q$, a very flat maximum induced by buoyancy, as described by eq. (24). Finally, at extremely small $q$, the intensity of the temperature fluctuations decreases as $q^2$ when $q \to 0$ [61,62].

Most importantly, the introduction of boundary conditions in the presence of gravity, yields also a perfectly valid convergent result for a range of positive Rayleigh numbers (*i.e.*, when heated from below), up to a limit that equals the well-known critical Rayleigh number for the appearance of convection in the system, as obtained from deterministic fluid dynamics. In this case (positive $Ra$), between the large-$q$ behavior as $q^{-4}$ and the small-$q$ behavior as $q^2$, a prominent maximum in the intensity of NE fluctuations develops, centered at a non-zero finite $q_\mathrm{m}$ whose height increases up to the critical Rayleigh number, where the fluctuations become macroscopic leading to convection patterns [6,62].

The impact of confinement on the spatial spectrum of NE fluctuations has been beautifully illustrated by the results of the GRADFLEX space experiment, performed in microgravity conditions [64–66,74,75]. As an example of the experimental results, we show in fig. 4 a comparison between the intensity of the NE temperature fluctuations in ground experiments (with gravity) and in experiments in space (microgravity) [75]. The experiments show the $q^2$-dependence due to confinement most clearly in microgravity, while the ground experiments were performed at such large and negative Rayleigh numbers so that the wave numbers at which the $q^2$-dependence should be evident were outside the experimental range of wave numbers. However, at microgravity conditions the maximum in the NE fluctuations as a crossover from $q^{-4}$ to $q^2$ is clearly apparent in the experimental results. We note that experimental evidence for confinement effects on the NE fluctuations was earlier observed by Wu *et al.* in supercritical $SF_6$ near but below the convection threshold [76].

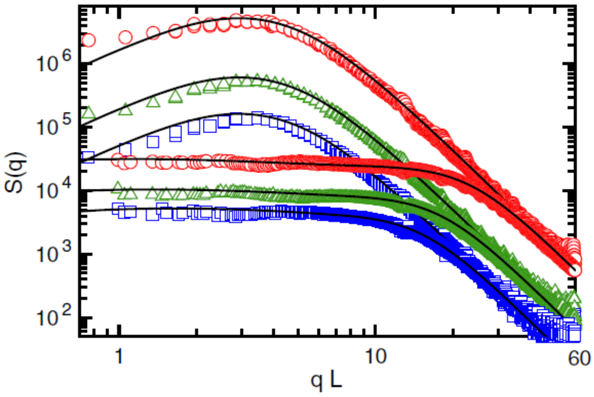

**Fig. 4.** Log-log plot of the NE enhancement of the temperature fluctuations in liquid $CS_2$ as a function of $qL$ as measured by Takacs *et al.* [75]. The symbols indicate the experimental data obtained from the GRADFLEX instrument at $\nabla T_0 = 17.9\,\mathrm{K \cdot cm^{-1}}$ (squares), at $\nabla T_0 = 34.5\,\mathrm{K \cdot cm^{-1}}$ (triangles), and at $\nabla T_0 = 101\,\mathrm{K \cdot cm^{-1}}$ (circles), in microgravity (upper curves) and on earth (lower curves). The curves represent the theoretical prediction from fluctuating hydrodynamics [62]. Figure reprinted from [75] with permission.

Regarding confinement effects on the intensity of NE concentration fluctuations, we first mention that an exact analytical solution for realistic boundary conditions has recently been obtained in the simpler case of the absence of gravity. For NE concentration fluctuations in the absence of gravity but with incorporation of the effect of confinement, the spatio-temporal correlation function is given by [72]

$$\begin{aligned}\langle \delta c^*(q',t)\delta c(q,0)\rangle_{\mathrm{NE}} = \frac{k_\mathrm{B}\overline{T_0}}{\rho}\frac{1}{\nu D}\frac{(\nabla c_0)^2}{q^4}\,[1+B_c(q)] \\ \times \exp\left(-t/\tau_c\right)(2\pi)^3\delta(q'-q), \quad (30)\end{aligned}$$

with

$$B_c(q) = \frac{4(1-\cosh(qL))}{qL(qL+\sinh(qL))} \quad (31)$$

and

$$\tau_c = \frac{1}{Dq^2}\,, \quad (32)$$

replacing eqs. (28) and (29) (at $g = 0$ or $q^4_{\mathrm{RO},c} = 0$). For simplicity, we have written only the NE part of the autocorrelation, the equilibrium fluctuations enter eq. (31) additively [72]. In fig. 2 it was already shown how eq. (30) nicely describes the experimental results of the GRADFLEX experiment for a binary mixture of polystyrene in toluene [64–66].

It is interesting to note that, in the limit $q \to 0$, the intensity of the NE concentration fluctuations reaches a constant non-zero limit independent of $q$, namely,

$$\frac{1+B_c(q)}{q^4} \xrightarrow{q\to 0} \frac{L^4}{720} + O(q^2). \tag{33}$$

In eq. (33), as well as in the experimental data of fig. 2, one observes that, while the NE temperature fluctuations vanish for very small $q$ as discussed earlier, the NE concentration fluctuations reach a finite limit for very large size as $q \to 0$. This difference is a direct consequence of the different boundary conditions to be satisfied by the temperature and the concentration fluctuations at the bounding plates. When gravity is incorporated, the exact solution can only be obtained numerically [71] and it becomes dependent on the solutal Rayleigh number $Ra_\mathrm{s} = \beta L^4 \mathbf{g}\cdot\nabla c_0/\nu D$. However, although eq. (33) applies only in microgravity, the qualitative effect of confinement remains similar if gravity is taken into account. This has been demonstrated both by Galerkin approximations [70] and by the numerical evaluation of the solution of the fluctuating hydrodynamics equations [71].

### 5.2 Finite-size effects on the dynamics of non-equilibrium fluctuations

There are few systematic studies on the effect of confinement on the dynamics of NE fluctuations. Only recently, the case of concentration fluctuations in a binary mixture has been considered in some detail [77,78]. It does not appear to be possible to obtain an analytical solution for the autocorrelation function when boundary conditions are included, but numerical calculations have been performed for different negative solutal Rayleigh numbers. These numerical calculations turn out be in good agreement with both experimental data and with computational fluid dynamics simulations [77,78]. The main impact of confinement is a slowing-down of the fluctuations with wave number $qL \leq 5.18$. In this range of very small wave numbers, the time constants are again diffusive-like with a reduced diffusion coefficient. Specifically, in the limit of small wave numbers [77,78]:

$$\lim_{q\to 0} \tau_\mathrm{conf} = \frac{1}{Dq^2\left(1-\frac{Ra_\mathrm{s}}{Ra_{\mathrm{s},c}}\right)}\,, \tag{34}$$

which replaces eq. (32) for $qL \ll 5.18$. Thus confinement changes the non-diffusive behaviour implied by eq. (29) as $q \to 0$, and diffusive behaviour is again recovered, but with a renormalized diffusion coefficient. As clearly shown in fig. 5, for stabilizing concentration gradients, the experimental decay times as a function of the wave number display a local minimum as a function of the wave number for any value of the solutal Rayleigh number and as $q \to 0$ the decay times crossover to the limiting behavior given by eq. (32).

A similar analysis of the effect of confinement on the NE temperature fluctuations is not yet available. The effect is expected to be somewhat different than the effect on the concentration fluctuations due to the different boundary conditions for the temperature fluctuations. For the NE concentration fluctuations, GRADFLEX experiments have confirmed that in microgravity ($q^4_{\mathrm{RO},c} = 0$) the dynamics of the NE concentration fluctuations is not affected by the gradients, in accordance with eq. (32) [64–66].

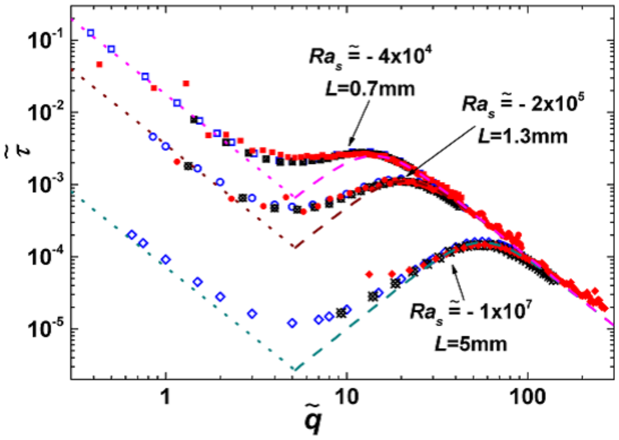

**Fig. 5.** Decay times of non-equilibrium concentration fluctuations in a binary mixture of 1,2,3,4-tetrahydronaphtalene and $n$-dodecane subjected to a stabilizing temperature gradient. Different symbols are for different thicknesses of the sample cell, thus resulting in different solutal Rayleigh numbers. Figure reproducing data already published in [77].

## 6 Non-equilibrium fluctuation-induced forces

Fluctuation-induced forces will appear in confined fluids when long-range fluctuations are present [80]. They are also often referred to as Casimir forces, since they originally were found as a result of quantum fluctuations of the electromagnetic field in vacuum [81]. A well-known example in fluids is the Casimir effect resulting from the long-range critical fluctuations earlier mentioned in sect. 2.3. The presence of Casimir forces due to the long-range non-equilibrium fluctuations has been predicted by Kirkpatrick *et al.* [9–13].

In a confined fluid layer subjected to a temperature gradient $\nabla T_0$ the non-equilibrium temperature fluctuations will induce a Casimir pressure, such that

$$p_\mathrm{NE}(\mathbf{r}) = \frac{\rho c_p(\gamma-1)}{2\overline{T}_0} B \left\langle (\delta T(\mathbf{r}))^2 \right\rangle_\mathrm{NE} \tag{35}$$

with a thermodynamic pre-factor

$$B = 1 - \frac{1}{\alpha c_p}\left(\frac{\partial c_p}{\partial T}\right)_p + \frac{1}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_p. \tag{36}$$

In eq. (35) $\gamma$ is the ratio of the isobaric and isochoric heat capacities and $\langle(\delta T(\mathbf{r}))^2\rangle_\mathrm{NE}$ is the intensity of the non-equilibrium temperature fluctuations at position $\mathbf{r}$ [9,10]. The effects of this non-equilibrium Casimir force are twofold, namely $p_\mathrm{NE}(\mathbf{r})$ causes a rearrangement of the local equilibrium density profile $\rho_0(\mathbf{r})$ and a deviation of the local equilibrium pressure $p_0$ [12]. Indeed, because of mass conservation one has

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) - \rho\kappa_T \left[p_{\mathrm{NE}}(\mathbf{r}) - \overline{p}_{\mathrm{NE}}\right], \tag{37}$$

with the actual (uniform) pressure being

$$p = p_0 + \overline{p}_{\mathrm{NE}}, \tag{38}$$

where $\kappa_T = \rho^{-1}(\partial\rho/\partial p)_T$ is the isothermal compressibility and $\overline{p}_{\mathrm{NE}}$ is the spatial average of $p_{\mathrm{NE}}(\mathbf{r})$. Just as in sect. 5, the detailed expression for $\langle(\delta T(\mathbf{r}))^2\rangle_{\mathrm{NE}}$ in eq. (35), but not the order of magnitude, depends on the boundary conditions at the surfaces of the plates confining the fluid. For a fluid layer between two thermally conducting plates and for stress-free conditions for the velocity fluctuations, Kirkpatrick *et al.* found a simple analytical solution such that [12]

$$\overline{p}_{\mathrm{NE}} = \frac{\rho c_p k_{\mathrm{B}} \overline{T}_0^{\,2}(\gamma - 1)}{29\pi a(\nu + a)} BL \left(\frac{\nabla T_0}{\overline{T}_0}\right)^2. \tag{39}$$

Thus for a given temperature gradient $\nabla T_0$, the non-equilibrium Casimir pressure will increase with the height $L$ of the fluid. For a fixed value of the temperature difference $\Delta T_0$ between the plates it will vary as $L^{-1}$. This is to be compared with a $L^{-4}$ dependence with the plate separation for electromagnetic Casmir forces, or a $L^{-3}$ dependence for critical Casimir forces [9].

In a layer of a binary fluid mixture with a concentration gradient $\nabla c_0$, Kirkpatrick *et al.* have also predicted a Casimir pressure due to the non-equilibrium concentration fluctuations [11,13]:

$$p_{\mathrm{NE}}(\mathbf{r}) = -\frac{\rho(\gamma - 1)}{2\alpha T} C \left\langle (\delta c(\mathbf{r}))^2 \right\rangle_{\mathrm{NE}} \tag{40}$$

with

$$C = \chi_{p,T}^{-1} - T\left(\frac{\partial \chi_{p,T}^{-1}}{\partial T}\right)_{p,c} - \frac{\rho c_p}{\alpha}\left(\frac{\partial \chi_{p,T}^{-1}}{\partial p}\right)_{T,c}. \tag{41}$$

In a binary-fluid layer between two impermeable walls and for no-slip boundary conditions for the velocity fluctuations, $\langle(\delta c(\mathbf{r}))^2\rangle_{\mathrm{NE}}$ can be readily evaluated consistent with eq. (30) [72], and one obtains for the Casimir pressure caused by NE concentration fluctuations [13]

$$\overline{p}_{\mathrm{NE}} = -\frac{k_{\mathrm{B}}(\gamma - 1)}{2\alpha\nu D} C\overline{F}L\left(\nabla c_0\right)^2, \tag{42}$$

where $\overline{F}$ is a numerical constant ($\overline{F} \simeq 0.006$).

Order-of-magnitude estimates for the predicted non-equilibrium Casimir pressures presented elsewhere [13] show that they are typically much larger than critical Casimir pressures [12]. One physical reason is that the intensity of the non-equilibrium fluctuations diverges for small $q$ as $q^{-4}$ in accordance with eqs. (19) and (23), while the intensity of critical fluctuations only diverges as $q^{-2}$ in accordance with eq. (12).

Again the equations above have been obtained from fluctuating hydrodynamics with local equilibrium values for the thermophysical properties. They predict in confined fluids a breakdown for the principle of local equilibrium for the thermophysical properties as discussed by Kirkpatrick *et al.* [10]. In principle one could iterate the procedure by using the actual NE values of the thermophyiscal properties. However, the non-equilibrium corrections to the thermophysical properties from the local equilibrium values are very small compared to the equilibrium values (cf., 1 Pa compared to $10^5$ Pa). Hence, one can continue to use the fluctuating hydrodynamics equations with local values of the thermophysical properties to predict accurately the deviations from local equilibrium in non-equilibrium fluids.

## 7 Conclusions

In this paper we have reviewed the intensity and dynamics of NE fluctuations in a variety of systems. The NE fluctuations are greatly enhanced over the corresponding equilibrium fluctuations, are long ranged extending over the entire system size, are affected by gravity and by finite-size effects. These non-local fluctuation phenomena have been predicted on the basis of the equations of fluctuating hydrodynamics assuming local equilibrium values for all thermophysical properties in the equations and in the noise correlation fluctuations. The excellent agreement of the predictions from these fluctuating-hydrodynamics equations with the experimentally observed non-local character of the NE fluctuations, as reviewed in the present paper, confirms the validity of the extension of fluctuating hydrodynamics with local equilibrium property values to non-equilibrium states.

Actually, the agreement between experiment and fluctuating hydrodynamics turns out to be so accurate that experimental investigation of NE fluctuations is becoming a new method for measuring transport properties of fluids and fluid mixtures. This new method has been verified first on a reference fluid mixture [82,83] for extracting mass diffusion and Soret coefficients from the dynamics of concentration NE fluctuations. Subsequently, the same approach has been used to determine these transport properties for fluid mixtures at high pressure [84]. The thermal diffusivity of fluids can be determined by measuring the dynamics of NE temperature fluctuations [85]. The Soret coefficient has also been determined from the analysis of the intensity NE concentration fluctuations obtained in microgravity conditions [65]. Applications of fluctuating hydrodynamics to study NE concentration fluctuations in ternary mixtures have also been initiated [79,86,87].

In the discussion above we have focused our attention to theoretical predictions and experimental verifications of the intensity and dynamics of NE fluctuations. It is important to mention that in the last decade also efforts have been made to apply Computational Fluid Dynamics for investigating different aspects of NE fluctuations. In particular computer simulations do not need some of the approximations that are introduced in the theory and are therefore able to investigate more complicated, and sometimes more interesting, problems. Among the important results obtained by this way we may mention the investigation of NE concentration fluctuations in microgravity experiments both at steady state [88,89] and during the transient state [66], the free diffusion of highly non-linear sample of glycerol and water [90], the effect of confinement on concentration NE fluctuations [77,78], the interaction with the presence of surface tension [91], chemical reactions [92] or electrostatic effects [93].

In non-equilibrium steady states, non-equilibrium fluctuations are always present. They have intensities much larger than their local equilibrium values, extend over the entire system and are strongly affected by gravity and confinement. The non-local fluctuation phenomena observed experimentally are in very good agreement with the features predicted from fluctuating hydrodynamics with thermophysical property values equal to their local equilibrium values. Hence, the assumption of local equilibrium in the equations of non-equilibrium thermodynamics is consistent with the presence of non-local fluctuations phenomena that are actually present in steady or quasi-steady NE states. By quasi-steady NE states we mean states in which the time dependence of the gradient is slow compared to the relevant relaxation rates of the fluctuations [94].

The fluctuating hydrodynamic equations not only predict non-local fluctuation phenomena, but also non-equilibrium contributions to the local equilibrium density and the local equilibrium pressure in confined fluid layers as discussed in sect. 6. Experimental confirmations of the latter deviations from local equilibrium are not yet available.

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