Non-Equilibrium is Different

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Abstract

Non-equilibrium and equilibrium fluid systems differ due to the existence of long-range correlations in non-equilibrium that are not present in equilibrium, except at critical points. Here we examine fluctuations of the temperature, of the pressure tensor, and of the heat current in a fluid maintained in a non-equilibrium stationary state (NESS) with a fixed temperature gradient, a system where the non-equilibrium correlations are especially long ranged. For this particular NESS our results show that (1) The mean-squared fluctuations in non-equilibrium differ markedly in their system size scaling compared to their equilibrium counterparts and (2) There are large, nonlocal, correlations of the normal stress in this NESS. These terms provide important corrections to the fluctuating normal stress in linearized Landau-Lifshitz fluctuating hydrodynamics.

In recent years fluctuations in fluids maintained in non-equilibrium steady states (NESS), and in non-equilibrium fluids in general, have attracted a large amount of attention. Of particular interest are the studies of Evans, Cohen and Morris (ECM) [1], Evans and Searles [2], and of Gallavotti and Cohen [3]. Later related work was done by Jarzynski [4] and by Crooks [5]. Particularly in the earlier work, a focus was on non-equilibrium currents and entropy production. For example, if $P_{xy \tau}$ is the time average of the microscopic stress tensor, $P_{xy}$, over a time interval $\tau$ then in a NESS with a steady shear rate, $\gamma$, ECM studied the probability distribution $\mathcal{P}(P_{xy \tau})$ in a $N-$particle system. Using an analysis based upon their computer simulations, they showed that,

$$\frac{\mathcal{P}(P_{xy \tau})}{\mathcal{P}(-P_{xy \tau})} = \exp \left\{ N\gamma \int_0^\tau d\tau P_{xy}[\Gamma(\tau)] \right\}$$

(1)

On the RHS the phase space time-dependence $\Gamma(\tau)$ is restricted such that only the dynamical states $i$ with a given value of $P_{xy \tau} = \int_0^\tau d\tau P_{xy}[\Gamma_i(\tau)]$ are taken into account. They also numerically determined $\mathcal{P}(P_{xy \tau})$ and found it had a sharp peak around it’s average value and that although the bulk of the distribution was consistent with positive entropy production, there was a tail part consistent with negative en-
tropy production. The system size or $N$-dependence of the width of the distribution, $\mathcal{P}(P_{xy})$ is an interesting open problem.

Prior to this work, it was established in the 1960's through the 1980's that correlations are very different in non-equilibrium fluid systems than they are equilibrium systems [6–8]. For example, in the early 1980's it was predicted [9] that the temperature and density correlations in a fluid in a NESS with a temperature gradient were extraordinarily long-ranged (in a sense growing with system size). This prediction was subsequently confirmed [10, 11] with great precision in small angle light scattering experiments. For very small angle scattering, the scattering was found to be larger than the equilibrium scattering by a factor of $10^5$. All of this implies that the statistics of fluctuations in non-equilibrium fluids will in general be very different than those for fluctuations in the same fluid in an equilibrium state. For reviews see [8, 11–13].

Here we will expand on this point by examining the system size dependence of not only the temperature fluctuations and distribution, but also the fluctuations and distributions of the pressure tensor, and heat current for a fluid in a NESS with a temperature gradient. This particular NESS (see also point 6 in the discussion) is unique because the correlations are so strong that they extend over the entire system size, see Eq.(3). This is very different then the correlations in other NESS, which typically decay as a power law. We find that that temperature and pressure or normal stress tensor fluctuations in a fluid with a temperature gradient are so large that many of the assumptions that are commonly made about non-equilibrium fluids when one uses equilibrium-like methods, such as maximum entropy formalisms, power series expansions, etc. to describe their properties, are called into question and may not be justified. We show that relative root mean square fluctuations of some thermodynamic and transport quantities do not in general scale with particle number, $N$, as $1/N^{1/2}$ as do their equilibrium counterparts. We also describe the distributions of these fluctuations, and point out their anomalous properties as well.

The new results in this paper are: (1) We show that the previously computed temperature fluctuations for a fluid in a temperature gradient scale as $1/N^{(d-2)/2}$ and not as $1/N^{1/2}$, (2) We compute for the first time the pressure or stress fluctuations for a fluid in a temperature gradient. These fluctuations are shown to scale as $1/N^{(d-2)}$, (3) We compute for the first time the heat current fluctuations for a fluid in a temperature gradient. These fluctuations do not exhibit anomalous scaling, (4) We discuss the implications of these fluctuation results for the distributions of temperature, pressure, and heat current,
(5) We argue that the linearized about the
NESS Landau and Lifshitz fluctuating hy-
drodynamics are not consistent with the long
range nature of the normal stress fluctua-
tions.

We start with the well-known expression
for the small wavenumber behavior of the
temperature fluctuations [9, 11],
\[
\langle |\delta T(k)|^2 \rangle_{NESS} = \frac{k_B T}{\rho D_T (\nu + D_T)} \left( k \nabla T \right)^2 \frac{k^6}{k^6}
\]
Here \( \rho, \nu \) and \( D_T \) are the mass density, the
kinematic viscosity, and thermal diffusivity of
the fluid. This result is valid as long as
\( k > 1/L \), with \( L \) the system size. Here we have
assumed that the temperature gradient is in,
say, the \( z \)-direction so that \( k = k_x^2 + k_y^2 \)
is the magnitude of the wavenumber parallel to
the confining walls. We note that this cor-
relation function is long ranged as indicated
by its \( k^{-4} \) behavior at small wave numbers,
while as the equilibrium temperature fluctu-
ations are localized in space with no singular
behavior of the corresponding Fourier trans-
forms at small wave numbers. In order to
determine the spatial correlation of the temper-
ature fluctuations one must invert the Fourier
transform to obtain the correlation function
\( C_{T,NESS}(r) \) [11]. Using Eq. (2) we find that
the spatial average of the temperature corre-
lations has a strikingly different size depen-
dence than the corresponding equilibrium
temperature correlation. That is
\[
\Delta_{T,NESS} \propto \frac{k_B T}{\rho D_T (\nu + D_T)} L^{4-d} (\nabla T)^2,
\]
where
\[
\tilde{\Delta}_{T,NESS} = \frac{1}{L^d} \int d\mathbf{r} C_{T,NESS}(\mathbf{r}),
\]
where \( L \) is the characteristic system size. In
general we will suppress numerical factors in
spatially averaged quantities. The \( N \) de-
pendence of this spatial average is easily found
to be of order \( N^{(4-d)/d} \) while the equilibrium
quantity would be
\[
\tilde{\Delta}_{T,eq} = \frac{k_B T^2}{L^d \rho c_v},
\]
where \( c_v \) is the specific heat per mass at
constant volume. The \( N \)-dependence quoted
above for Eq. (3) is for fixed \( \nabla T \). Physically,
and experimentally, it may be more reason-
able to use \( \nabla T = \Delta T/L \) with \( \Delta T \) the tem-
perature distance between the fluid confin-
ing plates in the direction of the temperature
gradient and fix \( \Delta T \). In this case the scaling
of Eq. (3) is \( \tilde{\Delta}_{T,NESS} \propto 1/L^{d-2} \propto 1/N^{(d-2)/d} \).
In either case \( \tilde{\Delta}_{T,NESS} \) is large compared to
\( \tilde{\Delta}_{T,eq} \) in the large system size limit. Below
we generally fix \( \Delta T \), to examine the system
size dependence. The theoretical results ap-
pear even more anomalous if the temperature
gradient is fixed.

For three dimensional systems a natural
length, \( l \), that occurs is
\[
l = \frac{k_B T}{\rho D_T (\nu + D_T)}.
\]
For water at STP, $l \approx 3 \times 10^{-9} \text{cm}$. The ratio of the non-equilibrium to equilibrium temperature fluctuations is

$$\frac{\Delta T_{\text{NESS}}}{\Delta T_{\text{eq}}} = \left( \frac{\rho c_v \ell}{n k_B \sigma} \right) n \sigma^3 \left( \frac{\Delta T}{T} \right)^2 \left( \frac{L}{\sigma} \right)^2 \tag{7}$$

with $\sigma$ a molecular diameter. This ratio is generally large if $L \gg \sigma$. Taking the reduced density to be unity, for water this requires, roughly,

$$\frac{L}{\sigma} > \epsilon = T \frac{\Delta T}{\left( n k_B \sigma \rho c_v \ell \right)^{1/2}} \tag{8}$$

or, $L/\sigma > 10$ for typical experiments. \[10, 11\] where $\Delta T/T < 1/5$. This sets the scale of the system size where non-equilibrium fluctuations become dominant. If we assume that the temperature fluctuations in the NESS have a Gaussian distribution, we find, again for three dimensions, that

$$P_{\text{NESS}}[\delta T] \sim \exp \left[ -\frac{L}{2\ell} \left( \frac{\delta T}{(\Delta T)^2} \right)^2 \right] \tag{9}$$

The corresponding probability distribution for equilibrium temperature fluctuations is

$$P_{\text{eq}}[\delta T] \sim \exp \left[ -L^3 \frac{\rho c_v (\delta T)^2}{2k_B T^2} \right]. \tag{10}$$

From a comparison of these two distributions one can see that the non-equilibrium distribution is dominant whenever the inequality given by Eq. (8) is satisfied. From Eq. (9) we see that in non-equilibrium the temperature fluctuations scale as $\delta T \sim 1/L^{1/2} \sim 1/N^{1/6}$ in three-dimensional systems (compared to $1/N^{1/2}$ in equilibrium systems).

Next we consider pressure or normal stress fluctuations in this NESS. It is important to note that the average pressure or normal stress at some point in the fluid has a non-equilibrium term that is proportional to the square of the temperature gradient. This follows from direct calculations, but it can be understood by symmetry arguments as well, since the pressure, for example, is a scalar quantity. The result for the most important non-equilibrium part of the (spatial and thermal) average pressure in three-dimensions is singular in the limit of large systems and is found to be \[14, 15\]

$$P_{\text{NESS}} \propto A \ell L (\nabla T)^2 = A \ell \frac{(\Delta T)^2}{L}, \tag{11}$$

with

$$A = \frac{\rho c_v (\gamma - 1)}{2T} \left[ 1 - \frac{1}{\alpha c_v} \left( \frac{\partial c_v}{\partial T} \right)_P + \frac{1}{\sigma^2} \left( \frac{\partial \alpha}{\partial T} \right)_P \right] \tag{12}$$

Here $c_v, \gamma, \alpha$ are, respectively the specific heat at constant pressure, the ratio of specific heats, and the coefficient of thermal expansion. More generally, the long distance part of the fluctuating pressure is \[14, 15\]

$$\tilde{P}(x) = A [\delta T(x)]^2 \tag{13}$$

Averaging this over the NESS and using Eq. (2) gives Eq. (11):

$$\langle \delta \tilde{P}(x) \rangle = A [\langle (\delta T(x))^2 \rangle]_{\text{NESS}}$$

The pressure fluctuations are

$$\delta \tilde{P}(x) = A [\langle (\delta T(x))^2 \rangle - \langle (\delta T(x))^2 \rangle_{\text{NESS}}]$$
and the non-equilibrium correlation function is \( C_{PP}(x, y) = \langle \delta P(x) \delta \bar{P}(y) \rangle_{NESS} \). Using a Gaussian approximation, we find this correlation function to be,

\[
C_{PP}(x, y) = 2A^2[\langle \delta T(x) \delta T(y) \rangle_{NESS}]^2
\]

The growth of the temperature correlations with distance implies that the spatially averaged \( C_{PP} \) behaves as,

\[
\Delta_{P,NESS} \propto \left[ \frac{\ell A (\Delta T)^2}{L} \right]^2 \propto \frac{1}{L^2}
\]

while in equilibrium,

\[
\Delta_{P,eq} = \frac{n k_B T}{L^3} \left( \frac{\partial P}{\partial n} \right)_s \propto \frac{1}{L^3}
\]

Again, the non-equilibrium fluctuations are large compared to the equilibrium ones at large length scales. Comparing Eqs. (15) and (16) and using Eq. (8), this roughly occurs when \( L/\sigma > \epsilon^4 \), or, in typical experiments, \( L/\sigma > 10^4 \).

If we assume Gaussian behavior then the normal stress fluctuation distributions in the NESS and in equilibrium are

\[
\mathcal{P}_{NESS}[\delta P] \sim \exp\left[ -\frac{L^2}{2} \left( \frac{\delta P}{A \ell (\Delta T)^2} \right)^2 \right]
\]

and

\[
\mathcal{P}_{eq}(\delta P) \sim \exp \left[ -\frac{L^3}{2n k_B T} \left( \frac{\partial n}{\partial P} \right)_s (\delta P)^2 \right].
\]

That is, in three-dimensional non-equilibrium systems the normal stress fluctuations scale as \( \delta P \sim 1/L \sim 1/N^{1/3} \) (compared to \( 1/N^{1/2} \) in equilibrium systems).

As a final example we consider the NESS fluctuations in the heat current in some direction, \( \delta j_{H,\alpha} \), where \( \alpha = (x, y, z) \). There are both linear and nonlinear (analogous to Eq. (13)) contributions to the heat flux. The linear contribution can be obtained by identifying the microscopic fluctuating heat current as \( \delta j_H(x) = -\lambda \nabla \delta T(x) \) with \( \delta T \) the fluctuating temperature gives,

\[
C_{LH,\alpha\beta}(x, y) = \lambda^2 \nabla_{x,\alpha} \nabla_{y,\beta} \langle \delta T(x) \delta T(y) \rangle_{NESS}
\]

The long ranged part of the temperature fluctuation in Eq. (19) is given by Eq. (2), with the final result for \( C_{LH} \) in Fourier space given by,

\[
C_{LH,\alpha\beta}(k) = \frac{c_p k_B T \lambda}{(\nu + D_T) k^2} \hat{k}_\alpha \hat{k}_\beta [k_\parallel \nabla T]^2
\]

This result can also be directly obtained with kinetic theory methods [16]. Here the \( \hat{k} \) denotes unit vectors. The \( 1/k^2 \) dependence in Eq. (20) implies that for systems in \( d \) dimensions, \( C_{LH}(r \to \infty) \sim 1/r^{d-2} \), that is, power law correlations. The angular factors don’t really change this in general. For example, it is easy to see that if in three-dimensions one look in the middle of the fluid at \( x_z = y_z \) and considers correlations along that plane (perpendicular to the direction of the temperature gradient) as a function of \( r_\perp \) one finds that the \( z \)-component of the current fluctuations is \( \sim 1/r_\perp \). Physically this means that
if there is a current fluctuation in the wrong direction then the fluctuations in that entire plane will likely also be in the wrong direction. To obtain a better measure of these correlations we consider the spatial average of $C_L^H(x)$,

$$\bar{\Delta}^L_{H,NESS} \propto \frac{k_B T c_p \lambda}{(D_T + \nu) L^{2-d}} (\nabla T)^2 \propto \frac{(\Delta T)^2}{L^d}$$

(21)

That is, even though the current correlations are of long-range, they are weighted by a factor of $(\nabla T)^2 \propto 1/L^2$, for fixed $\Delta T$, so that qualitatively scales just like $\bar{\Delta}_{H,eq} \propto 1/L^d$ and is, in fact, small compared to $\bar{\Delta}_{H,eq}$ because it is of relative order $(\Delta T/T)^2$.

In analogy with Eq.(13), the non-linear portion of the fluctuating heat current is $j_H(x) \propto \delta T(x) u(x)$, with $u$ the fluctuating fluid velocity. The fluctuation correlation of this quantity gives $C_{NL}^H(x)$. It can be readily computed [9, 11] and in space it decays as $\sim (\nabla T)^2/r^{2d-4} \sim (\Delta T)^2/[L^2 r^{2d-4}]$. To obtain a better measure of these correlations we consider the spatial average of $C_{NL}^H(x)$,

$$\bar{\Delta}^{NL}_{H,NESS} \propto \frac{(\Delta T)^2}{L^{2d-2}}$$

(22)

These correlations are even weaker then those from the linear portion of the fluctuating heat current and can therefore be neglected.

We conclude with a number of remarks:

1. The result for $\bar{\Delta}_{P,NESS}$, Eq.(15), has an important implication. In Landau and Lifshitz (L&L) fluctuating hydrodynamics an input is that the fluctuating stress tensor is local in space and time. Averaging the normal component of the L&L fluctuating stress tensor correlation function in three-dimensions over space and a microscopic time interval leads to a quantity $\bar{\Delta}$ that scales like $\bar{\Delta} \propto 1/L^3$ which should be compared with $\bar{\Delta}_{P,NESS} \propto 1/L^2$. That is, our results indicate that there are important corrections to the usual linearized L&L equations due to the very long-range correlations that exist, in at least some NESS.

In a non-linear fluctuating hydrodynamic description these anomalous terms will be generated by fluctuation or renormalization effects.

2. Compared to the pressure or stress fluctuations both the linear and non-linear heat current fluctuations are of relatively short range. This result is actually important: It is consistent with the local assumption for the fluctuating heat current in the L&L approach. This in part explains why conventional linearized fluctuating hydrodynamics can be used to successfully compute the very long range NESS temperature fluctuations [11, 17].
3. As another measure of just how anomalous the normal stress fluctuations are, note that if a fluctuation as large as the average value of $P_{NESS}$ is considered, Eq.(11), in $P_{NESS} \delta P$ then the probability of that fluctuation is of $O(L^0)$. That is, the normal stress is not a self-averaging quantity.

4. The correlations in a fluid with a constant velocity gradient (that is, the case studied by ECM) are very different (see, for example, [18]) then either a fluid with a temperature gradient, or in a mixture with a concentration gradient. Although there are power law correlations in the velocity gradient case, they are sufficiently weak that the normalized NESS stress-tensor correlation function does scale like $\sim 1/N^{1/2}$. This is true whether the velocity gradient, $\nabla u$, with $u$ the hydrodynamic velocity, is fixed or if $\nabla u = \Delta u/L$ is used, and $\Delta u$ is fixed.

5. In our presentation we have ignored a discussion of the boundaries, that must be present in this NESS. For the case of perfectly conducting walls the temperature fluctuation problem in a bounded geometry has been discussed and solved elsewhere [11].

6. Structurally identical results as those given here for a single component fluid with a temperature gradient are obtained in a fluid mixture with either a concentration gradient or a temperature gradient(see [11] and references therein). In this case, the temperature fluctuations, the concentration fluctuations, and the normal stress, or pressure, fluctuations are all found to obey anomalous statistics.

7. The profound difference between correlations in non-equilibrium and equilibrium systems means that many of the theoretical techniques developed to describe equilibrium systems cannot be applied to non-equilibrium systems. Non-equilibrium quantities do not have virial expansions [6]. A local expansion of the fluxes or currents in terms of powers of the gradients is also not possible [8, 19, 20]. Other techniques such as maximizing an entropy (for example, the so-called max cal method [21]) to obtain a non-equilibrium distribution function may not work, at least in their most naive form.

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