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Statistical mechanics of stationary states. III. Fluctuations in dense fluids with applications to light scattering

David Ronis,* Itamar Procaccia, and Irwin Oppenheim
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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The detailed structure of correlation functions in nonequilibrium stationary states is analyzed. The theory is applied to time-correlation functions and static-correlation functions in simple dense fluids. We find that the breaking of time-reversal symmetry induces important changes that cannot be predicted from local-equilibrium theories. The spectrum of light scattered from argon at 235 K and 1 g/cm^3 subject to a temperature gradient of 0.5 K/cm is computed. We find a pronounced asymmetry in the Brillouin peaks. The static-correlation functions that are usually zero due to time-reversal symmetry are calculated and found to be nonzero and show the existence of a long-range order (1/r decay in physical space). The connection to phenomenology is discussed and a regressionlike hypothesis is shown to be consistent with the microscopic theory once the changes due to symmetry breaking are made.

I. INTRODUCTION

In the first two papers of this series[1,2] (hereafter denoted as I and II), we have discussed some general properties of correlation functions in nonequilibrium stationary states (NESS). We have shown that the very existence of a NESS is associated with the breaking of time-reversal symmetry. The aim of this paper is to study the implications of this symmetry breaking on the detailed structure of the fluctuations in NESS, with emphasis on the changes in the spectrum of light scattered from dense fluids in NESS. We shall show that there is a significant change in the nature of the spectrum and that time-reversal symmetry breaking is a novel source of a long-range order which appears in NESS.

The traditional method for the calculation of time-correlation functions in hydrodynamic systems has been the use of Onsager's regression method.[3] Originally, the method was constructed for equilibrium-correlation functions, and was based on the assumption that small spontaneous fluctuations regress to equilibrium in the same fashion as the macroscopic variables. Thus the linearized macroscopic equations of motion and the static-correlation functions were sufficient to calculate the dynamic-correlation functions.

This method was generalized for the study of time-correlation functions in NESS.[4] There the equations of motion are linearized around the NESS and are then used to obtain a relation between the dynamic- and static-correlation functions. (For details see Ref. 4 or Sec. VI of this paper.) We shall show in this paper that faulty application of this method has led workers in this field to erroneous results. The reason is twofold. First, the time-correlation functions were assumed to be symmetric in time, and we have shown already[1,2] and will reiterate here, that this is not the case. Second, the nonequilibrium static-correlation functions have been evaluated incorrectly. The most common procedure has been to employ the local-equilibrium form for these quantities, and as we show later this is not an appropriate description of the system.

The experimental technique of scattering light from a macroscopic system,[5] offers an extremely accurate probe of long-wavelength (or hydrodynamic) fluctuations. The quantity measured in light scattering is proportional to the Fourier transform (in space and time) of the density-density time-correlation function. Due to time reversal symmetry, the spectrum of light scattered from equilibrium systems is perfectly symmetric in the frequency (shift). We have shown already in I and II that the spectrum of light scattered from NESS does not have this symmetry. The major part of this paper is devoted to the detailed study of this spectrum. We shall show that the asymmetry can be quite pronounced and indicates a preferential coupling of the NESS fluxes to one of the two sound modes at the expense of the other. The spectrum for argon at room temperature in a small temperature gradient is given.

One of the most striking results of this paper is that with the breaking of time-reversal symmetry there is associated an appearance of a long-range order. We shall show that static-correlation functions that vanish in equilibrium due to time-reversal symmetry are nonzero in the NESS and decay like $1/r$ for intermediate values of r.

The organization of this work is as follows: In Sec. II, we summarize the results of paper I that are needed here, and restate the general forms of correlation functions in NESS. In Sec. III, we present a general method for the calculation of the new terms in the correlation functions. This method is applicable to hydrodynamic systems. In Sec. IV, we apply the theory to simple fluids and calculate the transverse-velocity time-correlation function. Section V contains some of the most interesting results of this work. There, we calculate the NESS dynamic structure factor and the spectrum of light scattered from a fluid in NESS. Important changes from equilibrium spectra are predicted. In Sec. VI we tie our theory to phenomenology. We describe the connection to the regression hypotheses and analyze the implications of the breaking of time-reversal symmetry. Among these is the appearance of long-range order, reflected in a $1/k^2$ dependence (for intermediate wave vectors) of some static-correlation functions. Section VII offers summarizing remarks and discussions.

II. GENERAL CONSIDERATIONS

A. Summary of previous results

This section contains the relevant results found in I. As was shown there, when a macroscopic system is close to equilibrium, any arbitrary time-correlation function can be written as

$$\begin{aligned}\langle B(\vec{r},\sigma)C(\vec{r}\,')\rangle_{\rm NE} &= \langle B(\vec{r},\sigma)C(\vec{r}\,')\rangle_{\rm hom} + \langle B(\vec{r},\sigma)C(\vec{r}\,')\hat{\underline{A}}(\vec{r}_1)\rangle * (\vec{r}_1-\vec{r})\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r}) \\ &\quad - \int_0^\infty d\tau\,\langle B(\vec{r},\sigma)C(\vec{r}\,')\underline{I}_T(-\tau)\rangle\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r}) \\ &= \langle B(\vec{r},\sigma)C(\vec{r}\,')\rangle_{\rm hom} + \tfrac{1}{2}\langle[B(\vec{r},\sigma)C(\vec{r}\,')+B(\vec{r})C(\vec{r}\,',-\sigma)]\hat{\underline{A}}(\vec{r}_1)\rangle * (\vec{r}_1-\vec{r})\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r}) \\ &\quad - \tfrac{1}{2}\int_0^\infty d\tau\,\langle[B(\vec{r},\sigma)C(\vec{r}\,')+B(\vec{r})C(\vec{r}\,',-\sigma)]\underline{I}_T(-\tau)\rangle\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r})\,, \end{aligned} \tag{2.1}$$

where the second equality follows from stationarity. In the above expression, the symbols $\langle\;\rangle_{\rm NE}$, $\langle\;\rangle$, and "hom" denote averages in the NESS, equilibrium system, and the homogeneous equilibrium systems where $\underline{\Phi}=\underline{\Phi}(\vec{r})$, respectively, while $\hat{\underline{A}}$ is $\underline{A}-\langle\underline{A}\rangle$. As was discussed in I, $\underline{I}_T$ is the total dissipative flux and $\underline{\Phi}(\vec{r})$ corresponds to the deviation of the conjugate thermodynamic variables from their equilibrium values. Finally, the $*$ in Eq. (2.1) is used to represent integration over $\vec{r}_1$.

The set of variables $\underline{A}(\vec{r},t)$ consists of the slow variables which for our system are the densities of the conserved variables, i.e., $\underline{A}(\vec{r},t)\equiv\{N(\vec{r},t), E(\vec{r},t), \vec{P}(\vec{r},t)\}$ where the number, energy, and momentum densities are given by

$$N(\vec{r},t)\equiv\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j(t)) \tag{2.2a}$$

$$E(\vec{r},t)\equiv\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j(t))\times\left(\frac{p_j^2(t)}{2m}+\frac{1}{2}\sum_{j'\neq j}U(r_{jj'}(t))\right) \tag{2.2b}$$

and

$$\vec{P}(\vec{r},t)\equiv\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j(t))\vec{p}_j(t)\,. \tag{2.2c}$$

The conjugate thermodynamic variables corresponding to this set are

$$\Phi_N(\vec{r},t)\equiv\frac{\beta(\vec{r},t)}{\beta}\mu^*(\vec{r},t)-\mu\,, \tag{2.3a}$$

$$\Phi_E(\vec{r},t)\equiv 1-\beta(\vec{r},t)/\beta\,, \tag{2.3b}$$

$$\vec{\Phi}_P(\vec{r},t)\equiv\beta(\vec{r},t)\vec{v}(\vec{r},t)/\beta\,, \tag{2.3c}$$

where $\beta(\vec{r},t)\equiv[k_BT(\vec{r},t)]^{-1}$, $\vec{v}(\vec{r},t)$ is the fluid velocity, $\mu^*(\vec{r},t)$ is the local chemical potential, and β and μ are the corresponding equilibrium quantities. As has been argued in I the conjugate variables are governed by the usual phenomenological hydrodynamic equations.

The hydrodynamic variables, $\underline{A}(\vec{r},t)$ are the densities of conserved quantities and thus

$$\dot{\underline{A}}(\vec{r},t)\equiv\frac{\partial\underline{A}(\vec{r},t)}{\partial t}=-\vec{\nabla}\cdot\underline{J}(\vec{r},t)\,, \tag{2.4}$$

where the currents

$$\underline{J}(\vec{r},t) \equiv \{\vec{P}(\vec{r},t)/m,\ \vec{J}_E(\vec{r},t),\ \vec{\tau}(\vec{r},t)\}$$

with $\vec{J}_E(\vec{r},t)$ and $\vec{\tau}(\vec{r},t)$ being the microscopic energy current and stress tensor, respectively. As we discussed in I, the total dissipative fluxes are spatial integrals of the dissipative flux densities:

$$\underline{I}(\vec{r},t) \equiv \underline{\vec{J}}(\vec{r},t) - \underline{\vec{M}}(\vec{r}\,|\,\vec{r}\,';t) * \underline{\hat{A}}(\vec{r}\,',t)\,, \tag{2.5}$$

where

$$\underline{\vec{M}}(\vec{r}\,|\,\vec{r}\,';t) \equiv \langle \underline{\vec{J}}(\vec{r},t)\underline{\hat{A}}(\vec{r}_1)\rangle * \underline{K}^{-1}(\vec{r}_1\,|\,\vec{r}\,';t) \tag{2.6a}$$

and

$$\langle \underline{\hat{A}}(\vec{r},t)\underline{\hat{A}}(\vec{r}_1)\rangle * \underline{K}^{-1}(\vec{r}_1\,|\,\vec{r}\,';t) \equiv \delta(\vec{r}-\vec{r}\,')\underline{1}\,. \tag{2.6b}$$

We remind the reader that the dissipative fluxes are orthogonal to the slow variables in the sense that

$$\langle \underline{I}(\vec{r},t)\underline{\hat{A}}(\vec{r}_1)\rangle = 0\,. \tag{2.7}$$

For times t larger than some microscopic decay time τ_D (of the order 10^{-12} sec), is has been argued[6] that the quantity $\underline{\vec{M}}(\vec{r}\,|\,\vec{r}\,',t)$ becomes constant in time and will then be denoted by $\underline{\vec{M}}(\vec{r}\,|\,\vec{r}\,')$.

The significance of $\underline{\vec{M}}(\vec{r}\,|\,\vec{r}\,')$ lies in the fact that it governs[6] the macroscopic relaxation. That is for $t > \tau_D$

$$\dot{\underline{a}}(\vec{r},t) = -\vec{\nabla}\cdot\underline{\vec{M}}(\vec{r}\,|\,\vec{r}\,') * \hat{\underline{a}}(\vec{r}\,',t)\,, \tag{2.8}$$

where $\underline{a}(\vec{r},t)$ is the nonequilibrium average of $\underline{A}(\vec{r},t)$. It has been shown that Eq. (2.8) is equivalent to the linearized hydrodynamic equations and is correct to second order in the smallness parameter characterizing $\dot{\underline{A}}$. Finally, using the fact that the A's are slow allows us to set the time appearing in $\underline{\vec{M}}$ in Eq. (2.5) to zero thereby obtaining[6]

$$\vec{I}_N(\vec{r},t) = 0 \tag{2.9a}$$

$$\vec{I}_E(\vec{r},t) = \vec{J}_E(\vec{r},t) - (h/m\rho)\vec{P}(\vec{r},t) \tag{2.9b}$$

and

$$\vec{I}_P(\vec{r},t) = \vec{\tau}(\vec{r},t) - \left[\left(\frac{\partial p_h}{\partial \rho}\right)_e \hat{N}(\vec{r},t) + \left(\frac{\partial p_h}{\partial e}\right)_\rho \hat{E}(\vec{r},t)\right] - \langle\vec{\tau}\rangle\,, \tag{2.9c}$$

to lowest order in the slowness parameter. In the last equations, h, ρ, and e are the equilibrium enthalpy, number, and energy densities, and p_h is the pressure, respectively.

This completes our summary of the previous results which will be used in this work.

B. Correlation functions in NESS

As has already been discussed,[1] we consider systems which are translationally invariant and isotropic at equilibrium. This implies that the various terms appearing in Eq. (2.1) depend on $\vec{r} - \vec{r}\,'$ and parametrically on $\vec{r}$ only through the $\beta\underline{\Phi}(\vec{r})$. It is thus more convenient to consider a Fourier representation of the correlation functions:

$$\underline{C}(\vec{k},\sigma\,|\,\vec{r}) \equiv \int d\Delta\vec{r}\, e^{i\vec{k}\cdot\Delta\vec{r}} \langle \underline{\hat{A}}(\vec{r},\sigma)\underline{\hat{A}}(\vec{r}-\Delta\vec{r})\rangle_{\rm NE}\,. \tag{2.10}$$

Proceeding as in I we find from Eq. (2.1) that

$$\underline{C}(\vec{k},\sigma\,|\,\vec{r}) = \underline{C}^{\rm hom}(\vec{k},\sigma\,|\,\vec{r}) + \underline{C}^{nl}(\vec{k},\sigma\,|\,\vec{r}) + \underline{W}(\vec{k},\sigma\,|\,\vec{r})\,, \tag{2.11}$$

where

$$\underline{C}^{\rm hom}(\vec{k},\sigma\,|\,\vec{r}) \equiv (1/V)\langle \underline{A}_{\vec{k}}(\sigma)\underline{A}_{-\vec{k}}\rangle_{\rm hom}\,, \tag{2.12a}$$

$$\underline{C}^{nl}(\vec{k},\sigma\,|\,\vec{r}) \equiv \tfrac{1}{2}\int d\Delta\vec{r}\,d\vec{r}_1\, e^{i\vec{k}\cdot\Delta\vec{r}} \times\langle[\underline{\hat{A}}(\vec{r},\sigma)\underline{\hat{A}}(\vec{r}-\Delta\vec{r}) + \underline{\hat{A}}(\vec{r})\underline{\hat{A}}(\vec{r}-\Delta\vec{r},-\sigma)] \times\underline{\hat{A}}(\vec{r}_1)\rangle(\vec{r}_1-\vec{r})\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r})\,, \tag{2.12b}$$

and

$$\underline{W}(\vec{k},\sigma\,|\,\vec{r}) \equiv \frac{-1}{2V}\int_0^\infty d\tau\langle[\underline{A}_{\vec{k}}(\sigma)\underline{A}_{-\vec{k}} + \underline{A}_{\vec{k}}\underline{A}_{-\vec{k}}(-\sigma)] \times\underline{I}_T(-\tau)\rangle\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r})\,. \tag{2.12c}$$

In the last expressions, $\underline{A}_{\vec{k}}(\sigma)$ denotes the space Fourier transform [cf. Eq. (2.10)] of $\underline{A}(\vec{r},\sigma)$, etc. We remark that, if one considers the (N,N) component of Eq. (2.11), then Eq. (4.18) of paper I is obtained.

The various terms on the right-hand side of Eq. (2.11) may be interpreted as in I. From Eq. (2.12a) we see that $\underline{C}^{\rm hom}(\vec{k},\sigma\,|\,\vec{r})$ is given in terms of an equilibrium time-correlation function in a system where the thermodynamic state properties correspond to those in the NESS at the point $\vec{r}$. As such, the standard techniques for computing their small-k and large-σ forms may be used. In fact, using Eq. (2.6a), one may show that

$$\dot{\underline{C}}^{\rm hom}(\vec{k},\sigma\,|\,\vec{r}) = i\vec{k}\cdot\underline{\vec{M}}(\vec{k}\,|\,\vec{r})\cdot\underline{C}^{\rm hom}(\vec{k},\sigma\,|\,\vec{r})\,, \tag{2.13}$$

where $\underline{\vec{M}}(\vec{k}\,|\,\vec{r})$ is the Fourier transform of the long-time form of $\underline{\vec{M}}(\vec{r}\,|\,\vec{r}\,',t)$ evaluated in the appropriate homogeneous system. Thus

$$\underline{C}^{\rm hom}(\vec{k},\sigma\,|\,\vec{r}) = \exp[i\vec{k}\cdot\underline{\vec{M}}(\vec{k}\,|\,\vec{r})\sigma]\cdot\underline{C}^{\rm hom}(\vec{k},\sigma=0\,|\,\vec{r})\,. \tag{2.14}$$

Equation (2.14) is the Onsager regression hypothesis form for equilibrium time-correlation functions and is valid for times larger than τ_D and to second order in k.

The second term appearing on the right-hand side of Eq. (2.11) is a nonlocality correction associated with local-equilibrium averages. While these nonlocality corrections are unimportant for static quantities [see Eq. (3.12) of paper II], the nonlocality correction here may be important for large σ since the correlation length associated with this term may have time to grow. In principle the calculation of $\underline{C}^{nl}(\vec{k},\sigma\,|\,\vec{r})$ may be carried out using mode-coupling techniques[7] (i.e., multilinear hydrodynamics). To see this we note that Eq. (2.12b) can be reexpressed as

$$\underline{C}^{nl}(\vec{k},\sigma\,|\,\vec{r})=\frac{i}{2V}\lim_{\vec{k}'\to 0}\vec{\nabla}_{\vec{k}'}\cdot\langle[\underline{A}_{\vec{k}+\vec{k}'}(\sigma)\underline{A}_{-\vec{k}}+\underline{A}_{\vec{k}+\vec{k}'}\underline{A}_{-\vec{k}}(-\sigma)]\underline{A}_{-\vec{k}'}\rangle\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r})\,, \quad (2.15)$$

where the equilibrium translational invariance has been used. The equilibrium correlations appearing in Eq. (2.15) are between linear and bilinear variables and are thus subject to mode-coupling analysis.

As we shall now show, Eq. (2.15) can be evaluated without resorting to mode-coupling theory when one is interested in the diagonal elements of $\underline{C}^{nl}$ (i.e., in autocorrelation functions). The proof of this follows in exactly the same fashion as used in obtaining Eq. (4.15) of paper I. Starting with Eq. (2.12b) we have

$$C^{nl}_{\alpha\alpha}(\vec{k},\sigma\,|\,\vec{r})=\frac{1}{2V}\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 e^{i\vec{k}\cdot\vec{r}_{12}}\langle[\hat{A}_\alpha(\vec{r}_1,\sigma)\hat{A}_\alpha(\vec{r}_2)+\hat{A}_\alpha(\vec{r}_1)\hat{A}_\alpha(\vec{r}_2,-\sigma)]\underline{\hat{A}}(\vec{r}_3)\rangle\,(\vec{r}_3-\vec{r}_1)\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r})\,, \quad (2.16)$$

where translational invariance was used. Making use of time-reversal and inversion symmetries and the fact that the product of the signatures for this transformation is always equal to 1 for the hydrodynamic variables (cf. Sec. IV of paper I) Eq. (2.16) becomes

$$C^{nl}_{\alpha\alpha}(\vec{k},\sigma\,|\,\vec{r})$$

$$=\frac{i}{2V}\vec{\nabla}_{\vec{k}}\cdot\langle A_{\alpha,\vec{k}}(\sigma)A_{\alpha,-\vec{k}}\underline{\hat{A}}_T\rangle\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r}) \quad (2.17a)$$

$$=\frac{i}{2V}\vec{\nabla}_{\vec{k}}\cdot\left(\frac{\partial C^{\text{hom}}_{\alpha\alpha}(\vec{k},\sigma\,|\,\vec{r})}{\partial\beta\underline{\Phi}(\vec{r})}\right)_{\beta\underline{\Phi}=0}\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r})\,. \quad (2.17b)$$

Hence, Eq. (2.17b) in conjunction with Eq. (2.14) may be used to evaluate the nonlocality correction for NESS autocorrelation functions which are the subject of this paper.

The last term on the right-hand side of Eq. (2.11) is not simply related to equilibrium autocorrelation functions. Nonetheless, for NESS autocorrelation functions, it can be reexpressed in a simpler form by using time-reversal and inversion symmetries in Eq. (2.12c). The result is

$$W_{\alpha\alpha}(\vec{k},\sigma\,|\,\vec{r})=-\frac{1}{2V}\int_{-\infty}^{+\infty}d\tau\,\langle A_{\alpha,\vec{k}}(\sigma)\times A_{\alpha,-\vec{k}}\underline{I}_T(-\tau)\rangle\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r})\,. \quad (2.18)$$

In Sec. III we present a theory of the long-time and wavelength form of Eq. (2.18) in dense systems.

III. CALCULATION OF $\underline{W}$(k, σ | r) FOR AUTOCORRELATION FUNCTIONS

In I and II some information concerning $\underline{W}$ was obtained by examining its symmetries and low-density sum rules. Of much greater interest is the long-time dependence of long-wavelength fluctuations, since these play an important role in scattering experiments.[5]

In this section, the small-k and long-σ behavior of

$$\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma)\equiv\int_{-\infty}^{\infty}d\tau\,\langle A_{\alpha,\vec{k}}(\sigma)A_{\gamma,-\vec{k}}I_{\delta,T}(-\tau)\rangle \quad (3.1)$$

is investigated. The results will then be used [cf. Eq. (2.18)] to arrive at an expression for W. The function $\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma)$ has a number of symmetry properties which may be proved in the usual fashion[5]:

$$\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma)=\Lambda^{\alpha\gamma\delta}(-\vec{k},\sigma)^*\,, \quad (3.2a)$$

$$\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma)=-\lambda_\alpha\lambda_\gamma\lambda_\delta\Lambda^{\alpha\gamma\delta}(-\vec{k},\sigma)\,, \quad (3.2b)$$

$$\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma)=-\epsilon_\alpha\epsilon_\beta\epsilon_\delta\Lambda^{\alpha\gamma\delta}(\vec{k},-\sigma)\,, \quad (3.2c)$$

where the superscript * denotes complex conjugation, and λ_α and ϵ_α are the signatures of A_α under inversion and time reversal, respectively.

The calculation of $\Lambda^{\alpha\gamma\sigma}(\vec{k},\sigma)$ follows from the separation of time-scale assumption which is equivalent to the statement that correlations involving the dissipative fluxes decay quickly. We use this to advantage by writing the equation of motion for Λ in a form which exhibits as many dissipative fluxes as is possible. Thus, using Eqs. (3.2) and (2.4)–(2.6) we find

$$\dot{\Lambda}^{\alpha\gamma\delta}(\vec{k},\sigma)=M_{\vec{k}}^{\alpha\epsilon}(\sigma)\Lambda^{\epsilon\gamma\delta}(\vec{k},\sigma)+i\vec{k}\cdot\Omega^{\alpha\gamma\delta}(\vec{k},\sigma)\,, \tag{3.3}$$

where

$$\Omega^{\alpha\gamma\delta}(\vec{k},\sigma)\equiv\int_{-\infty}^{\infty}d\tau\langle I_{\alpha,\vec{k}}(\sigma)A_{\gamma,-\vec{k}}I_{\delta,T}(-\tau)\rangle\,, \tag{3.4}$$

$$M_{\vec{k}}^{\alpha\epsilon}(\sigma)\equiv i\vec{k}\cdot\{\langle \underline{J}_{\vec{k}}(\sigma)\underline{A}_{-\vec{k}}\rangle\cdot\langle \underline{A}_{\vec{k}}(\sigma)\underline{A}_{-\vec{k}}\rangle^{-1}\}^{\alpha\epsilon}\,, \tag{3.5}$$

and where the convention that repeated greek indices are to be summed over is adopted. The quantity appearing within the curly brackets in Eq. (3.5) is the Fourier transform of Eq. (2.6). It has been studied extensively for long times and long wavelengths by Selwyn and Oppenheim.[6] The main results concerning this quantity are that for small k (i.e., to order k^2) it becomes a constant for $\sigma>\tau_D$ and that it governs the macroscopic relaxation of $\underline{a}_{\vec{k}}(t)$ [cf. Eq. (2.8)]. Thus writing the equation of motion for Λ in the form given by Eq. (3.3) is useful since it makes part of its "macroscopic" evolution explicit.

Finally, writing the equation of motion for Λ in the form of Eq. (3.3) has the additional advantage that the "nonmacroscopic" part Ω appears multiplied by k and is thus small. On the other hand, one can easily verify that some of the Λ's diverge as $k\to 0$ [cf. Eq. (3.1)]. Therefore, we expect that the "macroscopic" part of Λ will be more important at long wavelengths.

For convenience, we rewrite Eq. (3.3) in matrix notation. We do so by regarding δ as an index that is fixed from the start (i.e., we consider couplings to $\vec{I}_E$ and $\vec{I}_P$ separately), and thus obtain

$$\underline{\dot{\Lambda}}^{\delta}(\vec{k},\sigma)=\underline{M}_{\vec{k}}(\sigma)\underline{\Lambda}^{\delta}(\vec{k},\sigma)+i\vec{k}\cdot\underline{\Omega}^{\delta}(\vec{k},\sigma)\,. \tag{3.6}$$

For $\sigma>\tau_D$ we can drop the σ dependence of $\underline{M}_{\vec{k}}(\sigma)$ and formally solve Eq. (3.6) for $\underline{\Lambda}^{\delta}$:

$$\underline{\Lambda}^{\delta}(\vec{k},\sigma)=\exp[\underline{M}_{\vec{k}}\sigma]\underline{\Lambda}^{\delta}(\vec{k},\sigma=0)+\int_0^{\sigma}d\tau[\exp\{\underline{M}_{\vec{k}}(\sigma-\tau)\}i\vec{k}\cdot\underline{\Omega}^{\delta}(\vec{k},\tau)]\,. \tag{3.7}$$

As was mentioned above, $\underline{\Lambda}$ may diverge as $k\to 0$, and for those cases the first term on the right-hand side of (3.7) should be more important at small k. We shall show, however, that for other cases the first term on the right-hand side of Eq. (3.7) vanishes by symmetry and then all the contribution arises from the second term which we now calculate.

Using Eq. (3.4), we may find an expression for the time dependence of $\underline{\Omega}^{\delta}(\vec{k},\sigma)$, at small k. Noting that for $\sigma>\tau_D$

$$\underline{\Omega}^{\delta}(\vec{k},\sigma)=\int_{-\infty}^{\infty}d\tau\,\langle \underline{I}_{\vec{k}}\underline{A}_{-\vec{k}}(-\sigma)I_{\delta,T}(-\tau)\rangle\,, \tag{3.8}$$

where $\underline{I}_{\vec{k}}(0)$ should be calculated using the long-time form of $\underline{M}(\vec{r}\,|\,\vec{r}\,';\sigma)$. The difference between this form and the forms (2.9) using $\underline{M}(\vec{r}\,|\,\vec{r}\,',0)$ is negligible to the pertinent orders in k. We see that $\underline{\Omega}^{\delta}(\vec{k},\sigma)$ may still have a "slow" part. In fact, at $k=0$, $\underline{\Omega}$ is constant in σ, since the A's are conserved. We use Eq. (3.8) to find the equation of motion

$$i\vec{k}\cdot\underline{\dot{\Omega}}^{\delta}(\vec{k},\sigma)=-i\vec{k}\cdot\underline{\Omega}^{\delta}(\vec{k},\sigma)\underline{M}^{T}_{-\vec{k}}(-\sigma)+i\vec{k}i\vec{k}:\int_{-\infty}^{\infty}d\tau\,\langle \underline{I}_{\vec{k}}\underline{I}_{-\vec{k}}(-\sigma)I_{\delta,T}(-\tau)\rangle\,, \tag{3.9}$$

where the superscript T denotes matrix transposition. Using Eq. (3.5) and time-reversal and inversion symmetries, it is easily shown that

$$\underline{M}_{-\vec{k}}(-\sigma)=-\underline{M}_{\vec{k}}(\sigma) \tag{3.10}$$

and thus Eq. (3.9) becomes (for $\sigma>\tau_D$)

$$i\vec{k}\cdot\underline{\dot{\Omega}}^{\delta}(\vec{k},\sigma)=i\vec{k}\cdot\underline{\Omega}^{\delta}(\vec{k},\sigma)\underline{M}_{\vec{k}}^{T}\,, \tag{3.11}$$

where we have used the long-time form of $\underline{M}_{\vec{k}}(\sigma)$. We have neglected the second term on the right-hand side of Eq. (3.9) since the correlation function appearing there contains only dissipative fluxes. In addition it is at least $O(k^2)$ and is of the same order of magnitude as the corrections that are omitted when the long-time form of $\underline{M}_{\vec{k}}(\sigma)$ is used.

The solution to Eq. (3.11) is

$$i\vec{k}\cdot\underline{\Omega}^{\delta}(\vec{k},\sigma)=i\vec{k}\cdot\underline{\Omega}^{\delta}(\vec{k},\sigma=0)\exp[\underline{M}_{\vec{k}}^{T}\sigma]\,. \tag{3.12}$$

Substituting Eq. (3.12) in Eq. (3.7) yields

$$\underline{\Lambda}^{\delta}(\vec{k},\sigma)=\exp[\underline{M}_{\vec{k}}\sigma]\underline{\Lambda}^{\delta}(\vec{k},\sigma=0)+\int_0^{\sigma}d\tau\exp[\underline{M}_{\vec{k}}(\sigma-\tau)]\,i\vec{k}\cdot\underline{\Omega}^{\delta}(\vec{k},\tau=0)\times\exp[\underline{M}_{\vec{k}}^{T}\tau],\quad \sigma>\tau_D\,. \tag{3.13}$$

This expression shows that all the time dependence of $\underline{\Lambda}^{\delta}$ is given in terms of the macroscopic evolution matrix $\underline{M}_{\vec{k}}$.

The matrix $\underline{M}_{\vec{k}}$ is diagonalizable; i.e., for some matrix $\underline{\tilde{P}}_{\vec{k}}$:

$$\underline{\tilde{P}}_{\vec{k}}^{-1}\cdot\underline{M}_{\vec{k}}\cdot\underline{\tilde{P}}_{\vec{k}}=\underline{\xi}(\vec{k})\,, \tag{3.14}$$

where $\underline{\xi}$ is a diagonal matrix. We note that in general the matrix elements are complex, $\mathrm{Re}(\xi_{\alpha,\alpha}(k))<0$ (in stable systems), and $\xi_{\alpha,\alpha}(k)\to 0$ as $k\to 0$. Using Eq. (3.13) in Eq. (3.12) gives

$$\underline{\Lambda}^{\delta}(\vec{k},\sigma)=\underline{\tilde{P}}_{\vec{k}}\Big(e^{\underline{\xi}(\vec{k})\sigma}(\underline{\tilde{P}}_{\vec{k}}^{-1})\underline{\Lambda}^{\delta}(\vec{k},\sigma=0)+\int_0^{\sigma}d\tau\, e^{\underline{\xi}(\sigma-\tau)}(\underline{\tilde{P}}_{\vec{k}}^{-1})i\vec{k}\cdot\underline{\Omega}^{\delta}(\vec{k},\tau=0)\times(\underline{\tilde{P}}_{\vec{k}}^{-1})^{T}e^{\underline{\xi}\tau}\underline{\tilde{P}}_{\vec{k}}^{T}\Big). \tag{3.15}$$

The integration in Eq. (3.15) can be now easily performed. Without going into the detailed structure of $\underline{M}_{\vec{k}}$ we see that the first term on the right-hand side of Eq. (3.15) decays exponentially whereas the second decays as either a pure exponential or as σ times an exponential. The detailed forms of the various terms are considered in the subsequent section.

We now turn our attention to the static quantities that appear in Eq. (3.15). From Eq. (3.1) we have

$$\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma=0)=(1-\epsilon_{\alpha}\epsilon_{\gamma}\epsilon_{\delta})\times\int_0^{\infty}d\tau\,\langle A_{\alpha,\vec{k}}A_{\gamma,-\vec{k}}I_{\delta,T}(-\tau)\rangle\,, \tag{3.16}$$

which follows by using time-reversal symmetry. In order to evaluate $\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma=0)$ we define

$$\Gamma^{\alpha\gamma\delta}(\vec{k},t)\equiv\langle A_{\alpha,\vec{k}}A_{\gamma,-\vec{k}}I_{\delta,T}(-t)\rangle=\langle A_{\alpha,\vec{k}}(t)A_{\gamma,-\vec{k}}(t)I_{\delta,T}\rangle\,, \tag{3.17}$$

where the second equality follows from time translational invariance. Using the techniques described above, an equation of motion for $\underline{\Gamma}$ is easily found. For $t>\tau_D$:

$$\dot{\underline{\Gamma}}^{\delta}(\vec{k},t)=\underline{M}_{\vec{k}}\cdot\underline{\Gamma}^{\delta}(\vec{k},t)+\underline{\Gamma}^{\delta}(\vec{k},t)\cdot\underline{M}_{\vec{k}}^{\dagger}+i\vec{k}\cdot[\langle\underline{I}_{\vec{k}}(t)\underline{A}_{-\vec{k}}(t)I_{\delta,T}\rangle-\langle\underline{A}_{\vec{k}}(t)\underline{I}_{-\vec{k}}(t)I_{\delta,T}\rangle]\,, \tag{3.18}$$

where the symbol $\dagger$ denotes Hermetian conjunction and where the long-time forms of $\underline{M}_{\vec{k}}(t)$ are used. The formal solution of the above equations is

$$\underline{\Gamma}^{\delta}(\vec{k},t)=\exp[\underline{M}_{\vec{k}}t]\cdot\underline{\Gamma}^{\delta}(\vec{k},t=0)\exp[\underline{M}_{\vec{k}}^{\dagger}t]+\int_0^{t}d\tau\exp[\underline{M}_{\vec{k}}(t-\tau)]\times i\vec{k}\cdot\langle\{\underline{I}_{\vec{k}}\underline{A}_{-\vec{k}}-\underline{A}_{\vec{k}}\underline{I}_{-\vec{k}}\}I_{\delta,T}(-\tau)\rangle\times\exp[\underline{M}_{\vec{k}}^{\dagger}(t-\tau)]\,, \tag{3.19}$$

which when used in conjunction with Eqs. (3.17) and (3.16) yields after some simple manipulations of the integrals

$$\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma=0)=(1-\varepsilon_{\alpha}\varepsilon_{\gamma}\varepsilon_{\delta})\Big(\int_0^{\infty}d\tau\exp[\underline{M}_{\vec{k}}\tau]\Big\{\underline{\Gamma}^{\delta}(\vec{k},t=0)+\int_0^{\infty}dt\, i\vec{k}\cdot\langle[\underline{I}_{\vec{k}}\underline{A}_{-\vec{k}}-\underline{A}_{\vec{k}}\underline{I}_{-\vec{k}}]I_{\delta,T}(-t)\rangle\Big\}\exp[\underline{M}_{\vec{k}}^{\dagger}\tau]\Big)^{\alpha\gamma}. \tag{3.20}$$

This last expression is the final result for $\Lambda^{\alpha\gamma\delta}(\vec{k},\sigma=0)$. Noting that $\underline{M}_{\vec{k}}\to 0$ as $k\to 0$, we see the source of the divergence in this quantity as $k\to 0$. The parts of the right-hand side of Eq. (3.20) not containing $\underline{M}_{\vec{k}}$ explicitly do not require a separate analysis. They are typical quantities which appear in nonlinear response theory as applied to conserved variables.[6(b)] They are well behaved as $k\to 0$ and it has been shown that $\underline{\Gamma}^{\delta}(\vec{k},\sigma=0)$ appears as the coefficients of the nonlinear reversible (or Euler) part of the hydrodynamic equations. The remaining quantities correspond to the nonlinear dissipative coefficients. In Sec. IV, the detailed form of these quantities will be given for a simple fluid.

The other static quantity that appears in Eq. (3.15) is

$$\Omega^{\alpha\gamma\delta}(\vec{k},\sigma=0)=(1+\varepsilon_{\alpha}\varepsilon_{\gamma}\varepsilon_{\delta})\int_0^{\infty}d\tau\,\langle I_{\alpha,\vec{k}}A_{\gamma,-\vec{k}}I_{\delta,T}(-\tau)\rangle \tag{3.21}$$

where the equality follows by using time-reversal invariance in Eq. (3.4). This shows that $\Omega^{\alpha\gamma\delta}(\vec{k},\sigma=0)$ is related to terms which appear on the right-hand side of Eq. (3.20) and hence the discussion presented above applies.

We remind the reader that the aim of this section is to evaluate Eq. (2.18), the new contribution to the autocorrelation function. Combining Eqs. (2.18), (3.1), (3.13), (3.20), and (3.21) gives

$$[W_{\alpha\alpha}(\vec{k},\sigma\,|\,\vec{r}) = -\frac{1}{2V}\Big\{[\exp(\underline{M}_{\vec{k}}\sigma)]^{\alpha\gamma}(1-\varepsilon_\gamma\varepsilon_\alpha\varepsilon_\delta)\Big(\int_0^\infty d\tau\,\exp(\underline{M}_{\vec{k}}\tau)[\underline{\Gamma}^\delta(\vec{k},0) + \int_0^\infty dt\, i\vec{k}\cdot\langle(\underline{I}_{\vec{k}}\underline{A}_{-\vec{k}} - \underline{A}_{-\vec{k}}\underline{I}_{-\vec{k}})I_{\delta,T}(-t)\rangle]\exp(\underline{M}_{\vec{k}}^\dagger\tau)\rangle\Big)^{\gamma\alpha} + \int_0^\sigma d\tau[\exp(\underline{M}_{\vec{k}}(\sigma-\tau))]^{\alpha\gamma} i\vec{k}\cdot(1+\varepsilon_\gamma\varepsilon_\phi\varepsilon_\delta) \times\int_0^\infty dt\,\langle I_{\gamma,\vec{k}}A_{\phi,-\vec{k}}I_{\delta,T}(-t)\rangle[\exp(\underline{M}_{\vec{k}}^T t)]^{\phi\alpha}\Big\}\cdot\vec{\nabla}\beta\Phi_\delta(\vec{r})\,, \tag{3.22}$$

where all repeated greek indices, except α, should be summed. With the help of Eq. (3.14) the integrals appearing in Eq. (3.22) may be performed. This form for $W_{\alpha\alpha}$ is valid for $\sigma > \tau_D$ and for long-wavelength phenomena. To be more specific, we note that k appears in Eq. (3.22) in two different fashions. In the first place we have the k dependence of $\underline{M}_{\vec{k}}$ which always appears multiplied by some microscopically long time (i.e., σ or a time integration variable $>\tau_D$) in an exponent. The other manner in which k appears is via the explicit k dependence associated with the static functions $\underline{\Gamma}(\vec{k},0)$ and $\underline{\Omega}(\vec{k},0)$. As was discussed earlier, these quantities do not diverge in k nor involve any long-time contributions. We are thus safe in expanding them in k, as they never appear multiplied by some possibly long time. In fact, for the remainder of this work, we shall consider only the leading nonvanishing contributions of these factors.

In the following sections we evaluate the new term appearing in the expression for the NESS autocorrelation functions for hydrodynamic fluctuations in simple fluids.

IV. APPLICATIONS TO SIMPLE FLUIDS: TRANSVERSE VELOCITY FLUCTUATIONS

A. Preliminaries

In the remaining parts of this work we consider only hydrodynamic systems and thus the set of variables are the number, energy, and momentum densities. Further, we may always choose the coordinate frame such that k is pointing in the x direction (i.e., $\vec{k}=\vec{e}_1 k$). Thus $P^x_{\vec{k}}$ is the longitudinal component of the momentum while the y and z components are the transverse ones.

In such a system the detailed structure of $\underline{M}_{\vec{k}}$ is given in Refs. 5 and 6(a). The result is

$$\underline{M}_{\vec{k}} = \begin{pmatrix} 0 & 0 & ik/m & 0 & 0 \\ -k^2\kappa_\rho & -k^2\kappa_e & ikh/m\rho & 0 & 0 \\ ik\chi_\rho & ik\chi_e & -k^2\nu_l & 0 & 0 \\ 0 & 0 & 0 & -k^2\nu_t & 0 \\ 0 & 0 & 0 & 0 & -k^2\nu_t \end{pmatrix}, \tag{4.1}$$

where we remind the reader that m is the particle mass, h is the equilibrium enthalpy density, ρ is the equilibrium number density,

$$\chi_\rho \equiv \left(\frac{\partial p_h}{\partial\rho}\right)_e, \quad \chi_e \equiv \left(\frac{\partial p_h}{\partial e}\right)_\rho; \qquad \kappa_\rho \equiv \lambda\left(\frac{\partial T}{\partial\rho}\right)_e, \quad \kappa_e \equiv \lambda\left(\frac{\partial T}{\partial e}\right)_\rho; \qquad \nu_l \equiv (\zeta + \tfrac{4}{3}\eta)/m\rho\,, \quad \nu_t \equiv \eta/(m\rho)\,; \tag{4.2}$$

and where λ, ζ, and η are the thermal conductivity, and bulk and shear viscosities, respectively. In Eq. (4.1) we have labeled the rows and columns according to the choice $\underline{A}_{\vec{k}} = [N_{\vec{k}}, E_{\vec{k}}, P^x_{\vec{k}}, P^y_{\vec{k}}, P^z_{\vec{k}}]^T$.

In this section we examine fluctuations in the absence of convection, and thus only the terms with $\delta = E$ in Eq. (3.22) arise. Using Eq. (3.17) we have

$$\underline{\Gamma}^E(\vec{k},0) = \langle\underline{A}_{\vec{k}}\underline{A}_{-\vec{k}}\vec{I}_{E,T}\rangle = \begin{pmatrix} 0 & 0 & \theta_\rho\vec{e}_1 & \theta_\rho\vec{e}_2 & \theta_\rho\vec{e}_3 \\ 0 & 0 & \theta_e\vec{e}_1 & \theta_e\vec{e}_2 & \theta_e\vec{e}_3 \\ \theta_\rho\vec{e}_1 & \theta_e\vec{e}_1 & 0 & 0 & 0 \\ \theta_\rho\vec{e}_2 & \theta_e\vec{e}_2 & 0 & 0 & 0 \\ \theta_\rho\vec{e}_3 & \theta_e\vec{e}_3 & 0 & 0 & 0 \end{pmatrix} + O(k^2)\,, \tag{4.3}$$

where as was discussed at the end of Sec. III, only the leading-order terms in k are kept. In obtaining Eq. (4.3) time-reversal and rotational invariances were used and

$$\theta_\alpha \equiv \tfrac{1}{3}\langle A_{\alpha,T}\vec{P}_T\cdot\vec{I}_{E,T}\rangle\,, \quad \alpha = N, E\,. \tag{4.4}$$

Using Eqs. (4.4) and (2.9b) gives

$$\theta_\rho = \langle N_T\rangle k_B T\left(\frac{\partial h/\rho}{\partial\beta\mu}\right)_{\beta,V},$$
$$\theta_e = -\langle N_T\rangle k_B T\left(\frac{\partial h/\rho}{\partial\beta}\right)_{\beta\mu,V}; \qquad (4.5)$$

which may easily be shown using the standard equilibrium fluctuation theories.

The last quantity which must be considered is $\underline{\Omega}^E(\vec{k},0)$. To lowest order in k

$$i\vec{k}\cdot\underline{\Omega}^E(\vec{k},0)=\begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ \Delta_\rho ik & \Delta_e ik & 0 & 0 & 0 \\ 0 & 0 & \Delta_{p_l} ik\vec{e}_1 & (\Delta_{p_l}-2\Delta_{p_t})ik\vec{e}_2 & (\Delta_{p_l}-2\Delta_{p_t})ik\vec{e}_3 \\ 0 & 0 & \Delta_{p_t} ik\vec{e}_2 & \Delta_{p_t} ik\vec{e}_1 & 0 \\ 0 & 0 & \Delta_{p_t} ik\vec{e}_3 & 0 & \Delta_{p_t} ik\vec{e}_1 \end{pmatrix} + O(k^2), \qquad (4.6)$$

where we have used Eq. (3.21), time reversal, and isotropy in evaluating $i\vec{k}\cdot\underline{\Omega}$. In this last expression

$$\Delta_\alpha \equiv \tfrac{2}{3}\int_0^\infty d\tau\,\langle \vec{I}_{E,T}\cdot\vec{I}_{E,T}(-\tau)\hat{A}_{\alpha,T}\rangle, \quad \alpha=N,E, \qquad (4.7a)$$

$$\Delta_{p_l} \equiv 2\int_0^\infty d\tau\,\langle I^{xx}_{P,T}P^x_T I^x_{E,T}(-\tau)\rangle, \qquad (4.7b)$$

and

$$\Delta_{p_t} \equiv 2\int_0^\infty d\tau\langle I^{xy}_{P,T}P^x_T I^y_{E,T}(-\tau)\rangle. \qquad (4.7c)$$

In Ref. 6(c) it was shown that

$$\Delta_\rho = 2V\left(\frac{\partial\beta\lambda}{\partial\beta\mu}\right)_{\beta,V}, \quad \Delta_e = -2V\left(\frac{\partial\beta\lambda}{\partial\beta}\right)_{\beta\mu,V}. \qquad (4.8)$$

In Ref. 6(d) it was proved that

$$\Delta_{p_l} = 2V\nu_l m\rho/\beta^2 \qquad (4.9a)$$

and that

$$\Delta_{p_t} = 2V\nu_t m\rho/\beta^2. \qquad (4.9b)$$

This completes the setup for the applications to simple fluids in nonconvecting NESS. As was asserted earlier none of the parameters which were introduced above is new since they all appear in the nonlinear hydrodynamic equations.

B. Transverse velocity fluctuations

A simple application of the theory presented above is found in the transverse-velocity time-autocorrelation function. The reason for the simplicity is the fact that the transverse velocity decouples from the longitudinal modes in the usual macroscopic relaxation to equilibrium. That is, the matrix $\underline{M}_{\vec{k}}$ [cf. Eq. (4.1)] is block diagonal with a diagonal transverse block. Further noting that $1-\varepsilon_p\varepsilon_p\varepsilon_e$ vanishes, we find

$$W_{p_y,p_y}(\vec{k},\sigma|\vec{r}) = \frac{1}{2V}\sigma e^{-\nu_t k^2\sigma}\Delta_{p_t} i\vec{k}\cdot\vec{\nabla}\beta(\vec{r}), \qquad (4.10a)$$

where we have employed Eqs. (3.21), (3.22), (4.1), and (4.6). Using Eq. (4.9a) for Δ_{p_t} this last expression becomes

$$W_{p_y,p_y}(\vec{k},\sigma|\vec{r}) = \sigma e^{-\nu_t k^2\sigma}\nu_t\frac{m\rho}{\beta^2}i\vec{k}\cdot\vec{\nabla}\beta(\vec{r}). \qquad (4.10b)$$

This equation is valid for $\sigma > \tau_D$. The connection to negative times is easily made using Eqs. (2.18) and (3.2c). They imply that $W_{p_y p_y}(\vec{k},\sigma|\vec{r})$ is odd in σ when convection is absent, i.e.,

$$W_{p_y p_y}(\vec{k},\sigma|\vec{r}) = \sigma e^{-\nu_t k^2|\sigma|}\nu_t\frac{m\rho}{\beta^2}i\vec{k}\cdot\vec{\nabla}\beta(\vec{r}), \qquad (4.10c)$$

where now $|\sigma| > \tau_D$.

Equation (4.10c) is only one of the three terms which appear in the expression for the transverse-velocity time autocorrelation function [cf. Eq. (2.11)]. The equilibrium part has been shown to equal

$$\frac{1}{V}\langle P^y_{\vec{k}}(\sigma)P^y_{-\vec{k}}\rangle = \exp(-\nu_t k^2|\sigma|)m\rho k_B T, \quad |\sigma| > \tau_D. \qquad (4.11)$$

Using this result in Eqs. (2.12a) and (2.17c) and finally in Eq. (2.11) yields for the NESS autocorrelation function

$$C_{p_yp_y}(\vec{k},\sigma\,|\,\vec{r})=\exp(-\nu_t k^2|\sigma|)m\rho(\vec{r})k_BT(\vec{r})\left\{1+|\sigma|\nu_t i\vec{k}\cdot\vec{\nabla}\ln\beta(\vec{r})\left[\frac{(|\sigma|+\sigma)}{|\sigma|}+T\left(\frac{\partial\ln\rho}{\partial T}\right)_{\mu/T}+T(1-\nu_t k^2|\sigma|)\left(\frac{\partial\ln\nu_t}{\partial T}\right)_{\mu/T}\right]\right\}, \tag{4.12}$$

which is valid for $|\sigma|>\tau_D$ *and* only to linear order in displacements from equilibrium for a system subject to thermal constraint.

The first term on the right-hand side of Eq. (4.12) is simply the local equilibrium transverse-velocity time-autocorrelation function and is even in k and σ. The remaining terms are odd in k and arise from both nonlocality and coupling to the dissipation. For relevant times, that is $\sigma\sim(k^2\nu_t)^{-1}$, and typical values for the temperature derivatives, it can be shown that the order of magnitude of the terms proportional to $\vec{\nabla}\ln\beta(\vec{r})$, divided by the local term is

$$|\vec{\nabla}\ln\beta(\vec{r})|/k\,. \tag{4.13}$$

For light-scattering wave vectors ($k\sim10^4$ cm^{-1}) and macroscopic temperature gradients ($\vec{\nabla}T\sim10$ K/cm, $T\sim100$ K) the above ratio is of the order of 10^{-5} and thus, for this case, the transverse-velocity autocorrelation function, all the new terms are extremely small. Clearly, at smaller k these terms become more important.

The size estimate of the new terms in Eq. (4.12) is not applicable to all autocorrelation functions. In fact the reason that the corrections were so small in this case is that the divergent terms associated with $\underline{\Gamma}^6(k,0)$ in Eq. (3.22) drop out by symmetry. As we now show this does not occur in the case of density fluctuations. Finally, we refer the reader to Sec. VI for a comparison of our result with the phenomenological approach.

V. DYNAMIC STRUCTURE FACTOR IN NONCONVECTING SYSTEMS

In this section we apply the theory to the calculation of the dynamic structure factor in a dense fluid. We refer the reader to paper I Sec. IV for a detailed discussion of the symmetry properties of this function. The aim of this section is to present an analytical expression for the k and σ dependence of this important quantity for a NESS subject to thermal constraint (i.e., $\Phi_N=0$, $\Phi_P=0$).

We first consider $W_{NN}(\vec{k},\sigma\,|\,\vec{r})$. In the case of the transverse-velocity autocorrelations Eq. (4.1) was used to prove that all the terms in Eq. (3.22) multiplied by the factor $(1-\varepsilon_\gamma\varepsilon_\alpha\varepsilon_6)$ vanish. This does not occur in the calculation of W_{NN}. Nonetheless, we need not consider all the terms in Eq. (3.22) since those multiplied by $(1-\varepsilon_\gamma\varepsilon_\alpha\varepsilon_6)$ diverge as $k\to0$, while the others do not. In what follows only the most divergent contributions are kept. Thus our starting expression is

$$W_{NN}(\vec{k},\sigma\,|\,\vec{r})=\frac{1}{V}[\exp(\underline{M}_{\vec{k}}\sigma)]^{NP_x}\times\left(\int_0^\infty d\tau\exp(\underline{M}_{\vec{k}}\tau)\underline{\Gamma}^E(\vec{k},0)\times\exp(\underline{M}_{\vec{k}}^\dagger\tau)\right)^{P_xN}\cdot\vec{\nabla}\beta(\vec{r})\,. \tag{5.1}$$

In arriving at Eq. (5.1) we have used the fact that N couples only to P_x in $\underline{M}_{\vec{k}}$ [cf. Eq. (4.1)] and the fact that $(1-\varepsilon_\gamma\varepsilon_N\varepsilon_E)$ vanishes unless $\gamma=\vec{P}$. Further, all static quantities of $O(k)$ or smaller were omitted. As was previously mentioned, M does not couple longitudinal and transverse modes and thus the transverse block is not needed. In Appendix A we show that

$$W_{NN}(\vec{k},\sigma\,|\,\vec{r})=\frac{1}{V}\frac{(\theta_\rho\chi_\rho+\theta_e\chi_e)}{2m^2c_0^3\Gamma_sk^3}\sin(kc_0\sigma)\times e^{-\Gamma_sk^2\sigma}i\vec{k}\cdot\vec{\nabla}\beta(\vec{r})+O(k^{-1})\,, \tag{5.2}$$

where the sound attenuation coefficient Γ_s, is given in Appendix A. In Appendix B we show that

$$W_{NN}(\vec{k},\sigma\,|\,\vec{r})=\frac{(k_BT)\rho}{2mc_0\Gamma_sk}\sin(kc_0\sigma)\times e^{-\Gamma_sk^2|\sigma|}\frac{i\vec{k}}{k^2}\cdot\vec{\nabla}\ln\beta(\vec{r})+O(k^{-1})\,, \tag{5.3}$$

where we have written the expression in a form which is valid for $|\sigma|>\tau_D$ and to linear order in displacements from equilibrium.

For many applications, the time Fourier transform of the dynamic structure factor is needed. The Fourier transform of Eq. (5.3) (cf. I, Sec. IV) is

$$W_{\vec{k}\omega}^{NN}(\vec{r})\equiv\int_{-\infty}^{\infty}d\sigma\,e^{-i\omega\sigma}W_{NN}(\vec{k},\sigma\,|\,\vec{r})=\frac{k_BT\rho}{2mc_0k}\vec{k}\cdot\vec{\nabla}\ln\beta(\vec{r})\left(\frac{1}{(\omega-kc_0)^2+(k^2\Gamma_s)^2}-\frac{1}{(\omega+kc_0)^2+(k^2\Gamma_s)^2}\right). \tag{5.4}$$

Note that Eq. (5.4) is odd both in k and in ω as was argued on general grounds in I.

Under the same type of approximations used in this paper, is has been shown that[5]

$$\frac{1}{V}\langle N_{\vec{k}\omega}N_{-\vec{k}}\rangle = k_B T\rho^2\gamma_P\left[\left(1-\frac{C_V}{C_P}\right)\frac{\Gamma_T k^2}{\omega^2+(\Gamma_T k^2)^2} + \frac{C_V}{C_P}\left(\frac{\Gamma_s k^2}{(\omega+kc_0)^2+(\Gamma_s k^2)^2} + \frac{\Gamma_s k^2}{(\omega-kc_0)^2+(\Gamma_s k^2)^2}\right)\right], \tag{5.5}$$

where a small non-Lorentzian correction has been neglected, since it is of the same order as the corrections to Eq. (A11) and thus to Eq. (5.4).

In Eq. (5.5) C_V, C_P, Γ_s, Γ_T, and γ_P are the heat capacities per particle at constant volume and pressure, the sound- and heat-mode attenuation constants, and the isothermal compressibility, respectively. (See Appendix A.)

As was done in Sec. IV, Eq. (5.5) is used in conjunction with Eqs. (2.17b), (2.12a), and (2.11) to obtain an expression for the NESS dynamic structure factor. As before, using typical values for the thermodynamic derivatives and for light scattering k's and ω's we find

$$\frac{C_{NN}^{nl}(\vec{k},\omega\,|\,\vec{r})}{C_{NN}^{\text{hom}}(\vec{k},\omega\,|\,\vec{r})} \sim \frac{|\vec{\nabla}\ln\beta(\vec{r})|}{k} \sim 10^{-4} \tag{5.6}$$

(where all quantities are Fourier transformed in time), and thus we may neglect the nonlocality terms. The remaining terms give

$$S_{\vec{k}\omega}(\vec{r}) \equiv C_{NN}(\vec{k},\omega\,|\,\vec{r}) = \left[\frac{k_B T\rho}{mc_0^2}\left(\frac{C_P}{C_V}-1\right)\frac{\Gamma_T k^2}{\omega^2+(\Gamma_T k^2)^2}\right]_{\text{hom}} + \frac{k_B T\rho\Gamma_s k^2}{mc_0^2}\left(\frac{1+\varepsilon(\vec{r})}{(\omega-kc_0)^2+(\Gamma_s k^2)^2} + \frac{1-\varepsilon(\vec{r})}{(\omega+kc_0)^2+(\Gamma_s k^2)^2}\right)_{\text{hom}}, \tag{5.7}$$

where

$$\varepsilon(\vec{r}) \equiv \frac{c_0}{2\Gamma_s k}\,\frac{\vec{k}\cdot\vec{\nabla}\ln\beta(\vec{r})}{k^2}, \tag{5.8}$$

where Eqs. (B3), (5.5), and (5.4) were used and where all thermodynamic parameters should be evaluated in the fashion indicated by the hom subscript.

We thus see that the NESS dynamic structure factor (and therefore the light-scattering spectrum) contains three Lorentzian peaks, whose positions and widths are unchanged with respect to their equilibrium values. The central or Rayleigh peak is unaffected by the temperature gradient. The most striking change is found in the sound or Brillouin doublet in that they are no longer symmetric. We find that correlations involving sound, propagating in the direction of the heat flux (i.e., $\vec{k}$ along $\vec{\nabla}\ln\beta$) are enhanced while those in the opposite direction are reduced.

From Eq. (5.7) we see that the relative size of the new effect is given by the ratio

$$|\vec{\nabla}\ln\beta(\vec{r})|/(2\Gamma_s k^2/c_0).$$

Since in the light-scattering regime, $\Gamma_s k/c_0 \sim 10^{-3}$ in most fluids, we see that we gain three orders of magnitude over the transverse-velocity estimate. Hence, we expect an effect of the order of a few percent. It should be stressed that the reason for the larger estimate lies in the fact that

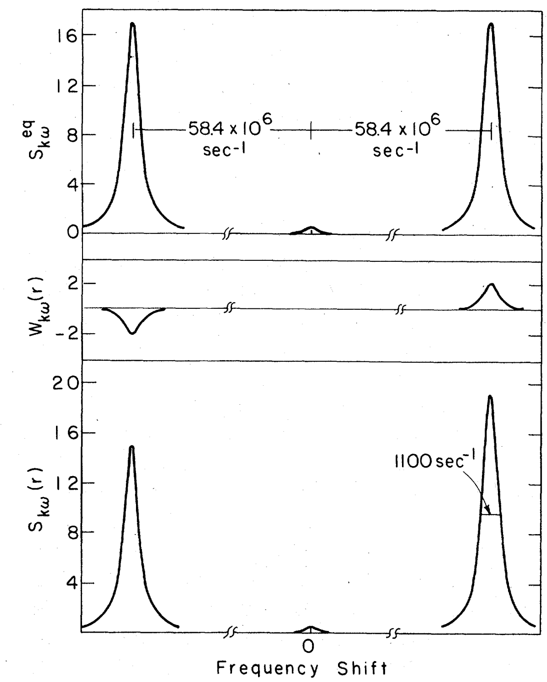

FIG. 1. Various contributions to the spectrum of light scattered from argon in a heat-conducting stationary state, all drawn to the same scale. Upper panel: spectrum of light scattered from argon in equilibrium (or local equilibrium) at 235 K and 1 g/cm^3 density. The wave vector here is $k = 852$ cm^{-1}. Middle panel: contribution due to the existence of a temperature gradient of 0.5 K/cm. It is antisymmetric in k and in ω and reflects the breaking of time-reversal symmetry. Lower panel: predicted full spectrum of light scattered from the stationary state. The smallness of the Rayleigh peak is due to the value of C_p/C_V which is almost unity. Notice the asymmetry in the Brillouin peaks. Here it amounts to about 25% difference in the peaks intensities. This asymmetry grows like $1/k^2$ for a given temperature gradient. For incident light with $k_{\text{in}} = 1\times10^5$ cm^{-1}, this spectrum can be observed at a scattering angle of 0.4°. Notice the break in the abscissas. The peaks are extremely sharp, with width ~ 1100 sec^{-1}.

the divergent terms in Eq. (3.22) now play a role. Using the ω or k assymmetries a differential experiment should easily be able to isolate these terms and thereby verify the existence of the dynamic broken symmetry associated with the heat flux. We caution the reader that Eq. (5.7) is valid only to linear order in displacements from equilibrium and, more importantly, for k's larger than the inverse macroscopic length scale. It cannot be directly used at hydrodynamic instabilities since among other things, Eq. (A11) is no longer valid. The extension to instabilities will be presented in a later paper.

Figure 1 graphically summarizes the results of this section for argon at 235 K and 1 g/cm^3 density. For this system $\Gamma_s = 0.8\times10^{-3}$ cm^2/sec, $\Gamma_T = 1.0\times10^{-3}$ cm^2/sec, $c_0 = 6.9\times10^4$ cm/sec, and $C_P/C_V = 1.028$. For Fig. 1 we choose $|\vec{\nabla}T| = 0.5$ K/cm and $k = 852$ cm^{-1} and points along $\vec{\nabla}T$ (see Fig. 1 of I). The first panel shows the structure factor in the absence of the temperature gradient. The Rayleigh peak is very small since C_P/C_V is close to unity. The second panel shows the contribution of Eq. (5.4). For the above choice of parameters, $\varepsilon = 0.12$. The third panel presents the predicted spectrum. The asymmetry is quite pronounced although each peak is Lorentzian. Due to the small k (scattering angle) the peaks are extremely sharp (the width is about 200 Hz) and the shifts are small (~10 MHz). Nonetheless, this spectrum should be readily measurable using modern light-scattering techniques. Note that the total scattered intensity is not changed by the temperature gradient and the Landau-Placzek ratio is obtained. From Eq. (5.7) it is clear that the ratio of the total intensities of the two Brillouin peaks is given by $(1+\varepsilon)/(1-\varepsilon)$, which in Fig. 1 is 1.27. Note that as the effect is given by the ratio of the macroscopic inverse length scale $(\vec{\nabla}\ln\beta(\vec{r}))$ to the inverse of the length scale on which sound is attenuated

$$(c_0/k^2\Gamma_s),$$

we require the steady-state system under observation to be several times larger than the sound-attenuation length.

VI. BROKEN SYMMETRY, STATIC-CORRELATION FUNCTIONS, AND THE CONNECTION TO PHENOMENOLOGY

The results of this work have one striking feature in common: all the parameters which appear in the expressions for the time-autocorrelation functions occur in the nonlinear hydrodynamic equations [cf. Eqs. (3.22), (2.13), and (2.17)]. Further, the nonlocality corrections were found to be negligible in all cases. This fact suggests that a connection to phenomenology is possible.

The common phenomenological approach has been to extend the Onsager regression hypothesis to the regime of the steady state. This assumes that once a fluctuation occurs, its relaxation is governed by the macroscopic equations of motion. Since the fluctuations are generally small, the macroscopic equations for the fluctuation are linearized around the steady state. That is,

$$\delta\underline{\dot{A}}_{\vec{k}}(\sigma) = \underline{M}_{SS}(\vec{k})\cdot\delta\underline{A}_{\vec{k}}(\sigma), \tag{6.1}$$

where $\delta\underline{A}_{\vec{k}}(\sigma)$ represents the values of the fluctuations and $\underline{M}_{SS}(\vec{k})$ governs the linearized macroscopic relaxation to NESS. Equation (6.1) is then solved subject to the initial values of the fluctuations $[\delta\underline{A}_{\vec{k}}(0)]$. The formal solution is multiplied by $\delta\underline{A}_{-\vec{k}}(0)$ and averaged, thereby giving

$$\langle\delta\underline{A}_{\vec{k}}(\sigma)\delta\underline{A}_{-\vec{k}}\rangle_{NE} = \exp[\underline{M}_{SS}(\vec{k})\sigma]\langle\delta\underline{A}_{\vec{k}}\delta\underline{A}_{-\vec{k}}\rangle_{NE}. \tag{6.2}$$

There are two problems associated with the use of Eq. (6.2). The first is that Eq. (6.2) is valid only for times σ larger than some microscopic time (τ_D). The regression hypothesis contains no information concerning how the initial values of the fluctuations are built up. This means that Eq. (6.2) cannot be directly used for negative times. In equilibrium this restriction is circumvented by using the connection between positive and negative times that is due to time-reversal symmetry. For autocorrelation functions this implies that they are even in time (or in ω). In many of the phenomenological studies,[4] this property was assumed to hold in NESS. We now know that this is unacceptable since time-reversal symmetry is broken in NESS.

Nonetheless, a connection to negative times can be made using the stationary property of NESS time-correlation functions.[8] This means that

$$\langle\underline{A}_{\vec{k}}(-\sigma)\underline{A}_{-\vec{k}}\rangle_{NE} = \langle\underline{A}_{\vec{k}}\underline{A}_{-\vec{k}}(+\sigma)\rangle_{NE} = \langle\underline{A}_{\vec{k}}(\sigma)\underline{A}_{-\vec{k}}\rangle^{\dagger}_{NE}, \tag{6.3}$$

where for simplicity we omit the δ notation for a fluctuation and where the second equality follows from the fact that $A_{\vec{k}}(\sigma)$ is the Fourier transform of a real quantity. It is this last expression which must be used in making the connection to negative times.

The second problem associated with the use of Eq. (6.2) lies in the fact that one must know the NESS values of the static-correlation functions. While this is straightforward in equilibrium, it was not clear how to make the extension to NESS. In many cases the practice has been to use the local equilibrium values for the static-correlation functions. In other cases low-density approximations have been used.[4,9] We shall now show that neither of these approaches is adequate in dense systems and then complete the connection to the phenomenological approach.

A. Static-correlation functions in NESS

The static-correlation functions can be computed using the theory developed in this series of papers. Neglecting nonlocality corrections and using Eq. (2.11) and the definition, Eq. (3.17), gives to linear order

$$\langle \underline{A}_{\vec{k}} \underline{A}_{-\vec{k}} \rangle_{\rm NE} = \langle \underline{A}_{\vec{k}} \underline{A}_{-\vec{k}} \rangle^{\rm hom} - \int_0^\infty d\tau\, \underline{\Gamma}^6(\vec{k},\tau)\cdot\vec{\nabla}\beta\Phi_6(\vec{r}) . \qquad (6.4)$$

When Eq. (3.15) is used for $\underline{\Gamma}^6(\vec{k},\tau)$ and only the most divergent terms are retained, Eq. (6.4) becomes

$$\langle \underline{A}_{\vec{k}} \underline{A}_{-\vec{k}} \rangle_{\rm NE} = \langle \underline{A}_{\vec{k}} \underline{A}_{-\vec{k}} \rangle^{\rm hom} - \int_0^\infty d\tau \exp[\underline{M}_{\vec{k}}\tau]\underline{\Gamma}^6(\vec{k},0) \times \exp[\underline{M}^\dagger_{\vec{k}}\tau]\cdot\vec{\nabla}\beta\Phi_6(\vec{r}) . \qquad (6.5)$$

Considering the somewhat simpler case of a nonconvecting NESS ($\Phi_P = 0$), Eqs. (4.3) and (A11) may be employed to calculate any component of Eq. (6.5). The results show that the static-correlation functions separate into two groups. The first contains all correlations between variables of the same time-reversal signature (e.g., $\langle N_{\vec{k}} N_{-\vec{k}} \rangle_{\rm NE}$, $\langle E_{\vec{k}} N_{-\vec{k}} \rangle_{\rm NE}$, $\langle P^x_{\vec{k}} P^y_{-\vec{k}} \rangle_{\rm NE}$, etc.). For this group we find that the static-correlation function is given by the local-equilibrium value, up to corrections $O(|\vec{\nabla}\ln\beta|/k)$. The second group contains the static correlations between variables of different time-reversal signature. These vanish in nonconvecting local-equilibrium theories, that is, the first term on the right-hand side of Eq. (6.5) vanishes. There are four types of correlations in this group for simple fluids. We find

$$\frac{1}{V}\langle P^x_{\vec{k}} N_{-\vec{k}} \rangle_{\rm NE} = \frac{k_B T\rho}{2k\Gamma_s}\frac{\vec{k}\cdot\vec{\nabla}\ln\beta(\vec{r})}{k^2} + O\left(\left|\frac{\nabla\ln\beta}{k}\right|\right) , \qquad (6.6a)$$

$$\frac{1}{V}\langle P^y_{\vec{k}} N_{-\vec{k}} \rangle_{\rm NE} = -\frac{\rho k_B T\gamma_T T}{k(\nu_t + \Gamma_T)}\frac{1}{k}\frac{\partial\ln\beta(\vec{r})}{\partial y} + O\left(\left|\frac{\nabla\ln\beta}{k}\right|\right) , \qquad (6.6b)$$

$$\frac{1}{V}\langle P^x_{\vec{k}} E_{-\vec{k}} \rangle_{\rm NE} = \frac{k_B T h}{2k\Gamma_s}\frac{\vec{k}\cdot\vec{\nabla}\ln\beta(\vec{r})}{k^2} + O\left(\left|\frac{\nabla\ln\beta}{k}\right|\right) , \qquad (6.6c)$$

and

$$\frac{1}{V}\langle P^y_{\vec{k}} E_{-\vec{k}} \rangle_{\rm NE} = -\frac{k_B T(h - \rho C_P/\gamma_T)T\gamma_T}{k(\nu_t + \Gamma_T)}\frac{1}{k}\frac{\partial\ln\beta(\vec{r})}{\partial y} + O\left(\frac{\nabla\ln\beta}{k}\right) , \qquad (6.6d)$$

where, as before, x is chosen as the longitudinal direction, y is one of the transverse directions, and where the thermodynamic identities of Appendix B were used.

As has been stressed throughout this series of papers, the existence of a NESS implies the breaking of time-reversal symmetry. In equilibrium systems with broken symmetries, it is commonly found[3] that certain static correlations diverge as k^{-2} which shows the appearance of a long-range order (i.e., the correlation decays in space as r^{-1}). Equation (6.6) show that in NESS a k^{-2} behavior is also found, thereby indicating the existence of long-range order. We note that the separation of time scales assumption forbids us from considering k too small. Thus, we cannot make any statements about the analyticity of the static correlations at $k=0$. In the r representation, this implies that the correlation decays like r^{-1} for r large, but less than the macroscopic length scale. Beyond this point this theory cannot be used and we plan to investigate the very long-distance behavior in a later publication. Another limitation on the size of k may be found through the Schwartz inequality, which implies, for example, that

$$\left|\frac{1}{V}\langle P^x_{\vec{k}} N_{-\vec{k}} \rangle_{\rm NE}\right|^2 \leq \frac{1}{V}\langle P^x_{\vec{k}} P^x_{-\vec{k}} \rangle_{\rm NE}\frac{1}{V}\langle N_{\vec{k}} N_{-\vec{k}} \rangle_{\rm NE} . \qquad (6.7)$$

Using the local-equilibrium values for the autocorrelation functions and Eq. (6.6a) we find

$$|\varepsilon| \leq \tfrac{1}{2}(C_P/C_V)^{1/2} , \qquad (6.8)$$

where ε is given by Eq. (5.8) and where we have employed Eq. (B3). The results presented in this work will not hold unless Eq. (6.8) is valid. We note that the argon system considered in Fig. 1 satisfies Eq. (6.8) and in fact for most fluid systems Eq. (6.8) poses no serious limitations.

There is a fundamental difference between the symmetry breaking found in NESS and in equilibrium. In the latter case the broken symmetries are usually continuous symmetries, such as translational or rotational symmetries, whereas in NESS it is a discrete symmetry which is broken. The important significance of this difference is that when a continuous symmetry is broken, new slow modes appear (i.e., the Goldstone modes)[3] and must be included in the set of variables. This does not occur when a discrete symmetry is broken and thus the use of the usual set of variables is sufficient.

We may now return to the analysis of the phenomenological approach.

B. Connection to phenomenology

Once the static-correlation functions are known, they may be substituted into Eq. (6.2) and thereby yield the NESS time-correlation function, as predicted by the regression hypothesis. In order to investigate the validity of the regression idea, we shall compute the (N,N) component of Eq. (6.2) and compare it with the results of Sec. IV. Thus

$$\langle N_{\vec{k}}(\sigma)N_{-\vec{k}}\rangle_{\mathrm{NE}}=\exp[\underline{M}_{SS}(\vec{k})\sigma]^{N\alpha}\langle A_{\alpha,\vec{k}}N_{-\vec{k}}\rangle_{\mathrm{NE}}\,. \qquad (6.9)$$

For k's in the light-scattering regime $\underline{M}_{SS}(\vec{k})$ can be replaced by $\underline{M}_{\vec{k}}$ defined in Eq. (3.5) since the macroscopic gradients play a minor role in the dynamics of fluctuations on the light-scattering length scale. Of the three static-correlation functions which appear on the right-hand side of Eq. (6.9), only $\langle P^x_{\vec{k}}N_{-\vec{k}}\rangle_{\mathrm{NE}}$ cannot be computed using local equilibrium. Hence, we rewrite Eq. (6.9) in the form

$$\langle N_{\vec{k}}(\sigma)N_{-\vec{k}}\rangle_{\mathrm{NE}}=\sum_{\alpha=N,E}\exp[\underline{M}_{\vec{k}}(\vec{r})\sigma]^{N\alpha}\langle A_{\alpha,\vec{k}}N_{-\vec{k}}\rangle_{\mathrm{hom}} +\exp[\underline{M}_{\vec{k}}(\vec{r})\sigma]^{NP^x}\langle P^x_{\vec{k}}N_{-\vec{k}}\rangle_{\mathrm{NE}}\,. \qquad (6.10)$$

The sum in Eq. (6.10) is simply the local-equilibrium dynamic structure factor [cf. Eq. (2.14)] whereas the second term is exactly $W_{NN}(\vec{k},\sigma\,|\,\vec{r})$ (to linear order) as is easily seen from Eqs. (5.1) and (6.5). This shows that the regression hypothesis is equivalent to the microscopic approach [cf. Eq. (5.7)] and may be used providing that the static-correlation functions are computed properly and the extension to negative times is made using stationarity. The other correlation functions may be treated in the same fashion, with the same result.

VII. DISCUSSION

We have shown in this paper that the breaking of time-reversal symmetry, which is associated with the very existence of the NESS, has profound implications on the fluctuations in the NESS. The NESS static-correlation functions which vanish in equilibrium or local equilibrium due to time-reversal symmetry may become large in the small-k regime. As a result, the time-correlation functions, which are related to the static ones through the regression method (which was shown to be consistent with our theory) acquire new properties that are absent in equilibrium. The dynamic structure factor is no longer symmetric in ω (or time) and this implies that the spectrum of scattered light is nonsymmetric. We have found that the density fluctuations are biased and there are different couplings to the sound modes that travel with and against the temperature gradient.

In a sense, this is a microscopic analog of the well-known phenomena of convection heating. There the appearance of a temperature gradient destroys the symmetry between the velocity directions through the nonlinear heating terms (i.e., the terms $\vec{v}\cdot\vec{\nabla}T$) which appear in the hydrodynamic equations. The same mechanism operates here except that on the microscopic level the fluctuations appear incoherently and therefore no macroscopic velocity field results.

An interesting result is embodied in Eqs. (6.6). We see there that the static-correlation functions that are now nonzero due to the breaking of time-reversal symmetry have a $1/k^2$ dependence. As noted, this is an indication of the appearance of long-range order, since this dependence in k space is equivalent to a $1/r$ dependence in real space, which is a very slow decay. This finding is common to many broken symmetry cases, except that usually (in equilibrium) it is continuous symmetry that is broken. Here we found that breaking a discrete symmetry yields similar consequences, and familiar features of broken symmetry appear. The one difference that needs stressing is that there is no indication of the appearance of a new slow mode (Goldstone mode). This difference is interesting and may warrant a separate treatment.

We stress that the results presented in Eqs. (6.6) are not an artifact of the method used here to derive them. In II (previous paper) we derived Eq. (6.6a) using an entirely different method [cf. Eq. (5.12) of paper II]. The fact that the same result was obtained by two completely different approaches is a strong indication that the method used here to calculate the correlation functions is correct. In addition, we now see that many of the results of II are not dependent on the choice of interparticle potential or density regime.

Within the context of the static correlations, we note that our results are significantly different from those already in the literature. For example, Hinton[9] has used a Boltzmann-equation approach to derive expressions for these quantities at low density. Contrary to our results he found no k

dependence in the static correlations (or no long-range order). In addition, he finds no correlation between density and velocity. The reason for this difference lies in his assumption that one can relate all the nonequilibrium higher-order distribution functions to products of lower-order ones. In particular [cf. Ref. 9 Eq. (25, 26)] he assumes that

$$W_{1,12}(\vec{x}_0, t_0; \vec{x}_1, \vec{x}_2, t)$$

$$\simeq W_{1,1}(\vec{x}_0, t_0; \vec{x}_1, t) \cdot W_{12}(\vec{x}_0, t_0; \vec{x}_2, t)/F(\vec{x}_0, t_0), \quad (7.1)$$

where the notation is of Ref. 9. Taking the limit $t \to t_0$ in Eq. (7.1) we find absolutely no correlation between particles 1 and 2. Thus, naturally, the static correlations cannot exhibit any long-range order. From the analysis of II we saw that is was precisely the correlation between particles 1 and 2 initially that brought about the new effects. In some of the phenomenological works,[4] Hinton's results were used to compute the spectrum of scattered light within the spirit of the regression hypotheses and thus it is not surprising that results different from ours were obtained.

Since the regression idea was found to be consistent with our theory, it seems that it may be generally proved within its context. The next paper in this series will indeed contain a proof of the regression hypotheses in a NESS. In addition, we shall discuss there fluctuation-dissipation theorems in far from equilibrium stationary states.

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APPENDIX A: PROOF OF EQ. (5.2)

The eigenvalues $\xi_\alpha(\vec{k})$ of the longitudinal block $\underline{M}_{\vec{k}}^l$, of $\underline{M}_{\vec{k}}$ are determined from the equation

$$0 = |\xi_\alpha \underline{1} - \underline{M}_{\vec{k}}^l|$$

$$= \xi_\alpha^3 + \xi_\alpha^2 k^2(\kappa_e + \nu_l) + \xi_\alpha k^2(c_0^2 + k^2 \nu_l \kappa_e)$$

$$+ k^4(\chi_\rho \kappa_e - \chi_e \kappa_\rho)/m, \quad \text{(A1)}$$

where we have used Eq. (4.1) and where the adiabatic sound speed is given by

$$c_0^2 \equiv \chi_\rho/m + \chi_e h/m\rho. \quad \text{(A2)}$$

It is well known that the three roots of Eq. (A1) [which we denote by $\xi_+(k)$, $\xi_-(k)$, and $\xi_T(k)$] have negative real parts, that $\xi_+ = \xi_-^*$, and ξ_T is real.

Corresponding to this block, the matrix $\underline{\tilde{P}}^l$ [cf. Eq. (3.14)] has columns equal to the eigenvectors, that is,

$$\underline{\tilde{P}}^l = \begin{pmatrix} m^{-1} & m^{-1} & \chi_e \\ \alpha_+ & \alpha_+^* & \chi_e \alpha_T m \\ \xi_+/ik & \xi_+^*/ik & m\chi_e \xi_T/ik \end{pmatrix}, \quad \text{(A3)}$$

where

$$\alpha_+ \equiv \frac{\xi_+ h/m\rho - k^2 \kappa_\rho/m}{\xi_+ + k^2 \kappa_e} \quad \text{(A4)}$$

and

$$\alpha_T \equiv \frac{\xi_T h/m\rho - k^2 \kappa_\rho/m}{\xi_T + k^2 \kappa_e}. \quad \text{(A5)}$$

The columns in the matrix in Eq. (A3) correspond to the ξ_+, ξ_-, and ξ_T eigenvectors of M_k^l, respectively. After some simple algebra we have

$$(\underline{\tilde{P}}^l)^{-1} = |\underline{\tilde{P}}^l|^{-1} \begin{bmatrix} m\chi_e(\alpha_+^* \xi_T - \alpha_T \xi_+^*)/ik, & \chi_e(\xi_+^* - \xi_T)/ik, & \chi_e(\alpha_T - \alpha_+^*) \\ m\chi_e(\alpha_T \xi_+ - \alpha_+ \xi_T)/ik, & \chi_e(\xi_T - \xi_+)/ik, & \chi_e(\alpha_+ - \alpha_T) \\ (\alpha_+ \xi_+^* - \alpha_+^* \xi_+)/ik, & (\xi_+ - \xi_+^*)/mik, & (\alpha_+^* - \alpha_+)/m \end{bmatrix} \quad \text{(A6)}$$

with

$$|\underline{\tilde{P}}^l| = (2\chi_e/k)\mathrm{Im}[\alpha_T \xi_+ - \xi_T \alpha_+ + \alpha_+ \xi_+^*] \quad \text{(A7)}$$

Using Eqs. (A3) and (A5) we see that

$$\exp(\underline{M}_k^l\sigma)=\underline{\tilde{P}}^l\exp(\underline{\xi}\sigma)(\underline{\tilde{P}}^l)^{-1}$$

$$=|\underline{\tilde{P}}^l|^{-1}\left[\begin{array}{l} \frac{\chi_e i}{k}\mathrm{Im}\{e^{\xi_T\sigma}\alpha_+\xi_-+e^{\xi_-\sigma}(\alpha_T\xi_+-\xi_T\alpha_+)\}, \\ \frac{2m\chi_e}{k}\mathrm{Im}\{e^{\xi_+\sigma}\alpha_+(\alpha_+^*\xi_T-\alpha_T\xi_+^*)+e^{\xi_T\sigma}\alpha_T\alpha_+\xi_+^*\}, \\ \frac{2m\chi_e i}{k^2}\mathrm{Im}\{e^{\xi_+\sigma}(\alpha_T|\xi_+|^2-\xi_+\alpha_+^*\xi_T)-e^{\xi_T\sigma}\xi_T\alpha_+^*\xi_+\}, \end{array}\right.$$

$$\left.\begin{array}{l} \frac{2\chi_e}{km}\mathrm{Im}\{e^{\xi_+\sigma}(\xi_--\xi_T)+e^{\xi_T\sigma}\xi_+\},\ \frac{2\chi_e i}{m}\mathrm{Im}\{e^{\xi_+\sigma}(\alpha_T-\alpha_+^*)+e^{\xi_T\sigma}\alpha_+^*\} \\ \frac{2\chi_e}{k}\mathrm{Im}\{e^{\xi_+\sigma}\alpha_+(\xi_--\xi_T)+\alpha_Te^{\xi_T\sigma}\xi_+\},\ 2\chi_e i\mathrm{Im}\{e^{\xi_+\sigma}\alpha_+(\alpha_T-\alpha_+^*)+e^{\xi_T\sigma}\alpha_T\alpha_+^*\} \\ -\frac{2\chi_e i}{k}\mathrm{Im}\{e^{\xi_+\sigma}\xi_+(\xi_--\xi_T)+e^{\xi_T\sigma}\xi_T\xi_+\},\ \frac{2\chi_e}{k}\mathrm{Im}\{e^{\xi_+\sigma}\xi_+(\alpha_T-\alpha_+^*)+e^{\xi_T\sigma}\xi_T\alpha_+^*\} \end{array}\right]. \tag{A8}$$

Equation (A8) is useful for a numerical calculation, but for our purpose the fact that k is small may be used to further simplify it. This is done by noting that

$$\xi_\pm(k)\sim\pm ikc_0-k^2\Gamma_s\,, \tag{A9}$$

and

$$\xi_T(k)\sim-k^2\Gamma_T\,,$$

with

$$\Gamma_T\equiv\lambda/\rho\overline{C}_p\,, \tag{A10}$$

and

$$\Gamma_s\equiv\tfrac{1}{2}[(C_P/C_V-1)\Gamma_T+\nu_l]\,.$$

In Eq. (A10) $\overline{C}_P$ and $\overline{C}_V$ are the heat capacities per particle at constant pressure and volume, respectively. Equation (A9) represents an expansion of the roots of Eq. (A1) to first order in $k\Gamma_s/c_0$, which is typically $O(10^{-3})$ in simple fluids at light scattering k's.

Equation (A8) is needed for long times [cf. Eq. (5.1)] and thus we must retain the $O(k^2)$ terms which appear multiplied by time. For the remaining factors, it is sufficient to retain only the leading k dependence. With this in mind, Eq. (A8) becomes

$$\exp(\underline{M}_k^l\sigma)=\frac{1}{2c_0^2}\begin{bmatrix} (e^{\xi_+\sigma}+e^{\xi_-\sigma})\chi_n/m+2e^{\xi_T\sigma}\chi_e h/mn, & \chi_e(e^{\xi_+\sigma}+e^{\xi_-\sigma}-2e^{\xi_T\sigma})/m, & c_0(e^{\xi_+\sigma}-e^{\xi_-\sigma})/m \\ \chi_n h(e^{\xi_+\sigma}+e^{\xi_-\sigma}-2e^{\xi_T\sigma})/mn, & \chi_e h(e^{\xi_+\sigma}+e^{\xi_-\sigma})/mn+2\chi_n{}^{\xi_T\sigma}/m, & c_0h(e^{\xi_+\sigma}-e^{\xi_-\sigma})/mn \\ c_0\chi_n(e^{\xi_+\sigma}-e^{\xi_-\sigma}), & c_0\chi_e(e^{\xi_+\sigma}-e^{\xi_-\sigma}), & c_0^2(e^{\xi_+\sigma}+e^{\xi_-\sigma}) \end{bmatrix}. \tag{A11}$$

Using Eqs. (A11) and (4.3) in (5.1), performing the indicated multiplications and integration gives on retaining the most divergent terms, Eq. (5.2).

APPENDIX B: PROOF OF EQ. (5.3)

In order to make the connection between Eqs. (5.2) and (5.3) we make use of the following thermodynamic identities:

$$\left(\frac{\partial h/\rho}{\partial\beta\mu}\right)_\beta=k_BT(1-T\gamma_T)\,, \tag{B1a}$$

$$\left(\frac{\partial h/\rho}{\partial\beta}\right)_{\beta\mu}=-k_BT(T\overline{C}_P+h(1-T\gamma_T)/\rho)\,, \tag{B1b}$$

$$\chi_\rho=-\frac{(h/\rho-\overline{C}_P/\gamma_T)}{\rho\overline{C}_P\gamma_P/\gamma_T-T\gamma_T}\,, \tag{B1c}$$

and

$$\chi_e=\frac{1}{\rho\overline{C}_P\gamma_P/\gamma_T-T\gamma_T}\,, \tag{B1d}$$

where

$$\gamma_T\equiv\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \gamma_P\equiv-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T. \tag{B2}$$

Further, using Eqs. (A2), (B1c), and (B1d) we obtain the well-known result that

$$mc_0^2=\frac{\overline{C}_P}{\rho\overline{C}_P\gamma_P-T\gamma_T^2}=\frac{C_P}{\rho\gamma_PC_V}\,, \tag{B3}$$

where the second equality follows by using the standard relationship between C_P and C_V.

From Eqs. (4.5), (B1), and (B3) it follows that

$$(1/V)(\theta_\rho\chi_\rho+\theta_e\chi_e)=(k_BTc_0)^2\rho m\,. \tag{B4}$$

Using this result in Eq. (5.2) yields Eq. (5.3).

*Present address: Dept. of Chemistry, University of California, Berkeley, Calif. 94720.

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