ESTIMATING HYDRODYNAMIC QUANTITIES IN THE PRESENCE OF MICROSCOPIC FLUCTUATIONS

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This paper discusses the evaluation of hydrodynamic variables in the presence of spontaneous fluctuations, such as in molecular simulations of fluid flows. The principal point is that hydrodynamic variables such as fluid velocity and temperature must be defined in terms of mechanical variables such as momentum and energy density). Because these relations are nonlinear and because fluctuations of mechanical variables are correlated, care must be taken to avoid introducing a bias when evaluating means, variances, and correlations of hydrodynamic variables. The unbiased estimates are formulated; some alternative, incorrect approaches are presented as cautionary warnings. The expressions are verified by numerical simulations, both at thermodynamic equilibrium and at a nonequilibrium steady state.

1. Introduction

Particle simulations are a useful tool in the study of continuum mechanics, especially fluid mechanics [15; 16], and a variety of particle-based algorithms (e.g., molecular dynamics [7], particle-in-cell (PIC) [12], direct simulation Monte Carlo (DSMC) [4], dissipative particle dynamics (DPD) [10], and lattice gas automata (LGA) [24]) are available to simulate hydrodynamic phenomena. In such simulations, the quantities of interest are not the precise trajectories of the particles but rather the hydrodynamic variables such as density, fluid velocity, temperature, pressure, etc. Compared to macroscopic systems, the number of particles in a simulation is small (typically fewer than 10^7) so the number of particles in a volume element is typically on the order of 10 to 100. For this reason, the spontaneous fluctuations in a volume element are significant and statistical samples are taken. The purpose of this paper is to establish the correct construction for measuring hydrodynamic variables and to point out some common errors that lead to biased results.

The bias described in this paper has already been studied in detail by Tysanner and Garcia [26; 25] for the measurement of mean fluid velocity. This paper extends that work in two important directions. First, we consider other hydrodynamic variables, most significantly temperature. Second, the study of hydrodynamic fluctuations is an important topic in a variety of fields ranging from nanoscale fluid mechanics [5; 13] to molecular biology [14; 23]. We therefore also consider the measurement of hydrodynamic fluctuations, such as the variance of fluid velocity and the correlation of density and temperature fluctuations.

The paper is organized as follows: Section 2 defines mechanical densities and relates them to hydrodynamic variables, specifically how the mean values of the latter are defined in terms of the former. Variances and correlations of hydrodynamic quantities are similarly described in Section 3. The bias observed when hydrodynamic quantities are measured incorrectly is described in Section 4 where the effects are illustrated by numerical results from simulations. Section 5 summarizes the main points and concludes with general remarks.

2. Mean Values

First let us establish some notation: Consider a fluid of particles of mass m. The position and velocity of particle k are $\mathbf{r}_k$ and $\mathbf{v}_k$. The measurement of mechanical variables in a cell, namely the instantaneous densities of mass, momentum, and kinetic energy, may be written as,

$$\rho = \frac{1}{V} \sum_{\mathbf{r}_k \in C} m \tag{1}$$

$$\mathbf{J} = \frac{1}{V} \sum_{\mathbf{r}_k \in C} m\mathbf{v}_k \tag{2}$$

$$K = \frac{1}{V} \sum_{\mathbf{r}_k \in C} \tfrac{1}{2}m|\mathbf{v}_k|^2 \tag{3}$$

where the sums are over particles located within cell C, which has volume V. One may define other mechanical variables but these suffice for the present discussion. For the equations of fluid dynamics these are the fundamental conserved variables.

For any of these mechanical variables ($\mathcal{M} = \rho$, $\mathbf{J}$, or K) we may write the sample mean as the average over S samples, that is,

$$\langle \mathcal{M} \rangle_s = \frac{1}{S} \sum_{j=1}^{S} \mathcal{M}_j \tag{4}$$

where the subscript j indicates individual samples, which may be from an ensemble of runs or, for steady state problems, samples taken at different times (i.e., a time

average). In the limit of infinitely many samples, this sample mean goes to the mean value, that is,

$$\overline{\mathcal{M}} = \langle \mathcal{M} \rangle_\infty \equiv \lim_{S \to \infty} \langle \mathcal{M} \rangle_s. \tag{5}$$

It is important to keep in mind that we are *not* considering the "thermodynamic limit" because our interest is in the measurement of fluid variables in relatively small volumes, so the number of particles, $N = \rho V/m = O(10^1\text{–}10^2)$, is by no approximation approaching infinity. Of course it is not necessary to take the thermodynamic limit in order to treat thermodynamic or hydrodynamic variables; one simply has to be careful to retain terms that are $O(1/N)$.

From the sample measurements of the mechanical variables one may obtain estimates of hydrodynamic variables, such as fluid velocity and temperature. However it is important to understand that for a hydrodynamic variable, $\mathcal{H}$, the mean is defined in terms of the means of mechanical variables. Specifically,

$$\overline{\mathcal{H}} = \mathcal{H}(\overline{\rho}, \overline{\mathbf{J}}, \overline{K}) \neq \lim_{S \to \infty} \langle \mathcal{H}(\rho, \mathbf{J}, K) \rangle_s, \tag{6}$$

With this in mind, we introduce the notation

$$\langle \mathcal{H} \rangle_s^* = \mathcal{H}(\langle \rho \rangle_s, \langle \mathbf{J} \rangle_s, \langle K \rangle_s) \tag{7}$$

with $\overline{\mathcal{H}} = \langle \mathcal{H} \rangle_\infty^*$. The asterisk reminds us that the estimated mean of a hydrodynamic variable is constructed from the sample means of mechanical variables.

Landau and Lifshitz (§49, [18]) warn of this subtlety in defining quantities such as temperature and pressure: "Strictly speaking, in a system which is not in thermodynamic equilibrium, such as a fluid with velocity and temperature gradients, the usual definitions of thermodynamic quantities are no longer meaningful, and must be ... defined as being the same functions of [mechanical variables] "as they are in thermal equilibrium. [...] The introduction of any further terms (for example, the inclusion in the mass flux density of terms proportional to the gradient of density or temperature) has no physical meaning.... Worse still, the inclusion of such terms may violate the necessary conservation laws." Such a violation is demonstrated in [26] and is discussed here in Section 4.1.

Intensivity (i.e., invariance with volume) is an important property that is lost when hydrodynamic variables are measured incorrectly. Intensive and extensive variables are familiar from equilibrium statistical mechanics, temperature and entropy being examples of each, respectively. The property of intensivity requires that for two volume elements A and B for which $\overline{\mathcal{M}}_A = \overline{\mathcal{M}}_B$, we have $\overline{\mathcal{H}}_{A+B} = \overline{\mathcal{H}}_A = \overline{\mathcal{H}}_B$ if $A + B$ is the union of the two elements.Intensivity is guaranteed when hydrodynamic variables are defined in terms of mechanical densities as $\overline{\mathcal{H}} = \mathcal{H}(\overline{\mathcal{M}})$. On the

other hand,

$$\langle \mathscr{H}(\mathcal{M}) \rangle_\infty = \overline{\mathscr{H}} + \tfrac{1}{2}\overline{\delta\mathcal{M}^2}\left(\frac{\partial^2 \mathscr{H}}{\partial \mathcal{M}^2}\right)_{\overline{\mathcal{M}}} + \dots \tag{8}$$

where $\delta\mathcal{M} = \mathcal{M} - \overline{\mathcal{M}}$ is the fluctuation of mechanical variables, and $\overline{\delta\mathcal{M}^2}$ is their covariance. Because the covariance is *not* intensive (e.g., $\overline{\delta\rho^2} = m\overline{\rho}/V$ for a dilute gas at equilibrium) one cannot guarantee that $\langle \mathscr{H}(\mathcal{M}) \rangle_\infty$ remains intensive (though in some cases, typically at thermodynamic equilibrium, $\langle \mathscr{H}(\mathcal{M}) \rangle_\infty = \overline{\mathscr{H}}$). This generic analysis is illustrated in the next two subsections for the specific examples of fluid velocity and temperature.

2.1. *Fluid Velocity.* The simplest example of a hydrodynamic variable is fluid velocity, which from the development of the equation of continuity (§1, [18]) is defined as

$$\overline{\mathbf{u}} = \frac{\overline{\mathbf{J}}}{\overline{\rho}} = \lim_{S\to\infty} \frac{\langle \mathbf{J} \rangle_s}{\langle \rho \rangle_s} \tag{9}$$

The unbiased sample mean for the fluid velocity is

$$\langle \mathbf{u} \rangle_s^* = \frac{\langle \mathbf{J} \rangle_s}{\langle \rho \rangle_s} = \frac{S^{-1}\sum_j^S \mathbf{J}_j}{S^{-1}\sum_j^S \rho_j}, \tag{10}$$

so $\overline{\mathbf{u}} = \lim_{S\to\infty}\langle \mathbf{u} \rangle_s^*$.

It is important to note that

$$\langle \mathbf{u} \rangle_s^* \neq \langle \hat{\mathbf{u}} \rangle_s = \frac{1}{S}\sum_j^S \hat{\mathbf{u}}(\rho_j, \mathbf{J}_j, K_j) \tag{11}$$

where $\hat{\mathbf{u}}$ is any general function that defines an instantaneous fluid velocity in terms of the instantaneous mechanical state.

Specifically, note that the instantaneous center-of-mass velocity, $\hat{\mathbf{u}}_j = \mathbf{J}_j/\rho_j$, when averaged over samples, may be written as

$$\langle \hat{\mathbf{u}} \rangle_s = \frac{1}{S}\sum_{j=1}^S \hat{\mathbf{u}}_j = \frac{1}{S}\sum_{j=1}^S \frac{\mathbf{J}_j}{\rho_j} = \left\langle \frac{\mathbf{J}}{\rho} \right\rangle_s, \tag{12}$$

so one might be tempted to define fluid velocity as the center of mass velocity. This definition, though commonly used (eg. §9-4-1, [12]) for fluid velocity, is problematic for two reasons.

First, there is an ambiguity since $\hat{\mathbf{u}}_j$ is not well defined for samples at which $\rho_j = \mathbf{J}_j = 0$, that is, when the instantaneous number of particles N_j is zero. There are two ways to remove this ambiguity: One could take $\hat{\mathbf{u}}_j = 0$ for those samples, an unacceptable approach because it introduces a bias proportional to $1 - S_0/S$ where

S_0 is the number of samples for which $\rho_j = 0$ (see equation (61)). The acceptable approach is to define

$$\langle \hat{\mathbf{u}} \rangle_s = \frac{1}{S - S_0} \sum_{j=1}^{S} \frac{\mathbf{J}_j}{\rho_j} (1 - \delta_{0, N_j}) \tag{13}$$

that is, to skip those samples with zero particles, which we shall implicitly assume is how the averaging of samples is performed.

The second and far more serious issue is that using (12) to define fluid velocity is biased when the fluid is not at equilibrium. To see why, recall that

$$\langle \hat{\mathbf{u}} \rangle_s = \left\langle \frac{\mathbf{J}}{\rho} \right\rangle_s \neq \frac{\langle \mathbf{J} \rangle_s}{\langle \rho \rangle_s} = \langle \mathbf{u} \rangle_s^*, \tag{14}$$

The inequality should not be surprising since the instantaneous values of ρ and $\mathbf{J}$ are correlated (e.g., if the instantaneous mass is greater than average then most likely so is the instantaneous momentum). These correlations happen to cancel out at equilibrium (even when $\bar{\mathbf{u}} \neq 0$) but out of equilibrium (e.g., temperature gradient) the measurement of fluid velocity as $\langle \hat{\mathbf{u}} \rangle_s$ is biased and incorrect. This effect is discussed further in Section 4.1.

2.2. Temperature. Next we consider the measurement of temperature (or more specifically of translational temperature), which is defined from the principle of equipartition of kinetic energy as

$$\overline{T} = \frac{1}{c_v \overline{\rho}} \left(\overline{K} - \frac{|\overline{\mathbf{J}}|^2}{2\overline{\rho}} \right), \tag{15}$$

where $c_v = d\, k_B / 2m$ is the heat capacity per unit mass due to the d translational degrees of freedom. From the discussion above, the unbiased sample mean for temperature is

$$\langle T \rangle_s^* = \frac{1}{c_v \langle \rho \rangle_s} \left(\langle K \rangle_s - \frac{|\langle \mathbf{J} \rangle_s|^2}{2 \langle \rho \rangle_s} \right) \tag{16}$$

$$= \frac{1}{c_v} \left(\frac{\langle K \rangle_s}{\langle \rho \rangle_s} - \frac{1}{2} |\langle \mathbf{u} \rangle_s^*|^2 \right), \tag{17}$$

so $\lim_{S \to \infty} \langle T \rangle_s^* = \overline{T}$.

There are several alternative (and incorrect) hydrodynamic definitions for temperaturein common use. The most naive is to define temperature in terms of the

instantaneous internal energy per particle:

$$\hat{T}_j = \frac{1}{c_v \rho_j} \left(K_j - \frac{|\mathbf{J}_j|^2}{2\rho_j} \right) \tag{18}$$

$$= \frac{1}{c_v} \left(\frac{K_j}{\rho_j} - \frac{1}{2}|\hat{\mathbf{u}}_j|^2 \right). \tag{19}$$

Note that this definition is problematic if $\rho_j = 0$, in the same fashion as already discussed for $\hat{\mathbf{u}}_j$, so the evaluation of the mean value should exclude those samples. A more serious flaw with this definition of temperature is that it is biased, even at equilibrium with $\overline{\mathbf{u}} = 0$, because it fails to account for the fluctuations of the center-of-mass velocity, as shown in Section 4.2. This definition appears in the standard literature of computational statistical mechanics (e.g., §2.4,[2]) and its use is appropriate in the canonical ensemble (fixed N) but not in general.

A simple modification improves the above definition. Arguing that the unbiased estimate of variance must account for the statistical degree of freedom lost in estimating $\hat{\mathbf{u}}_j$, one writes the improved estimate thus:

$$\hat{T}_j = \frac{K_j - \frac{1}{2}\rho_j|\hat{\mathbf{u}}_j|^2}{c_v(\rho_j - m/V)} = \frac{K_j - \frac{1}{2}\rho_j|\hat{\mathbf{u}}_j|^2}{c_v m(N_j - 1)/V}. \tag{20}$$

Note that in this case averages are computed omitting samples where $N_j = 0$ or 1. This construction may be used in equilibrium simulations (e.g., §4.1, [7]) but in Section 4.2 we show that it is biased out of equilibrium.

2.3. *Other Hydrodynamic Variables.* In this paper we focus on the hydrodynamic variables of fluid velocity and translational temperature, but there are many others. If the molecules have internal structure, one may separately define temperatures for other degrees of freedom (e.g., rotational, vibrational) [4]. Here we only consider a single species fluid but the more general case would include concentration as a hydrodynamic variable.

The pressure in a fluid is defined by the equation of state, which may be quite complicated in general. A simple case, however, is the ideal gas law $\overline{P} = \overline{\rho}R\overline{T}$, where $R = k_B/m$ is the gas constant and k_B is Boltzmann's constant. Using mechanical variables, the unbiased sample estimate of the mean pressure is then

$$\langle P \rangle_s^* = \frac{R}{c_v} \left(\langle K \rangle_s - \frac{|\langle \mathbf{J} \rangle_s|^2}{2\langle \rho \rangle_s} \right) = \frac{R}{c_v} \left(\langle K \rangle_s - \frac{1}{2}\langle \rho \rangle_s |\langle \mathbf{u} \rangle_s^*|^2 \right). \tag{21}$$

The stress tensor and heat flux are also complicated in general, but for an ideal gas they may be expressed in terms of moments of the molecular velocity distribution.

Evaluating means and variances from sample averages of instantaneous hydrodynamic variables isprone to the biases found for fluid velocity and temperature.

Since the analysis for other variables follows the same lines, for brevity we simply reiterate that unbiased estimates are only guaranteed when defining means and variances in terms of mechanical variables.

3. Variances and Correlations

To formulate the measurement of variances and correlations, recall that our hydrodynamic variables are defined in terms of mechanical variables as $\overline{\mathcal{H}} = \mathcal{H}(\overline{\rho}, \overline{\mathbf{J}}, \overline{K})$. We define a fluctuation in $\mathcal{H}$ as

$$\delta\mathcal{H} = \mathcal{H}(\rho, \mathbf{J}, K) - \mathcal{H}(\overline{\rho}, \overline{\mathbf{J}}, \overline{K}) \tag{22}$$

$$= \mathcal{H}(\overline{\rho} + \delta\rho, \overline{\mathbf{J}} + \delta\mathbf{J}, \overline{K} + \delta\mathbf{J}) - \mathcal{H}(\overline{\rho}, \overline{\mathbf{J}}, \overline{K}) \tag{23}$$

$$= \delta\rho \left.\frac{\partial\mathcal{H}}{\partial\rho}\right|_{\overline{\rho},\overline{\mathbf{J}},\overline{K}} + \delta\mathbf{J} \cdot \left.\frac{\partial\mathcal{H}}{\partial\mathbf{J}}\right|_{\overline{\rho},\overline{\mathbf{J}},\overline{K}} + \delta K \left.\frac{\partial\mathcal{H}}{\partial K}\right|_{\overline{\rho},\overline{\mathbf{J}},\overline{K}} + O(\delta\mathcal{M}^2), \tag{24}$$

Note that

$$\langle\delta\mathcal{H}\rangle_s^* = \mathcal{H}(\langle\rho\rangle_s, \langle\mathbf{J}\rangle_s, \langle K\rangle_s) - \mathcal{H}(\overline{\rho}, \overline{\mathbf{J}}, \overline{K}), \tag{25}$$

so $\lim_{S\to\infty}\langle\delta\mathcal{H}\rangle_s^* = \overline{\delta\mathcal{H}} = 0$. In general, the exact means are unknown so for estimating $\delta\mathcal{H}$ we implicitly take $\overline{\mathcal{M}} = \langle\mathcal{M}\rangle_s$ and also drop the higher order terms. This construction allows us to formulate the variance of hydrodynamic variables in terms of the variances of mechanical variables, which may be estimated from samples. The remainder of this section presents expressions for variances and correlations involving fluid velocity and temperature.

3.1. *Fluid Velocity Fluctuations.* First consider fluid velocity, whose fluctuations are expressed in terms of fluctuations of mechanical variables as

$$\delta\mathbf{u} = \frac{\delta\mathbf{J}}{\overline{\rho}} - \frac{\overline{\mathbf{J}}}{\overline{\rho}^2}\delta\rho = \frac{1}{\overline{\rho}}\left(\delta\mathbf{J} - \overline{\mathbf{u}}\,\delta\rho\right), \tag{26}$$

or for the x-component,

$$\delta u_x = \frac{1}{\overline{\rho}}\left(\delta J_x - \overline{u}_x\,\delta\rho\right). \tag{27}$$

The correlation of mass density fluctuations in cell C and fluid velocity fluctuations in cell C' is

$$\langle\delta\rho\,\delta u_x'\rangle_s^* = \frac{1}{\overline{\rho}'}\left(\langle\delta\rho\,\delta J_x'\rangle_s - \overline{u}_x'\langle\delta\rho\,\delta\rho'\rangle_s\right) \tag{28}$$

with similar expressions for the other components.

The sample estimated variance of the x-component of fluid velocity is

$$\langle \delta u_x^2 \rangle_s^* = \frac{1}{\bar{\rho}^2} \langle (\delta J_x - \bar{u}_x \, \delta \rho)^2 \rangle_s \tag{29}$$

$$= \frac{1}{\bar{\rho}^2} \left(\langle \delta J_x^2 \rangle_s - 2\bar{u}_x \langle \delta \rho \, \delta J_x \rangle_s + \bar{u}_x^2 \langle \delta \rho^2 \rangle_s \right). \tag{30}$$

If the system is isotropic (i.e., $\bar{\mathbf{u}} = 0$), then $\overline{|\delta \mathbf{u}|^2} = d \, \overline{\delta u_x^2} = d \, \overline{\delta J_x^2}/\bar{\rho}^2$, where d is the dimensionality. The correlations of velocity components are similarly obtained, for example,

$$\langle \delta u_x \, \delta u_y' \rangle_s^* = \frac{1}{\bar{\rho} \, \bar{\rho}'} \left(\langle \delta J_x \, \delta J_y' \rangle_s - \bar{u}_x \langle \delta \rho \, \delta J_y' \rangle_s - \bar{u}_y' \langle \delta \rho' \, \delta J_x \rangle_s + \bar{u}_x \bar{u}_y' \langle \delta \rho \, \delta \rho' \rangle_s \right), \tag{31}$$

with similar results for the other components.

3.2. *Temperature Fluctuations.* In terms of mechanical variables, the fluctuation of temperature may be written as

$$\delta T = \frac{1}{c_v \bar{\rho}} \left\{ \delta K - \bar{\mathbf{u}} \cdot \delta \mathbf{J} - \left(c_v \bar{T} - \tfrac{1}{2} |\bar{\mathbf{u}}|^2 \right) \delta \rho \right\}$$

$$= \frac{1}{c_v \bar{\rho}} \left\{ \delta K - \delta G - \overline{Q} \, \delta \rho \right\}, \tag{32}$$

where $\delta G \equiv \bar{\mathbf{u}} \cdot \delta \mathbf{J}$ and $\overline{Q} \equiv c_v \bar{T} - \tfrac{1}{2} |\bar{\mathbf{u}}|^2$. From this, the estimated sample correlation of temperature fluctuations is

$$\langle \delta T \delta T' \rangle_s^* = \frac{1}{c_v^2 \bar{\rho} \, \bar{\rho}'} \left\{ \langle \delta K \delta K' \rangle_s + \langle \delta G \delta G' \rangle_s + \overline{Q} \, \overline{Q}' \langle \delta \rho \, \delta \rho' \rangle_s \right.$$

$$- \langle \delta K \delta G' \rangle_s - \langle \delta G \delta K' \rangle_s - \overline{Q}' \langle \delta K \delta \rho' \rangle_s - \overline{Q} \langle \delta \rho \, \delta K' \rangle_s$$

$$\left. + \overline{Q}' \langle \delta G \, \delta \rho' \rangle_s + \overline{Q} \langle \delta \rho \, \delta G' \rangle_s \right\}. \tag{33}$$

The covariance of density and temperature fluctuations is

$$\langle \delta \rho \, \delta T' \rangle_s^* = \frac{1}{c_v \bar{\rho}'} \left\{ \langle \delta \rho \, \delta K' \rangle_s - \langle \delta \rho \, \delta G' \rangle_s - \overline{Q}' \langle \delta \rho \, \delta \rho' \rangle_s \right\}. \tag{34}$$

The covariance of fluid velocity and temperature is

$$\langle \delta u_x \, \delta T' \rangle_s^* = \frac{1}{c_v \bar{\rho} \, \bar{\rho}'} \left\{ \langle \delta J_x \, \delta K' \rangle_s - u_x \langle \delta \rho \, \delta K' \rangle_s \right.$$

$$\left. - \langle \delta J_x \, \delta G' \rangle_s + u_x \langle \delta \rho \, \delta G' \rangle_s - \overline{Q}' \langle \delta J_x \, \delta \rho' \rangle_s + u_x \overline{Q}' \langle \delta \rho \, \delta \rho' \rangle_s \right\}. \tag{35}$$

4. Biases due to Fluctuations

We now consider the possible bias in the statistical measurements of hydrodynamic variables due to fluctuations. To derive and illustrate these results we consider four separate approaches, two for equilibrium and two for nonequilibrium systems. The first is the direct evaluation of statistical means at thermodynamic equilibrium; this methodology is straightforward and details of the calculations are collected in Appendix A. Results for the variances and correlations are compared with fluctuating hydrodynamic theory, which is summarized in Appendix B. The second approach is similar to the first but uses stochastic numerical simulations to generate random samples (see Appendix C). These numerical results illustrate the predicted phenomena and verify the accuracy of various approximate results.

For nonequilibrium systems, various definitions for mean values of fluid velocity and temperature are compared to quadratic order in fluctuations, indicating how a bias may be introduced by nonequilibrium correlations. The predicted bias is confirmed by the fourth approach—molecular simulations of a dilute gas in a closed system with a temperature gradient (see Appendix D). Note that the four approaches are intertwined in the presentation below.

4.1. *Bias for Fluid Velocity.* First we consider two ways to estimate the mean value of fluid velocity, $\langle \mathbf{u} \rangle_s^*$ and $\langle \hat{\mathbf{u}} \rangle_s$, as introduced in Section 2.1. By direct evaluation (see (55), (56) and (59)) we find that both definitions are unbiased at equilibrium (even if $\overline{\mathbf{u}} \neq 0$), a result confirmed by numerical simulation. However, $\langle \mathbf{u} \rangle_s^*$ and $\langle \hat{\mathbf{u}} \rangle_s$ are not equivalent out of equilibrium. To see why, note that the sample mean of the center-of-mass velocity from equation (12) may be written as

$$\langle \hat{\mathbf{u}} \rangle_s = \left\langle \frac{\mathbf{J}}{\rho} \right\rangle_s = \left\langle \frac{\overline{\mathbf{J}} + \delta\mathbf{J}}{\overline{\rho} + \delta\rho} \right\rangle_s \tag{36}$$

$$= \frac{\overline{\mathbf{J}}}{\overline{\rho}} \left\langle \left(1 + \frac{\delta\mathbf{J}}{\overline{\mathbf{J}}}\right)\left(1 - \frac{\delta\rho}{\overline{\rho}} + \frac{\delta\rho^2}{\overline{\rho}^2}\right) \right\rangle_s + O(\delta\mathcal{M}^3) \tag{37}$$

$$= \overline{\mathbf{u}} \left(1 + \frac{\langle \delta\rho^2 \rangle_s}{\overline{\rho}^2}\right) - \frac{\langle \delta\rho \, \delta\mathbf{J} \rangle_s}{\overline{\rho}^2} + O(\delta\mathcal{M}^3). \tag{38}$$

From (26), $\delta\mathbf{J} = \overline{\rho}\delta\mathbf{u} + \overline{\mathbf{u}}\delta\rho$, so in the limit where the number of samples $S \to \infty$,

$$\langle \hat{\mathbf{u}} \rangle_\infty = \overline{\mathbf{u}} - \frac{\overline{\delta\rho \, \delta\mathbf{u}}}{\overline{\rho}} + O(\delta\mathcal{M}^3). \tag{39}$$

The correlation $\overline{\delta\rho \, \delta\mathbf{u}}$ is zero at equilibrium (see Appendix B) but, in general, nonzero for nonequilibrium systems [20]. The correlation $\overline{\delta\rho\delta\mathbf{u}} \propto \nabla T$ and the fact

that $\langle \hat{\mathbf{u}} \rangle_\infty \neq 0$ in a closed system indicates a violation of mass conservation, as cautioned by Landau and Lifshitz (see Section 2 above). Finally, since $\overline{\delta\rho\,\delta\mathbf{u}} \propto V^{-1}$, the quantity $\langle \hat{\mathbf{u}} \rangle_\infty$ is not an intensive variable.

This bias of the center-of-mass fluid velocity is studied at length in [26] where it is shown that the nonequilibrium correlation $\overline{\delta\rho\,\delta\mathbf{u}}$ leads to an anomalous flow, as measured by $\langle \hat{\mathbf{u}} \rangle_s$, in closed systems.[1] For the simulation parameters listed in Appendix D the anomalous flow velocity is about $10^{-4}c$ for the large system and $10^{-3}c$ for the small system, where c is the sound speed.

At equilibrium, the variance of fluid velocity is (see Appendix B),

$$\overline{|\delta\mathbf{u}|^2} = d\,\frac{k_B\overline{T}}{\overline{\rho}V} = d\,\frac{C_T^2}{\overline{N}}.\tag{40}$$

By direct evaluation, the definition based on the variances of mechanical variables is found to be unbiased, that is $\langle|\delta\mathbf{u}|^2\rangle_\infty^* = \overline{|\delta\mathbf{u}|^2}$, (see equation (62)) whereas the center-of-mass definition gives (see equation (66)),

$$\langle|\delta\hat{\mathbf{u}}|^2\rangle_\infty \approx \overline{|\delta\mathbf{u}|^2}\left(1 + \frac{\overline{\delta N^2}}{\overline{N}^2}\right).\tag{41}$$

Figure 1 shows the fractional errors in the sample estimate for the variance of fluid velocity, that is

$$\frac{\langle|\delta\mathbf{u}|^2\rangle_s^* - \overline{|\delta\mathbf{u}|^2}}{\overline{|\delta\mathbf{u}|^2}}\qquad\text{and}\qquad\frac{\langle|\delta\hat{\mathbf{u}}|^2\rangle_s - \overline{|\delta\mathbf{u}|^2}}{\overline{|\delta\mathbf{u}|^2}}.$$

In the simulations N is Poisson-distributed, so $\overline{\delta N^2} = \overline{N}$; thus the error goes roughly as $1/\overline{N}$. Note that this fractional error is significant (e.g., about 5% for $\overline{N} = 20$).

4.2. *Bias for Temperature.* Section 2.2 introduced three definitions for the sample mean temperature, specifically the definition in terms of mean values of mechanical variables, $\langle T\rangle_s^*$ (equation (16)), and two definitions based on instantaneous temperature. The latter may be combined and written as

$$\hat{T}_\alpha = \frac{K - \frac{1}{2}\rho|\hat{\mathbf{u}}|^2}{c_V(\rho - \alpha m/V)},\tag{42}$$

where $\alpha = 0$ for equation (18) and $\alpha = 1$ for equation (20).

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[1]In [26] the quantity $\langle\mathbf{u}\rangle_s^*$ is referred to as the Cumulative-Averaged-Measurement (CAM) of fluid velocity and $\langle\hat{\mathbf{u}}\rangle_s$ is called the Sample-Averaged-Measurement (SAM) of velocity.
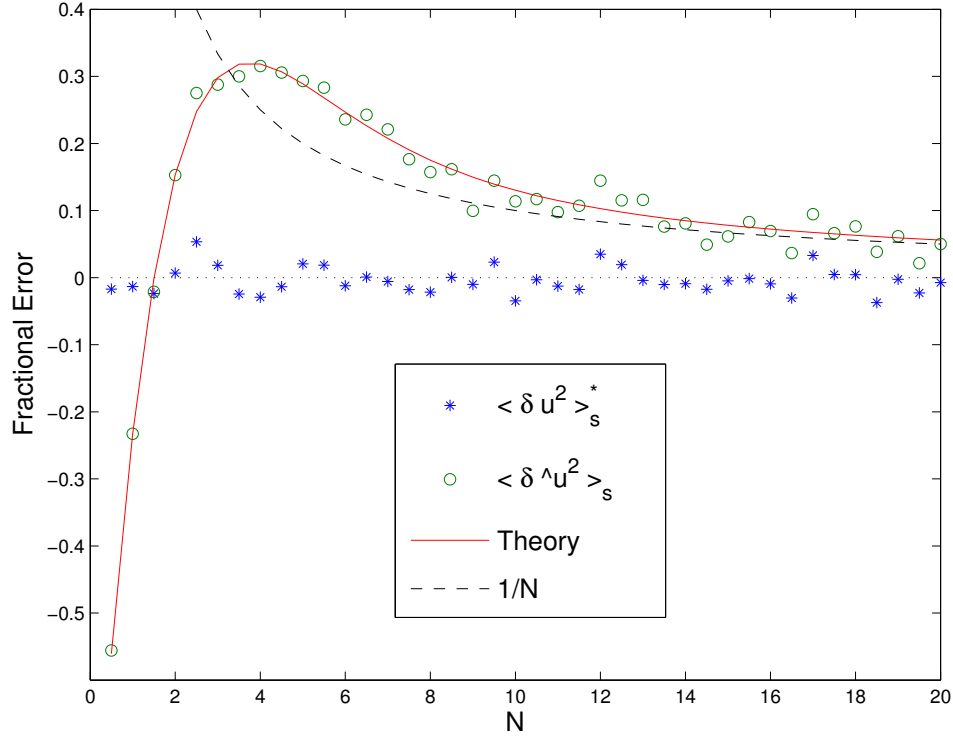
Figure 1. Fractional error in the sample variance of fluid velocity versus $\overline{N}$ for: $\langle|\delta\mathbf{u}|^2\rangle_s^*$ (asterisks); $\langle|\delta\hat{\mathbf{u}}|^2\rangle_s$ (circles). Solid line given by equation (63); dashed line is $1/\overline{N}$ (dashed line).

By direct evaluation (see (73), (76)), we find that $\langle T\rangle_\infty^* = \langle\hat{T}_1\rangle_\infty = \overline{T}$ at equilibrium, while

$$\langle\hat{T}_0\rangle_\infty \approx \left(1 - \frac{1}{\overline{N}}\right)\overline{T}. \tag{43}$$

Figure 2 confirms these results, showing the fractional error in the sample mean of temperature (relative to $\overline{T}$) versus the mean number $\overline{N}$ of particles. Note that the fractional error for $\langle\hat{T}_0\rangle_\infty$ is significant (e.g., about 5% for $\overline{N} = 20$).

For a more general result, applicable to nonequilibrium cases, we write the sample mean of instantaneous temperature as

$$\langle\hat{T}_\alpha\rangle_s = \frac{1}{c_V}\left\langle\frac{K - \frac{1}{2}\rho|\hat{\mathbf{u}}|^2}{\rho - \alpha m/V}\right\rangle_s \tag{44}$$

$$= \left(1 + \frac{\alpha m}{\overline{\rho}V}\right)\overline{T} - \frac{1}{\overline{\rho}c_V}\left\langle\frac{\delta\rho}{\overline{\rho}}\left(\delta K - \frac{1}{2}\delta\rho|\overline{\mathbf{u}}|^2 - \rho\overline{\mathbf{u}}\cdot\delta\mathbf{u}\right)\right\rangle_s + O(\delta\mathcal{M}^3).$$
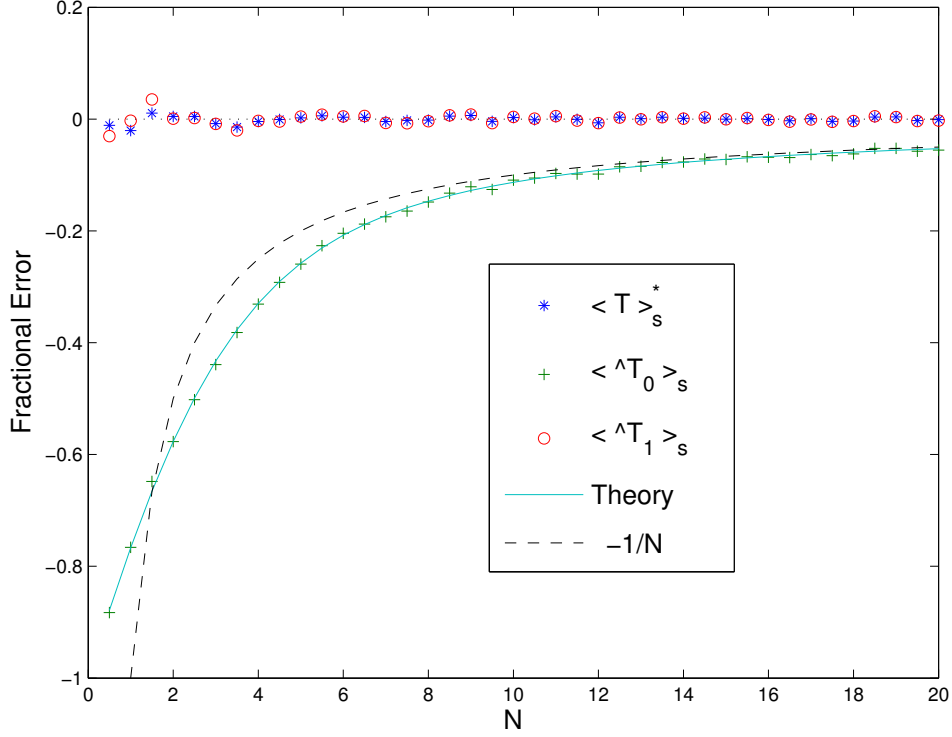
Figure 2. Fractional error in the sample mean of temperature versus $\overline{N}$ for: $\langle T \rangle_s^*$ (asterisks), $\langle \hat{T}_0 \rangle_s$ (crosses) and $\langle \hat{T}_1 \rangle_s$ (circles). Solid line given by equation (73); dashed line is $-1/\overline{N}$.

Using the results from Section 3, after some algebra, we find

$$\langle \hat{T}_\alpha \rangle_s = \left[1 + \frac{\alpha}{\overline{N}} - \frac{\langle \delta \rho^2 \rangle_s}{\overline{\rho}^2} \right] \overline{T} - \frac{\langle \delta \rho \, \delta T \rangle_s^*}{\overline{\rho}} + O(\delta \mathcal{M}^3). \tag{45}$$

At equilibrium $\overline{\delta \rho \delta T} = 0$ so by comparison with the results from direct evaluation we have

$$\langle \hat{T}_1 \rangle_\infty = \overline{T} - \frac{\overline{\delta \rho \, \delta T}}{\overline{\rho}} + O(\delta \mathcal{M}^3). \tag{46}$$

This result is verified by molecular simulations of a nonequilibrium system at a steady state, specifically a dilute gas between a pair of thermal walls at different temperatures (see Appendix D). The predicted bias from (46) is in good agreement with the bias measured in both the large (132 particles per sample cell) and small (8.2 particles per sample cell) systems. In the latter case the absolute temperature bias is a few Kelvin (about 1% of the mean), while in the large system the bias is smaller by a factor of $132/8.2 \approx 16$, since $\overline{\delta \rho \, \delta T} \propto V^{-1}$. This result confirms the
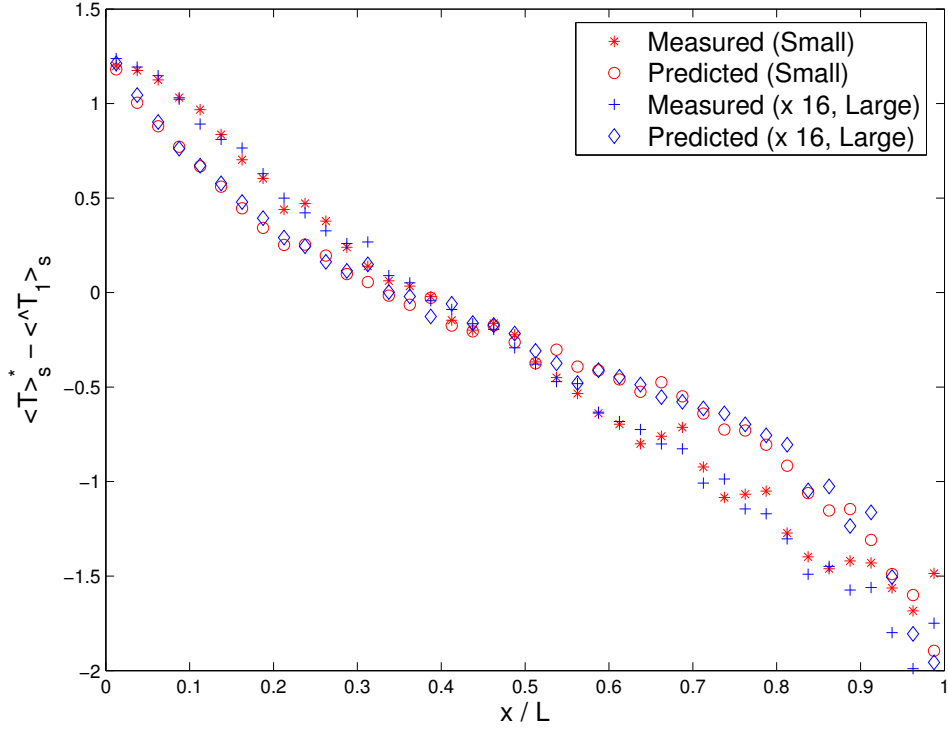
Figure 3. Measured temperature difference $\langle T \rangle_s^* - \langle \hat{T}_1 \rangle_s$ [small (asterisks), large (crosses) systems] and theory prediction, $\langle \delta\rho \, \delta T \rangle_s^* / \langle \rho \rangle_s$ [small (circles), large (diamonds) systems] versus position. Results for the large system are scaled by a multiplicative factor of 16. Wall temperatures are 273 and 809 Kelvin; see Appendix D for other parameters.

warning given in Section 2 that the means of instantaneous hydrodynamic variables are not intensive quantities.

Finally, we consider the measurement of temperature fluctuations, choosing among the many possible examples the correlation of density and temperature fluctuations. As mentioned above, at equilibrium $\overline{\delta\rho \, \delta T} = 0$; by direct evaluation we get $\langle \delta\rho \, \delta T \rangle_\infty^* = 0$ (see Appendix A), while for the two definitions of instantaneous temperature we find (see eqns. (78) and (79)),

$$\langle \delta\rho \, \delta \hat{T}_0 \rangle_\infty = \overline{\rho}\overline{T} \sum_{N=1}^{\infty} \left(\frac{N-1}{\overline{N}} - \frac{N-1}{N} \right) \frac{P(N)}{1 - P(0)} \tag{47}$$

$$\approx \overline{\rho}\overline{T} \, \frac{\overline{\delta N^2}}{\overline{N}^3} \tag{48}$$

and

$$\langle \delta\rho\, \delta\hat{T}_1 \rangle_\infty = \frac{\overline{\rho}\,\overline{T}}{\overline{N}} \left(\frac{\overline{N}P(0) + (\overline{N}-1)P(1)}{1 - P(0) - P(1)} \right), \tag{49}$$

where $P(N)$ is the probability distribution for N. When this is the Poisson distribution, then

$$\langle \delta\rho\, \delta\hat{T}_0 \rangle_\infty \approx \frac{\overline{\rho}\,\overline{T}}{\overline{N}^2} \tag{50}$$

and

$$\langle \delta\rho\, \delta\hat{T}_1 \rangle_\infty = \overline{\rho}\,\overline{T}\,\overline{N}e^{-\overline{N}}. \tag{51}$$

These results are illustrated and verified in Figure 4 where the scaled error (relative to $(\overline{\delta\rho^2}\,\overline{\delta T^2})^{1/2}$) in the correlation of density and temperature versus $\overline{N}$ is presented for equilibrium simulation measurements (see Appendix C). The bias for $\langle \delta\rho\, \delta\hat{T}_0 \rangle_\infty$ is significant (scaled error of about 7% for $\overline{N} = 20$) while the bias for $\langle \delta\rho\, \delta\hat{T}_1 \rangle_\infty$ decreases quickly with $\overline{N}$ (scaled error is less than 1% for $\overline{N} = 10$). On the other hand, the bias in the variance $\langle \delta\hat{T}_1^2 \rangle_\infty$ turns out to be significant (e.g., over 10% for $\overline{N} = 20$).

5. Summary and Concluding Remarks

In this paper we demonstrate that in the presence of spontaneous fluctuations the statistical measurement of hydrodynamic quantities, such as fluid velocity and translational temperature, should be done by sampling mechanical variables, such as momentum and kinetic energy densities. The correct constructions for means and variances are given in sections 2 and 3, respectively. In those sections we caution that using definitions based on instantaneous fluid velocity and instantaneous temperature leads to biased statistical results (as shown in Section 4).

Molecular simulations have been used in the study of fluids for nearly half a century, so why are the results presented in this paper not well known? First, one should recall that most molecular dynamics simulations are of equilibrium systems for the purpose of computing thermodynamic properties, such as the equation of state. The computation of means and fluctuations of thermodynamic quantities in the various ensembles of statistical mechanics is certainly well known [2; 7].

Molecular dynamics simulations of hydrodynamic phenomena are more recent (e.g. [17]) and often focus on qualitative features (e.g., appearance of vortex shedding).[2] Other molecular algorithms, such as direct simulation Monte Carlo [4] and lattice gases [24], have always been applied to nonequilibrium flows, yet, as with molecular dynamics, the biases due to fluctuations were not identified. Errors due to these biases were either dismissed as small numerical artifacts (e.g., finite time

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[2]Evan's nonequilibrium molecular dynamics (NEMD) approach is not designed for hydrodynamic flows but rather is a method for obtaining transport properties, such as viscosity [6].
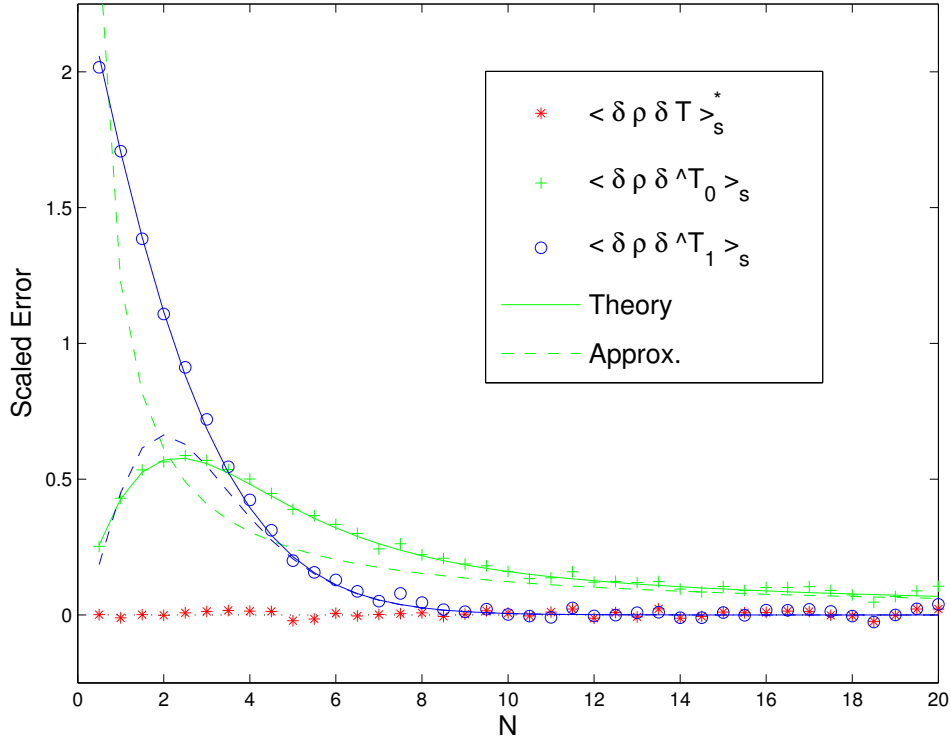
Figure 4. Scaled error in the correlation of density and temperature (relative to $(\overline{\delta\rho^2}\,\overline{\delta T^2})^{1/2}$) versus $\overline{N}$ for: $\langle\delta\rho\,\delta T\rangle_s^*$ (asterisks), $\langle\delta\rho\,\delta\hat{T}_0\rangle_s$, (crosses) and $\langle\delta\rho\,\delta\hat{T}_1\rangle_s$ (circles). Solid lines are theoretical predictions (47) and (49); dashed lines are approximations (50) and (51).

step effects) or masked by other errors (e.g., large statistical uncertainties). Since the bias in the mean values is usually quite small (about 0.1 Kelvin for the large system in Figure 3) either possibility is plausible.

Another possibility is that, in some cases, no errors were made in measuring hydrodynamic quantities because the sampling happened to be equivalent to the unbiased formulation using mechanical variables (e.g., programs in [4]). Unfortunately, one rarely finds a detailed description in the literature of how statistical measurements are performed, especially for fluid velocity.

In molecular simulations of hydrodynamic flows, variances are usually measured only for the purpose of estimating error bars [11]. As such, the effects described in this paper are unlikely to have been noticed by many computational scientists. On the other hand, my own research is in the field of nonequilibrium

fluctuations, which is how these effects came to my attention. The recent computational studies of nano-scale and multi-scale flows, as well as of Brownian motors, may also profit from this paper's analysis regarding the measurement of microscopic fluctuations in molecular simulations. The importance of these fluctuations is appreciated by noting that a typical molecular motor protein consumes ATP at a power of roughly 10^{-16} watts while operating in a background of 10^{-8} watts of thermal noise power, which has been said tobe "as difficult as walking in a hurricane is for us." [3]

Finally, we have focused on the effect of fluctuations in particle-based simulations, yet these effects have a physical rather than numerical origin so the discussion also applies to continuum methods for stochastic partial differential equations. The deterministic hydrodynamic equations can be augmented by the inclusion of stochastic fluxes due to thermal fluctuations. These fluctuating hydrodynamic equations [18] accurately capture equilibrium and nonequilibrium effects and can be computed numerically (see [9] for a simple, finite-difference scheme). Any numerical computation of hydrodynamic phenomena that includes spontaneous fluctuations may be susceptible to the effects presented in this paper. *Caveat ratiocinator*.

Appendix A: Direct Evaluation at Equilibrium

In this appendix we obtain, by direct evaluation, mean values and variances of mechanical and hydrodynamic variables at thermodynamic equilibrium. To perform this analysis, we first need to say something about the probability distributions for the fluid particles, specifically, $P(\mathbf{v})$, the probability that a particle has velocity $\mathbf{v}$ and $P(N)$, the probability that a cell has N particles.

From the principle of equipartition, at thermodynamic equilibrium the velocities of classical particles are Gaussian-distributed with mean $\overline{\mathbf{v}} = \overline{\mathbf{u}}$ and variance $\overline{|\mathbf{v} - \overline{\mathbf{v}}|^2} = \overline{|\delta\mathbf{v}|^2} = d\,C_T^2 = d\,k_B\overline{T}/m$ where C_T is the thermal speed. Note that thermodynamic equilibrium does *not* imply $\overline{\mathbf{u}} = 0$ since a system is in equilibrium in all inertial frames of reference.

The distribution for N depends on the equation of state for the fluid. For the present analysis we only require the mean $\overline{N} = \overline{N}$ and variance $\overline{\delta N^2} = \sigma_N^2$. In dense fluids σ_N^2 is small since it is proportional to the fluids' compressibility; in the case of a dilute gas, N is Poisson-distributed with $\sigma_N^2 = \overline{N}$.

For some definitions of instantaneous variables (e.g., eqns. (12) and (18)) we need to exclude the state $N = 0$, in which case we use the distribution

$$P_0(N) = \frac{1}{1 - P(0)}\, P(N) \tag{52}$$

for $N = 1, \ldots, \infty$. For the alternative temperature definition, equation (20), we need to exclude the states $N = 0$ or 1, in which case we use the distribution

$$P_{01}(N) = \frac{1}{1 - P(0) - P(1)} \, P(N) \tag{53}$$

for $N = 2, \ldots, \infty$.

Mean values may be obtained by direct evaluation,

$$\langle X \rangle_\infty = \sum_{N=0}^{\infty} \int d\mathbf{v}_1 \ldots \int d\mathbf{v}_N \, X(N, \mathbf{v}_1, \ldots, \mathbf{v}_N) P(N) P(\mathbf{v}_1) \ldots P(\mathbf{v}_N), \tag{54}$$

with the minor modification that the sum starts at $N = 1$ or $N = 2$ if P_0 or P_{01} is used in place of $P(N)$. For the mechanical variables, we easily find

$$\begin{aligned}
\langle \rho \rangle_\infty &= \frac{1}{V} \sum_{N=0}^{\infty} \int d\mathbf{v}_1 \ldots \int d\mathbf{v}_N \left(\sum_{k=1}^{N} m \right) P(N) P(\mathbf{v}_1) \ldots P(\mathbf{v}_N) \\
&= \frac{1}{V} \sum_{N=0}^{\infty} \left(Nm \right) P(N) = \frac{m\overline{N}}{V} = \overline{\rho}.
\end{aligned} \tag{55}$$

Similarly,

$$\begin{aligned}
\langle \mathbf{J} \rangle_\infty &= \frac{1}{V} \sum_{N=0}^{\infty} \int d\mathbf{v}_1 \ldots \int d\mathbf{v}_N \left(\sum_{k=1}^{N} m\mathbf{v}_k \right) P(N) P(\mathbf{v}_1) \ldots P(\mathbf{v}_N) \\
&= \frac{1}{V} \sum_{N=0}^{\infty} \left(Nm\overline{\mathbf{v}} \right) P(N) = \frac{m\overline{N}}{V} \overline{\mathbf{v}} = \overline{\rho} \, \overline{\mathbf{u}}
\end{aligned} \tag{56}$$

and

$$\begin{aligned}
\langle K \rangle_\infty &= \frac{1}{V} \sum_{N=0}^{\infty} \int d\mathbf{v}_1 \ldots \int d\mathbf{v}_N \left(\sum_{k=1}^{N} \tfrac{1}{2} m |\mathbf{v}_k|^2 \right) P(N) P(\mathbf{v}_1) \ldots P(\mathbf{v}_N) \\
&= \frac{m\overline{N}}{V} \, \tfrac{1}{2} \overline{|\mathbf{v}|^2} = \overline{\rho}(c_v \overline{T} + \frac{1}{2} |\overline{\mathbf{u}}|^2),
\end{aligned} \tag{57}$$

confirming the expected result that $\langle \mathcal{M} \rangle_\infty = \overline{\mathcal{M}}$.

The variances and covariances of the mechanical variables may be evaluated directly. For example,

$$\langle \delta \rho^2 \rangle_\infty = \frac{1}{V^2} \sum_{N=0}^{\infty} \int d\mathbf{v}_1 \dots \int d\mathbf{v}_N \left[\left(\sum_{k=1}^{N} m \right) - \bar{\rho} \right]^2 P(N) P(\mathbf{v}_1) \dots P(\mathbf{v}_N)$$

$$= \frac{1}{V^2} \sum_{N=0}^{\infty} \left[Nm - \bar{N}m \right]^2 P(N) = \frac{m^2}{V^2} \overline{\delta N^2} = \bar{\rho}^2 \frac{\sigma_N^2}{\bar{N}^2}. \tag{58}$$

The procedure is straightforward (though tedious) for the other variables; the results are the same as in eqns. (83)–(88) in Appendix B.

Fluid Velocity. From the results above, the mean fluid velocity

$$\langle \mathbf{u} \rangle_\infty^* = \langle \mathbf{J} \rangle_\infty / \langle \rho \rangle_\infty = \bar{\mathbf{J}}/\bar{\rho} = \bar{\mathbf{u}}.$$

At equilibrium we find for the center-of-mass velocity,

$$\langle \hat{\mathbf{u}} \rangle_\infty = \sum_{N=1}^{\infty} \int d\mathbf{v}_1 \dots \int d\mathbf{v}_N \left(\frac{\mathbf{v}_1 + \dots \mathbf{v}_N}{N} \right) P_0(N) P(\mathbf{v}_1) \dots P(\mathbf{v}_N) \tag{59}$$

$$= \sum_{N=1}^{\infty} \frac{N\bar{\mathbf{v}}}{N} P_0(N) = \bar{\mathbf{u}}, \tag{60}$$

where the $N = 0$ case is excluded. An alternative approach would be to take $\hat{\mathbf{u}}_j = 0$ when $N_j = 0$ which gives

$$\langle \hat{\mathbf{u}}' \rangle_\infty = \sum_{N=0}^{\infty} \frac{N\bar{\mathbf{u}}}{N} (1 - \delta_{N,0}) P(N) = \bar{\mathbf{u}} \left(\sum_{N=0}^{\infty} P(N) \right) - \bar{\mathbf{u}} P(0)$$

$$= (1 - P(0))\bar{\mathbf{u}}, \tag{61}$$

so at equilibrium this definition for the mean of the center-of-mass velocity does not equal the fluid velocity except when $\bar{\mathbf{u}} = 0$.

From (29), the variance of fluid velocity as obtained from mechanical variables is

$$\langle |\delta \mathbf{u}|^2 \rangle_\infty^* = \frac{1}{\bar{\rho}^2} (\overline{|\delta \mathbf{J}|^2} - 2\bar{\mathbf{u}} \cdot \overline{\delta \rho \mathbf{J}} + |\bar{\mathbf{u}}|^2 \overline{\delta \rho^2}). \tag{62}$$

Using (80), (83), and (86), we find $\langle|\delta\mathbf{u}|^2\rangle^*_\infty = dC_T^2/\overline{N} = \overline{|\delta\mathbf{u}|^2}$. By direct evaluation, the variance of the center-of-mass velocity is

$$\langle|\delta\hat{\mathbf{u}}|^2\rangle_\infty = \sum_{N=1}^\infty \int d\mathbf{v}_1 \ldots \int d\mathbf{v}_N \left|\frac{\mathbf{v}_1 + \ldots + \mathbf{v}_N}{N} - \bar{\mathbf{u}}\right|^2 P_0(N) P(\mathbf{v}_1) \ldots P(\mathbf{v}_N)$$

$$= \sum_{N=1}^\infty \frac{N\overline{|\delta\mathbf{v}|^2}}{N^2} P_0(N) = d\, C_T^2 \sum_{N=1}^\infty \frac{1}{N} P_0(N). \tag{63}$$

By Jensen's inequality

$$\sum_{N=1}^\infty \frac{1}{N} P_0(N) > \sum_{N=1}^\infty \frac{1}{N} P(N) \geq \left(\sum_{N=1}^\infty N P(N)\right)^{-1} = \frac{1}{\overline{N}}, \tag{64}$$

with equality only if $P_0(N) = \delta_{N,\overline{N}}$. Excluding this trivial case, $\langle|\delta\hat{\mathbf{u}}|^2\rangle_\infty > \overline{|\delta\mathbf{u}|^2}$. Since

$$\overline{N^{-1}} = \frac{1}{\overline{N}}\left(1 + \frac{\sigma_N^2}{\overline{N}^2} + O(\delta N^3)\right), \tag{65}$$

we have

$$\langle|\delta\hat{\mathbf{u}}|^2\rangle_\infty = \overline{|\delta\mathbf{u}|^2}\left(1 + \frac{\sigma_N^2}{\overline{N}^2} + O(\delta N^3)\right). \tag{66}$$

If N is Poisson-distributed, then

$$\langle|\delta\hat{\mathbf{u}}|^2\rangle_\infty = \overline{|\delta\mathbf{u}|^2}\left(1 + \frac{1}{\overline{N}} + O(\delta N^3)\right) \tag{67}$$

Finally, note that we may write

$$\langle|\delta\hat{\mathbf{u}}|^2\rangle_\infty = \sum_{N=1}^\infty \langle|\delta\hat{\mathbf{u}}|_N^2\rangle_\infty P_0(N), \tag{68}$$

where

$$\langle|\delta\hat{\mathbf{u}}|_N^2\rangle_\infty = \frac{d\, C_T^2}{N} \tag{69}$$

is the variance of the center-of-mass velocity for a given value of N, a result used below.

Temperature. From (16), (55), (56), and (57) we find $\langle T\rangle^*_\infty = \overline{T}$. Turning to the two definitions of instantaneous temperature, equation (18) and (20), note that they may be combined as

$$\hat{T}_{\alpha;j} = \frac{1}{2c_V(N_j - \alpha)} \sum_k^{N_j} |\mathbf{v}_{k,j} - \hat{\mathbf{u}}_j|^2 \tag{70}$$

where $\alpha = 0$ or 1 and

$$\hat{\mathbf{u}}_j = \frac{1}{N_j} \sum_{k}^{N_j} \mathbf{v}_{k,j} \tag{71}$$

is the instantaneous center-of-mass velocity. First, consider the case $\alpha = 0$, by direct evaluation the mean value is,

$$\langle \hat{T}_0 \rangle_\infty = \frac{1}{2c_V} \sum_{N=1}^{\infty} \int d\mathbf{v}_1 \dots \int d\mathbf{v}_N \left(\frac{1}{N} \sum_{k=1}^{N} |\mathbf{v}_k - \hat{\mathbf{u}}|^2 \right) P_0(N) P(\mathbf{v}_1) \dots P(\mathbf{v}_N)$$

$$= \frac{1}{2c_V} \sum_{N=1}^{\infty} \left(\overline{|\mathbf{v}|^2} - \overline{|\hat{\mathbf{u}}|^2} \right) P_0(N) \tag{72}$$

In general $\langle \hat{T}_0 \rangle_\infty < \overline{T}$ since $|\delta\hat{\mathbf{u}}|^2 \to 0$ only in the limit $\overline{N} \to \infty$. From the above result for the variance of the center-of-mass velocity,

$$\langle \hat{T}_0 \rangle_\infty = \overline{T} \left(1 - \sum_{N=1}^{\infty} \frac{1}{N} P_0(N) \right) \tag{73}$$

$$\approx \left(1 - \frac{1}{\overline{N}} - \frac{\sigma_N^2}{\overline{N}^3} \right) \overline{T}, \tag{74}$$

so to leading order the bias for this definition of temperature is $O(1/\overline{N})$.

For the alternative definition of instantaneous temperature, equation (20), we have

$$\langle \hat{T}_1 \rangle_\infty = \frac{1}{2c_V} \sum_{N=2}^{\infty} \int d\mathbf{v}_1 \dots \int d\mathbf{v}_N \left(\frac{1}{N-1} \sum_{k=1}^{N} |\mathbf{v}_k - \hat{\mathbf{u}}|^2 \right) P_{01}(N) P(\mathbf{v}_1) \dots P(\mathbf{v}_N)$$

$$= \overline{T} \sum_{N=2}^{\infty} \frac{N}{N-1} \left(1 - \frac{\overline{|\delta\hat{\mathbf{u}}|_N^2}}{d\, C_T^2} \right) P_{01}(N), \tag{75}$$

where $\overline{|\delta\hat{\mathbf{u}}|_N^2}$ is the variance of the center-of-mass velocity for a given value of N. From (69),

$$\langle \hat{T}_1 \rangle_\infty = \frac{d\, C_T^2}{2c_V} \sum_{N=2}^{\infty} \frac{N}{N-1} \left(1 - \frac{1}{N} \right) P_{01}(N) \; = \; \overline{T} \tag{76}$$

so using this definition gives the correct mean value.

Finally, consider thecorrelation of density and temperature fluctuations; from (34) and the results for mechanical variables, $\langle \delta\rho\, \delta T \rangle_\infty^* = \overline{\delta\rho\, \delta T}$. To obtain the correlation for instantaneous temperature, we use $\langle \delta\rho\, \delta\hat{T}_\alpha \rangle_\infty = \langle \rho\hat{T}_\alpha \rangle_\infty - \overline{\rho}\langle \hat{T}_\alpha \rangle_\infty$;

direct evaluation for $\hat{T}_0$ equation (18) gives

$$\langle\rho\hat{T}_0\rangle_\infty = \frac{m}{2c_V V}\sum_{N=1}^\infty\int d\mathbf{v}_1\ldots\int d\mathbf{v}_N N\left(\frac{1}{N}\sum_{k=1}^N|\mathbf{v}_k-\hat{\mathbf{u}}|^2\right)P_0(N)P(\mathbf{v}_1)\ldots P(\mathbf{v}_N)$$

$$= \frac{m\overline{T}}{V}\sum_{N=1}^\infty N\left(1-\frac{\overline{|\delta\hat{\mathbf{u}}|_N^2}}{d\,C_T^2}\right)P_0(N) = \overline{\rho}\overline{T}\sum_{N=1}^\infty\frac{N-1}{\overline{N}}P_0(N), \tag{77}$$

so

$$\langle\delta\rho\,\delta\hat{T}_0\rangle_\infty = \overline{\rho}\overline{T}\sum_{N=1}^\infty\left(\frac{N-1}{\overline{N}}-\frac{N-1}{N}\right)P_0(N). \tag{78}$$

For the alternative definition of instantaneous temperature (equation (20)) we get

$$\langle\rho\hat{T}_1\rangle_\infty$$

$$= \frac{m}{2c_V V}\sum_{N=1}^\infty\int d\mathbf{v}_1\ldots\int d\mathbf{v}_N N\left(\frac{1}{N-1}\sum_{k=2}^N|\mathbf{v}_k-\hat{\mathbf{u}}|^2\right)P_{01}(N)P(\mathbf{v}_1)\ldots P(\mathbf{v}_N)$$

$$= \frac{m\overline{T}}{V}\sum_{N=2}^\infty\frac{N^2}{N-1}\left(1-\frac{\overline{|\delta\hat{\mathbf{u}}|_N^2}}{d\,C_T^2}\right)P_{01}(N)$$

$$= \overline{\rho}\overline{T}\sum_{N=2}^\infty\frac{N}{\overline{N}}P_{01}(N) = \frac{\overline{\rho}\overline{T}}{\overline{N}}\left(\frac{\overline{N}-P(1)}{1-P(0)-P(1)}\right),$$

so

$$\langle\delta\rho\,\delta\hat{T}_1\rangle_\infty = \frac{\overline{\rho}\overline{T}}{\overline{N}}\left(\frac{\overline{N}P(0)+(\overline{N}-1)P(1)}{1-P(0)-P(1)}\right). \tag{79}$$

Appendix B: Variances from Fluctuating Hydrodynamics

This appendix lists the variances and covariances of mechanical and hydrodynamic variables in the case of thermodynamic equilibrium at the mean state, $\overline{\rho}$, $\overline{\mathbf{u}}$, and $\overline{T}$. These results are from the theory of fluctuating hydrodynamics (§132, [18]) as developed from equilibrium statistical mechanics (§112, [19]).

The variance of mass density depends on the compressibility (i.e., the equation of state) of the fluid. In general,

$$\overline{\delta\rho^2} = \overline{\rho}^2\,\frac{\sigma_N^2}{\overline{N}^2}, \tag{80}$$

where $\overline{N} = \overline{\rho} V / m$ and σ_N^2 is the variance of N at equilibrium. For example, for an ideal gas N is Poisson-distributed so $\sigma_N^2 = \overline{N}$ and $\overline{\delta \rho^2} = \overline{\rho}^2 / \overline{N}$. The more general result is $\sigma_N^2 = -(k_B \overline{T} \ \overline{N}^2 / V^2)(\partial V / \partial \overline{P})_T$.

The variances of fluid velocity and temperature are

$$\overline{|\delta \mathbf{u}|^2} = d \, \frac{k_B \overline{T}}{\overline{\rho} V} = d \, \frac{C_T^2}{\overline{N}} \tag{81}$$

$$\overline{\delta T^2} = \frac{k_B \overline{T}^2}{c_v \overline{\rho} V} = \frac{C_T^2 \overline{T}}{c_v \overline{N}} \tag{82}$$

where $C_T = \sqrt{k_B \overline{T} / m}$ is the thermal speed (and the standard deviation of the Maxwell-Boltzmann distribution). The covariances are $\overline{\delta \rho \, \delta \mathbf{u}} = \overline{\delta \rho \, \delta T} = \overline{\delta \mathbf{u} \, \delta T} = 0$.

From the results above and those formulated in Section 3, the variances and covariances of the mechanical densities at equilibrium are

$$\overline{\delta \rho \delta \mathbf{J}} = \overline{\rho} \overline{\mathbf{J}} \Delta_\rho, \tag{83}$$

$$\overline{\delta \rho \delta K} = \overline{\rho} \overline{K} \Delta_\rho, \tag{84}$$

$$\overline{\delta J_\alpha \delta J_\beta} = \overline{J}_\alpha \overline{J}_\beta \Delta_\rho + \overline{\rho}^2 C_T^2 \Delta_u \delta_{\alpha,\beta}, \tag{85}$$

$$\overline{|\delta \mathbf{J}|^2} = |\overline{\mathbf{J}}|^2 \Delta_\rho + d \, \overline{\rho}^2 C_T^2 \Delta_u, \tag{86}$$

$$\overline{\delta \mathbf{J} \, \delta K} = \overline{\mathbf{J}} \, \overline{K} \Delta_\rho + \overline{\mathbf{J}} \, \rho C_T^2 \Delta_u, \tag{87}$$

$$\overline{\delta K^2} = \overline{K}^2 \Delta_\rho + |\overline{\mathbf{J}}|^2 C_T^2 \Delta_u + c_v^2 \overline{\rho}^2 \overline{T}^2 \Delta_T, \tag{88}$$

where $\overline{\mathbf{J}} = \overline{\rho} \, \overline{\mathbf{u}}$ and $\overline{K} = c_v \overline{\rho} \overline{T} + \frac{1}{2} \overline{\rho} |\overline{\mathbf{u}}|^2$; the dimensionless variances are defined by (80), (81), and (82) normalized as $\Delta_\rho = \overline{\delta \rho^2} / \overline{\rho}^2$, $\Delta_u = \overline{\delta u_x^2} / C_T^2$, and $\Delta_T = \overline{\delta T^2} / \overline{T}^2$.

Appendix C: Equilibrium Simulations

Simple stochastic simulations of a dilute gas at thermodynamic equilibrium were performed to verify and illustrate the results obtained by direct evaluation (see Appendix A). Sample means and variances of fluid velocity and temperature, using the various definitions, were computed and compared with theoretical predictions, as shown in the figures in Section 4.

From the principle of equipartition, at thermodynamic equilibrium the velocities of the particles are Maxwell–Boltzmann-distributed,

$$P(\mathbf{v}) = \left(\frac{m}{2\pi k_B \overline{T}} \right)^{d/2} \exp(-m |\mathbf{v}_{k,j} - \overline{\mathbf{u}}|^2 / 2 k_B \overline{T}), \tag{89}$$

with mean $\overline{\mathbf{v}} = \overline{\mathbf{u}}$ and variance $\overline{|\mathbf{v} - \overline{\mathbf{v}}|^2} = \overline{|\delta \mathbf{v}|^2} = d \, C_T^2$ where $C_T \equiv \sqrt{k_B \overline{T} / m}$ is the thermal speed. Note that this distribution is not restricted to a dilute gas

but applies to any classical fluid at equilibrium. Also note that thermodynamic equilibrium does *not* imply $\bar{\mathbf{u}} = 0$ since a system is in equilibrium in all inertial frames of reference.

The number of particles in a given sample, N_j, is a random variable whose distribution depends on the equation of state for the fluid. For the simulations we take the case of a dilute gas, so N_j is Poisson-distributed,

$$P(N_j) = \frac{e^{-\bar{N}}\bar{N}^{N_j}}{N_j!} \tag{90}$$

with mean $\bar{N} = \bar{N}$ and variance $\overline{\delta N^2} = \bar{N}$.

Each simulation run consisted of $S = 5000$ samples for fixed $\bar{N}$, varying from 0.5 to 20, and arbitrary $\bar{\mathbf{u}}$ and $\bar{T}$. For each sample, given (90), a random value of N_j was generated and then that many random particle velocities were generated according to (89). Means, variances, and correlations were estimated by the various definitions presented in sections 2 and 3; note that for some definitions (e.g., (12), (18), (20)) samples containing zero or one particle are omitted in evaluating sample means.

Appendix D: Non-equilibrium Simulations

In Section 4.2 the mean instantaneous temperature $\langle\hat{T}_1\rangle_s$ is predicted to have a bias due to nonequilibrium correlations of density-temperature fluctuations. To test this prediction, molecular simulations of a dilute gas were performed to measure $\langle T\rangle_s^*$, $\langle\hat{T}_1\rangle_s$, and $\langle\delta\rho, \delta T\rangle_s^*$ (see equation (46) and Figure 3). The simulations were of a nonequilibrium state, specifically a temperature gradient produced by parallel thermal walls at different temperatures. Similar simulations in [26] verified the predicted bias in the instantaneous center-of-mass fluid velocity (see equation (39)).

The simulations used the direct simulation Monte Carlo (DSMC) algorithm, a well-known method for computing gas dynamics at the molecular scale; see [1; 8] for pedagogical expositions on DSMC, [4] for a complete reference, and [27] for a proof of the method's equivalence to the Boltzmann equation. As in molecular dynamics, the state of the system in DSMC is given by the positions and velocities of particles. In each time step, the particles are first moved as if they did not interact with each other. After moving the particles and imposing any boundary conditions, collisions are evaluated by a stochastic process, conserving momentum and energy and selecting the postcollision angles from their kinetic theory distributions. DSMC is a stochastic algorithm but the statistical variation of the physical quantities has nothing to do with the "Monte Carlo" portion of the method. The equilibrium and nonequilibrium variations in DSMC are the physical spectra of spontaneous thermal fluctuations, as confirmed by excellent

Molecular diameter (Argon)	3.66×10^8
Molecular mass (Argon)	6.63×10^{23}
Reference mass density	1.78×10^{-3}
Reference temperature	273
Sound speed	33700
Specific heat c_v	3.12×10^6
Wall temperature (left)	273
Wall temperature (right)	819
System length	1.25×10^4
Reference mean free path	6.26×10^{-6}
System volume (large)	1.96×10^{-16}
System area (small)	1.23×10^{-17}
Number of particles (large)	5265
Number of particles (small)	329
Number of sampling cells	40
Number of samples, S	2.5×10^7
DSMC time step	1.0×10^{-11}
DSMC grid size	2.09×10^{-6}

Table 1. System parameters (in cgs units) for DSMC simulations of a dilute gas between thermal walls.

agreement with fluctuating hydrodynamic theory [9; 20] and molecular dynamics simulations [21; 22].

The nonequilibrium system we consider is a dilute monatomic hard-sphere gas between a pair of parallel thermal walls. The left wall is at the reference temperature of 273 Kelvin and the right wall's temperature is three times greater. Two cases, hydrodynamically equivalent, are simulated. The distance between the walls is the same in the two cases, but one system is 16 times larger in volume (and has 16 times more particles) than the other. All other parameters (e.g., mean free path, transport coefficients) were the same in the two systems (see Table 1). Samples are taken in forty rectangular cells sliced parallel to the thermal walls; in the large system these cells are 16 times larger than in the small system. Starting near the steady state (approximately linear temperature profile) the simulations of these two systems are run for 2.5×10^7 time steps to dissipate any initial transients. After allowing the systems to relax, samples are taken at each time step for a total of $S = 2.5 \times 10^7$ samples.

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