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Thermal Fluctuations in Non-Equilibrium Thermodynamics

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Abstract

Thermal fluctuations in fluids and fluid mixtures in stationary non-equilibrium states are spatially long ranged. This long-ranged nature of the non-equilibrium fluctuations is caused by a coupling between hydrodynamic modes through the non-equilibrium fluxes or gradients. The phenomena are discussed with some illustrative examples in fluids and fluid mixtures.

1. Introduction

The theory of fluctuations in fluids that are in thermodynamic equilibrium is well established. For instance, the intensity of density fluctuations will be proportional to the isothermal compressibility. Such density fluctuations can be probed experimentally by light scattering: the integrated intensity $S(\mathbf{q})$ of the scattered light at a scattering wave vector $\mathbf{q}$ is proportional to the Fourier transform of the spatial equal-time correlation function of the refractive-index fluctuations, which in turn is directly related to that of the (mass) density ρ. For fluids in thermodynamic equilibrium, the correlation functions associated with the thermal fluctuations are spatially short ranged, except for states near a critical point.

In this paper, we discuss the nature of thermal fluctuations in fluid and fluid mixtures that are in stationary non-equilibrium states. Non-equilibrium fluids can exhibit a large variety of complex fluctuation phenomena such as those associated with convection patterns or turbulence. Here we restrict ourselves what at first sight may seem to be a much simpler problem, namely

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fluctuations in non-equilibrium fluids in the absence of convection or turbulence. As an example, one may consider a fluid with positive thermal-expansion coefficient, confined between two horizontal parallel plates that are maintained at two different temperatures, to which we refer as the Rayleigh–Bénard problem. The relevant dimensionless parameter is the Rayleigh number,

$$Ra = -\frac{\alpha g L^4 \nabla T_0}{\nu a}, \tag{1}$$

where α is the thermal-expansion coefficient of the fluid, g the acceleration of gravity, L the distance between the two bounding plates, ∇T_0 the temperature gradient maintained across the fluid layer, ν the kinematic viscosity, and a the thermal diffusivity. Convection will be absent when the fluid layer is heated from above, corresponding to negative values of Ra, and when the fluid is heated from below at values of Ra smaller than a critical Rayleigh number Ra_c associated with the onset of convection.

A fundamental concept underlying non-equilibrium thermodynamics is that of local equilibrium. That is, at each position $\mathbf{r}$ and time t the local state is specified by local values of the thermodynamic variables like a local density $\rho(\mathbf{r}, t)$, a local temperature $T(\mathbf{r}, t)$, and a local pressure $p(\mathbf{r}, t)$. These local thermodynamic variables and all other associated local thermodynamic properties remain interrelated by the same relations as for a thermodynamic equilibrium state with $\rho \equiv \rho(\mathbf{r}, t)$ and $T \equiv T(\mathbf{r}, t)$.

Traditionally, it had been expected that in the absence of any hydrodynamic instabilities, like convection or turbulence, the thermal fluctuations would also satisfy the hypothesis of local equilibrium. That is, one would expect that the intensity of the density fluctuations in a stationary quiescent non-equilibrium state would be proportional to the local value of the compressibility. During the past two decades, it has become evident that the assumption of local equilibrium is only valid for the thermodynamic properties themselves, but not for the correlations among these properties. In equilibrium fluids the spatial extent of diffusive fluctuations, like temperature, viscous, or concentration fluctuations, are generically short ranged on a hydrodynamic scale. However, in non-equilibrium fluids correlations among the fluctuations at two spatial points exist even when large macroscopic distances separate these two points. Therefore, correlations extend over a much larger spatial range than one would expect in the basis of a local equilibrium assumption for these properties.

In this paper we discuss some examples of thermal fluctuations in fluids in stationary non-equilibrium states using the Rayleigh–Bénard problem as an illustrative example. For a comprehensive treatment of the subject, the reader is referred to a recent book on hydrodynamic fluctuations in fluids and fluid mixtures [1].

2. Mode-coupling phenomena

About fifty years ago an approach to develop a systematic statistical mechanics theory for dealing with non-equilibrium fluids was proposed by Bogoliubov [2]. It was based on a postulate that a fluid away from equilibrium would proceed to a thermodynamic equilibrium state in two distinct stages: first, a microscopic kinetic stage with a time scale of the order of the time between molecular collisions, which for dense fluids or liquids is of the same order as the duration of the molecular collisions, after which local equilibrium is established; second, a macroscopic hydrodynamic stage during which the fluid evolves in accordance with the equations of hydrodynamics. Since in practice temperature differences in fluids over microscopic molecular distances remain negligibly small, this postulate would justify the assumption of local equilibrium not only for the thermodynamic properties, but also for the fluctuations, except for thermally excited sound waves that do propagate over hydrodynamic distances and, hence, would be affected by the presence of a temperature gradient [3].

An important consequence of Bogoliubov's postulate is that fluids consisting of molecules with short-ranged interactions cannot exhibit long-ranged dynamic correlations because of the randomizing nature of the molecular collisions. This postulate was consistent with the classical theory of critical phenomena, where the spatial extent of the static correlations become long ranged due to the divergence of the compressibility in accordance with the theory of Ornstein and Zernike, but where the dynamic correlations remain short ranged in accordance with the classical theory of the slowing down of the critical fluctuations formulated by Van Hove. However, this picture failed when it was discovered that transport properties like the thermal conductivity diverge at the critical point. A sharp distinction between a short-ranged kinetic stage and a long-ranged hydrodynamic stage could not longer be maintained and there is an additional mesoscopic stage in which the slow hydrodynamic modes become coupled due to nonlinear hydrodynamic interactions between the long-wavelength fluctuations [4]. For instance, a coupling between temperature fluctuations (heat mode) and transverse momentum fluctuations (viscous mode) causes a divergence of the thermal conductivity at the vapour–liquid critical point. Some time later it turned out that the same mode-coupling theory could also account for the phenomena of long-time tails in the Green–Kubo correlation functions for the transport coefficients that were originally noticed in computer simulations of molecular dynamics [5, 6]. Around 1980 it became evident that mode-coupling phenomena would also strongly affect the nature of thermal fluctuations in fluids that are kept in stationary non-equilibrium states [7–9].

For fluids in thermodynamic equilibrium, fluctuations at hydrodynamic spatiotemporal scales can be determined by the method of fluctuating hydrodynamics in conjunction with the fluctuation–dissipation theorem [10, 11]. The mode-coupling phenomena described above are a consequence of nonlinear terms in the equations of fluctuating hydrodynamics. It is possible to extend the method of fluctuating hydrodynamics to fluids in non-equilibrium states by adopting a local version of the fluctuation–dissipation theorem. For non-equilibrium fluids, the hydrodynamic modes become coupled through the externally imposed dissipative fluxes and associated gradients. As a consequence, these types of mode-coupling phenomena can be treated within the framework of linear fluctuating hydrodynamics, as explained elsewhere [1].

3. Non-equilibrium fluctuations in fluids

When a one-component fluid is subjected to a stationary temperature gradient, ∇T_0, there appears a coupling between the temperature fluctuations and the fluctuations of the velocity component parallel to the gradient. Such a coupling causes an enhancement in the intensity of non-equilibrium refractive-index fluctuations, $S(\mathbf{q})$. Working out the theory in detail from the random Boussinesq equations, one finds [7, 12–14]:

$$S(\mathbf{q}) = S_{\mathrm{E}}\left[1 + \frac{c_p(\nabla T_0)^2}{a^2 T(Pr+1)}\frac{q_\parallel^2}{q^6}\right], \tag{2}$$

where S_{E} is the intensity of refractive-index fluctuations in equilibrium, which is isotropic and does not depend on the scattering vector $\mathbf{q}$, c_p is the isobaric specific heat capacity, and $Pr = \nu/a$ the Prandtl number. The non-equilibrium enhancement is represented by the second term inside the brackets in Eq. (2); it is proportional to the square of the temperature gradient and is anisotropic, since $q_\parallel^2 = q_x^2 + q_y^2$ is the component of the scattering vector perpendicular to the direction of the gradient. For small scattering angles $q_\parallel^2/q^6 \simeq 1/q^4$, and such a dependence of $S(\mathbf{q})$ on the wave number q clearly indicates the long-ranged nature of the corresponding equal-time correlation functions.

In the case of a binary mixture, an externally imposed temperature gradient induces a concentration gradient through the Soret effect. Such an induced stationary concentration gradient causes a new coupling between concentration

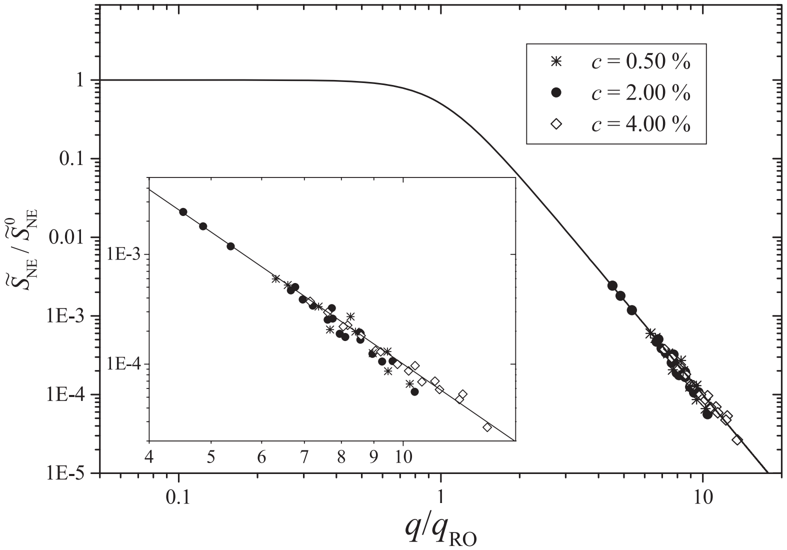

Figure 1 Normalized non-equilibrium enhancement of concentration fluctuations in a solution of polystyrene in toluene heated from above. The insert shows the range where the actual experimental data have been obtained. The solid curve is a plot of Eq. (4) using the known thermophysical properties of the mixture. From ref. [15].

fluctuations and fluctuations of the fluid velocity component parallel to the gradient. Further complications in mixtures arise from the presence of both temperature and concentration fluctuations, which may not be independent depending on the experimental conditions. However, in many important practical cases the dominant contribution to the structure factor is that of concentration fluctuations. On the basis of the theory of fluctuating hydrodynamics in mixtures, one finds for the structure factor associated with the concentration fluctuations [15]

$$S(\mathbf{q}) = S_\mathrm{E}\left[1 + \frac{(\nabla c_0)^2}{\chi \nu D}\frac{q_\parallel^2}{q^6}\right], \tag{3}$$

where χ is the osmotic compressibility, D the binary diffusion coefficient, and ∇c_0 the magnitude of the concentration gradient. Just as the intensity of the non-equilibrium temperature fluctuations, the intensity of the non-equilibrium concentration fluctuations will vary as $1/q^4$.

It is worth emphasizing that the most salient features of the theory of non-equilibrium fluctuations have been verified by experiments. As an example, we show in Figure 1 a double-log plot of the intensity enhancement of non-equilibrium concentration fluctuations ($\tilde{S}_\mathrm{NE}(\mathbf{q}) = (S(\mathbf{q}) - S_\mathrm{E})/S_\mathrm{E}$) in a solution of polystyrene in toluene at different concentrations and normalized by a corresponding prefactor ($\tilde{S}^0_{\rm NE} = (\nabla c_0)^2/\chi D\nu L^4$). The straight line in the insert that shows the actual experimental data represents the $1/q^4$ proportionality predicted by the theory, with a slope calculated from the known thermophysical properties of the solution without any fitting parameters. Theory and experiments are in excellent agreement.

4. Buoyancy effect on fluctuations

Equations (2) and (3) do not account for any effects of gravity or effects of the presence of boundaries on the fluctuations. The variation of the intensity of the non-equilibrium fluctuations as $1/q^4$, which corresponds to a spatial dependence proportional to the distance r between the two points where fluctuations are correlated, cannot go on indefinitely as $q \to 0$. Indeed, buoyancy modifies that dependence, and when gravity is stabilizing (like for a binary mixture with positive separation ratio, when heated from above) it causes the intensity of non-equilibrium fluctuations to become saturated and reach a constant limit at $q \to 0$. Again, on the basis of fluctuating hydrodynamics, one can show that the (dominant) contribution of concentration fluctuations to the non-equilibrium structure factor, when buoyancy effects are included and the adiabatic temperature gradient is identified with the actual temperature gradient, can be expressed as

$$S(\mathbf{q}) = S_{\rm E}\left[1 + \frac{(\nabla c_0)^2}{\chi\nu D}\,\frac{q_\parallel^2}{q^6 + q_{\rm RO}^4 q_\parallel^2}\right], \tag{4}$$

where buoyancy effects are included in the "roll-off" wave number $q_{\rm RO}$, defined by

$$q_{\rm RO}^4 = -\psi\frac{aRa}{DL^4}, \tag{5}$$

with ψ the separation ratio. Notice that, for positive ψ, and heating from above ($Ra < 0$) the RHS of Eq. (5) is positive, and the "roll-off" wave number is a well-defined quantity. However, if buoyancy is destabilizing ($Ra > 0$), there exists an unphysical divergence in Eq. (4) for some wave vectors, and confinement effects need to be included in the theory to obtain valid theoretical results. This is considered in the next section.

We note that, for large q, Eq. (4) reproduces Eq. (3), which was deduced without considering buoyancy. However, for small q, the intensity of the non-equilibrium concentration fluctuations no longer increases without limit (as predicted by Eq. (3)), but a constant limit is reached instead. This small wave-number quenching of non-equilibrium fluctuations is also shown in Figure 1, where we note that the straight line corresponding to the $1/q^4$ proportionality crosses over to a constant limit for values of the wave number around q_{RO}. The experimental points displayed in Figure 1 were obtained for q values larger than q_{RO}, so that the quenching due to gravity could not be observed. However, the quenching of the intensity of non-equilibrium fluctuations due to buoyancy has been confirmed by Vailati and Giglio [16].

5. Confinement effects on non-equilibrium fluctuations

When buoyancy has a destabilizing effect, the presence of boundaries has to be taken into account explicitly to describe the intensity of non-equilibrium fluctuations. Since the non-equilibrium fluctuations in the presence of a temperature or a concentration gradient extend spatially over the entire system, they will be affected at small wave numbers (i.e., at long wavelengths) by the finite size of the fluid layer. A systematic incorporation of confinement effects in the theory of non-equilibrium fluctuations has been obtained [17, 18] by requiring that the fluctuating fields satisfy appropriate boundary conditions, which depend on the problem under consideration. The most important conclusion of these investigations is that the long-wavelength behavior of the non-equilibrium fluctuations is indeed strongly affected by the boundary conditions. The detailed expression that fluctuating hydrodynamics gives for the intensity of non-equilibrium fluctuations is generally involved and depends on the boundary conditions considered. The case of a one-component fluid with free-slip boundary conditions is particularly instructive because the calculation can be performed analytically to yield [17]

$$S(\mathbf{q}) = S_{\mathrm{E}}\left\{1 + \frac{c_p(\nabla T_0)^2}{a^2 T(Pr+1)}\frac{1}{L^4}\tilde{S}_{\mathrm{NE}}(\mathbf{q})\right\}, \tag{6}$$

with the dimensionless enhancement $\tilde{S}_{\mathrm{NE}}(\mathbf{q})$ of non-equilibrium fluctuations given by

$$\tilde{S}_{\mathrm{NE}}(\mathbf{q}) = \frac{\tilde{q}_{\parallel}^2}{\tilde{q}^6 - Ra\tilde{q}_{\parallel}^2} + \frac{2\tilde{q}_{\parallel}}{3Ra}\sum_{j=0}^{2}\frac{\xi_j\sqrt{\xi_j - \tilde{q}_{\parallel}^{4/3}}}{[\tilde{q}^2 - \xi_j\tilde{q}_{\parallel}^{2/3}]^2}\,\frac{\cos(\tilde{q}_z) - \cos(\tilde{q}_{\parallel}^{1/3}\sqrt{\xi_j - \tilde{q}_{\parallel}^{4/3}})}{\sin(\tilde{q}_{\parallel}^{1/3}\sqrt{\xi_j - \tilde{q}_{\parallel}^{4/3}})}, \tag{7}$$

in terms of a dimensionless wave vector $\tilde{\mathbf{q}} = \mathbf{q}L$. In Eq. (7), ξ_j represents the three complex cubic roots of the Rayleigh number, see Eq. (3) in ref. [17]. The first term in Eq. (7) represents the effects of buoyancy and has a structure

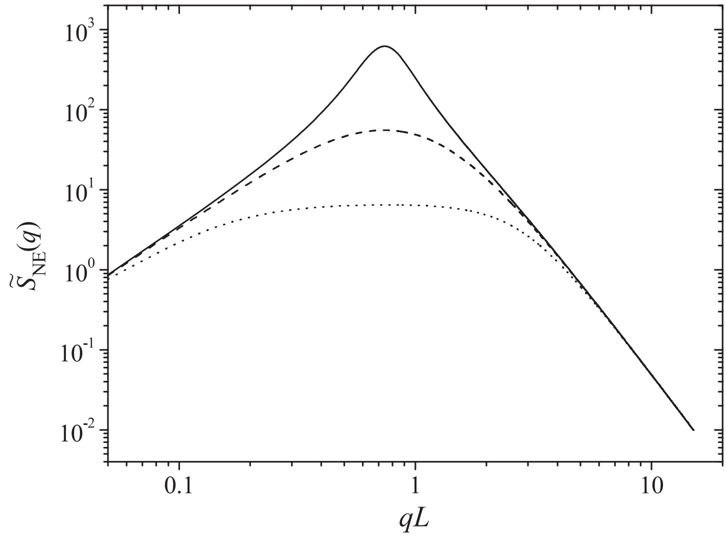

Figure 2 Normalized non-equilibrium enhancement of temperature fluctuations for a one-component fluid with free slip boundary conditions as given by Eq. (7), and for three values of the Rayleigh number; from ref. [17].

similar to Eq. (4) for a binary mixture. The second term in Eq. (7), expressed as a sum over the ξ_j, represents the confinement effects. The most salient features included in Eq. (7) are as follows: First, it gives valid (convergent) results not only for negative *Ra* (heating from above), but also for positive *Ra* up to a critical $Ra_c = 27\pi^4/4$ that coincides with the well-known critical Rayleigh number obtained from linear instability analysis. Second, the intensity of non-equilibrium temperature fluctuations vanishes proportionally to q^2 when $q \to 0$, as a consequence of the boundary conditions. To illustrate these features, we show in Figure 2 a plot of Eq. (7) for three different values of the *Ra* number. The upper curve corresponds to a positive *Ra* close to the convective instability, the intermediate curve is for $Ra \simeq 0$ (i.e., in microgravity), and the lower curve is for a large and negative *Ra*, similar to the values employed in small-angle light-scattering experiments.

We clearly observe in Figure 2 the features mentioned above, and how the $1/q^4$ dependence obtained in Eq. (2) when no boundaries are considered, crosses over to a q^2 dependence for extremely small q. As a consequence, fluctuations become maximally enhanced for a certain non-zero value of the wave number q_m. It is to be noted that the position of the peak in Figure 2, a problem sometimes referred to as wave-number selection, cannot be correctly predicted on the basis of traditional hydrodynamic instability analysis for the decay rate of the fluctuations. One must account for the intrinsic stochastic nature of hydrodynamics to make these kinds of predictions, i.e., the value of q_m [18]. For the non-equilibrium fluctuations with wave numbers close to q_m, we observe in Figure 2 that when Ra approaches the critical value for the onset of convection, Ra_c, the intensity of those fluctuations increases dramatically. Eventually, when $Ra = Ra_c$, the intensity of non-equilibrium fluctuations diverges (within the linear theory employed to deduce Figure 2). This observation demonstrates a close connection between a divergence of non-equilibrium fluctuations and the appearance of hydrodynamic instabilities.

Long-wavelength fluctuations can be probed by shadowgraphy. Experiments performed by Wu et al. [19] in sulphur hexafluoride have confirmed the main features of the theory. However, since the experiments were conducted near the critical point, non-Boussinesq effects become important, which have not yet been incorporated into the theory in a systematic way [20].

Confinement effects on non-equilibrium fluctuations in mixtures have been also recently examined theoretically. The case of mixtures is complicated by the presence of simultaneous temperature and concentration fluctuations, which leads to the existence of two hydrodynamic modes and two competing instability mechanisms. As a consequence, the intensity of non-equilibrium temperature fluctuations for a typical binary mixture presents a surprising bimodal distribution. For a more detailed study on this topic, we refer the reader to a paper by Ortiz de Zárate et al. [21].

6. Discussion

In this paper, we have focused our attention on non-equilibrium fluctuations in fluids in the presence of a temperature or a concentration gradient. However, mode-coupling phenomena are generically present in non-equilibrium systems like in fluids in plane Couette flows or mixtures with non-equilibrium chemical reactions [1]. In general, we can make the following conclusions regarding non-equilibrium fluctuations:

1. The principle of local thermodynamic equilibrium in non-equilibrium thermodynamics is valid for the thermodynamic properties, but not for the fluctuations of those properties, even far away from any hydrodynamic instability.
2. The non-equilibrium fluctuations are always stronger and spatially longer ranged than would be the case if the hypothesis of local equilibrium for the fluctuations was valid.
3. While linear fluctuating hydrodynamics ceases to be valid at and beyond the appearance of hydrodynamic instabilities, it does give a description at all stable non-equilibrium states, even rather close to the appearance of an

instability like convection. On the other hand, traditional hydrodynamic instability analysis, based on the deterministic hydrodynamic equations, i.e., without the inclusion of random noise terms, does not yield a correct description of the amplitude of the non-equilibrium fluctuations as a function of the wave number.

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