Probability density functions in binary mixtures

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Abstract. A theory of probability distributions of temperature and concentration fluctuations in turbulence of binary mixtures is presented. The Soret and Dufour effects couple concentration and temperature fluctuations modifying the scalar dissipation rates and the fluctuation–dissipation relations usual in one-component systems.

1. Introduction

Probability density function (PDF) of fluctuations is of increasing interest in turbulence. Recently much experimental and numerical data for derivatives and differences of velocity and scalar fields have been accumulated. The PDFs of these quantities are found to be non-Gaussian [1–3]. The discovery of nearly exponential temperature fluctuations in convection has stimulated a considerable number of studies on PDFs [4–7].

In one-component systems, the equations of the fluctuations of passive scalars, temperature fluctuation T and concentration fluctuation c, diffusing in a random incompressible velocity field are

$$\frac{\partial T}{\partial t} + v \cdot \nabla T = k \Delta T \tag{1}$$

$$\frac{\partial c}{\partial t} + v \cdot \nabla c = D \Delta c \tag{2}$$

and

$$\nabla \cdot v = 0 \tag{3}$$

where k and D are the thermal conductivity and the matter diffusion coefficient.

Using equations (1) and (3), Sinai and Yakhot [4] derived a fluctuation–dissipation relation for the case when the system is homogeneous and the temperature field is not forced. Moreover, using these relations the above authors obtained a closed form for the asymptotic PDF of the decaying temperature fluctuations in homogeneous systems.

Later, Ching [7] extended these results to the case of turbulent convection. The theoretical predictions of this author agree quite well (except for very limiting cases) with the experimental data.

The description of a binary fluid mixture requires additional parameters. Soret and Dufour's effects introduce important differences with the case of one-component fluids. Walden *et al* [8] studied Rayleigh–Bénard convection in alcohol–water mixtures, in which the diffusion of concentration oppose convection via the Soret effect. Near onset, the convection rolls are found to move continuously as travelling waves, in contrast to the

stationary roll patterns observed in homogeneous fluids. On the other hand, Linz proposed [9], that internal temperature variations, which are driven by the Dufour effect, can have a significant influence on the stability boundaries of the quiescent state of a convective binary mixture.

The crossed effects can also be present in turbulence. One of the most important features of turbulent flows is the enhancement of diffusivity and other transport coefficients. The rates of transfer and mixing are several orders of magnitude greater than the rates due to molecular diffusion. The author, in collaboration with Llebot, has considered the importance of the crossed fluxes in the framework of turbulent theories [10]. A calculation based on kinetic theory shows that Soret and Dufour's effects are enhanced by turbulence.

Taking into account all of these considerations which suggest the existence of some differences between one-component systems and mixtures it seems to be necessary to study fluctuation–dissipation relations and PDFs of temperature and concentration in binary mixtures.

This paper is organized as follows. In section 2 we derive the fluctuation–dissipation relations for binary mixtures in the case where the scalar fluctuations of temperature and concentration are not forced. In section 3 we use the fluctuation–dissipation relations obtained in the previous section to derive the PDFs in decaying turbulence. In section 4 we present the extension of the above results to the case of convective turbulence. Finally, in section 5, we emphasize the main results of this paper and consider if the results obtained in the previous sections can be experimentally tested.

2. Fluctuation–dissipation relations

As it is well known from non-equilibrium thermodynamics [11], when Soret and Dufour effects are taken into account, equations (1) and (2) transform into

$$\frac{\partial T}{\partial t} + \boldsymbol{v} \cdot \nabla T = k\Delta T + H\Delta c \tag{4}$$

and

$$\frac{\partial c}{\partial t} + \boldsymbol{v} \cdot \nabla c = D\Delta c + S\Delta T. \tag{5}$$

The new terms, $-H\nabla c$ and $-S\nabla T$, represent the Dufour heat flux, driven by a gradient of concentration fluctuations, and the Soret matter flux, driven by a gradient of temperature fluctuations. H and S are phenomenological coefficients.

We now discuss the validity of the basic equations presented. Equations (1) and (2) have been systematically used in nonturbulent and turbulent problems reproducing quite well the experimental results [4, 7, 11]. On the other hand, equations (4) and (5) agree quite well with the experiments in nonturbulent situations [8, 9, 11]. Then, taking into account the validity of the related equations (1) and (2) in both regimes, we can expect that equations (4) and (5) will be adequate to describe the turbulent behaviour of temperature and concentration in binary mixtures. In equations (1) and (4) the term describing the viscous dissipation [11, 12], has been neglected. This term is usually neglected in comparison with the direct conduction term in the case of turbulent single fluids, justifying its absence in equation (1) and in accordance with numerous theoretical and experimental evidence [4, 12]. We can expect that this viscous term can also be neglected in comparison with the crossed or Dufour conduction term in the most interesting situations. Effectively, in nonturbulent systems in the usual situations the viscous term is always much smaller than the Dufour one [12]. In the situations interesting for the crossed effects (those in which the effects can be

measured) the crossed effects must be comparable to the direct ones. In [10] it was shown that the order of magnitude of the ratio between direct and crossed effects is equal in the turbulent and nonturbulent regimes. Then, if in these types of situations the magnitude of the turbulent viscous term was comparable to those of the turbulent Dufour term it would also be comparable (in these situations the direct and crossed effects are comparable) to the direct one in contrast to our previous considerations. On the other hand, it is well known that equation (2) can only be rigorously derived in isothermal conditions [11]. However, it agrees quite well with experimental data even in the highly nonisothermal conditions of the hard-turbulence convection [1]. Therefore, equation (2) is adequate to describe these types of problems. Arguments similar to those presented for the case of the neglected viscous term justify the use of equation (5) even in these highly nonisothermal conditions. We must remark that the validity of these equations, finally, must only rest in the agreement of their predictions with the experimental studies. The transport coefficients show, in general, dependence on the different thermodynamic variables. In particular, the mass diffusion coefficient dependence on temperature, $D = D(T)$, must be studied carefully because a dependence of these form represents a new type of coupling between mass transfer and temperature differences that can be superposed to the Soret effect. The importance of these coupling effect depends on the particular mixture considered, the actual values of the thermodynamic variables, etc and we cannot obtain general conclusions about the magnitude of the effect. From an experimental point of view we can analyse separately both types of contributions. We can study experimentally the dependence $D = D(T)$ of every component of the mixture as a single fluid. Using this information and studying the behaviour of the mixture we can, essentially, separate both types of effects. In the case of nonturbulent flows these coupling can be neglected in comparison with the Soret effect. Using an argument similar to those presented in the discussion of the validity of the basic equations we can expect that in the turbulent regime these coupling will also be smaller than the Soret effect. Note, finally, that the sign of the mass diffusion coefficient does not change with the variation of the temperature whereas the sign of the Soret coefficient can change with the variation of the concentration and temperature of the mixture. First, we consider the fluctuation–dissipation relations of temperature fluctuations. Note that the above equations are only valid when we consider fluctuations of scalars that are not forced and the scalar fluctuations are, as a result, decaying. Multiplying equation (4) by T and taking spatial averages we derive an equation for $Q = \langle T^2 \rangle$, the covariance of the temperature fluctuation

$$\frac{\partial Q}{\partial t} = -2\langle k(\nabla T)^2 + H(\nabla T) \cdot (\nabla c) \rangle. \tag{6}$$

To obtain equation (6) we have used the following boundary conditions, $v \cdot \mathrm{d}S = 0$, $\nabla T \cdot \mathrm{d}S = 0$ and $\nabla c \cdot \mathrm{d}S = 0$ with S the normal vector to the surface of the boundary. These are the usual conditions for a rigid boundary with no interchange of mass or heat. This form is imposed by the characteristics of the problem considered here, decaying turbulence without interchange of mass in a closed vessel. These boundary conditions give the following properties of the spatial average, $\langle v \cdot \nabla T^2 \rangle = 0 = \langle \Delta T^2 \rangle$ and $\langle T \Delta c \rangle = -\langle \nabla c \cdot \nabla T \rangle$, that have been used to derive equation (6). Note that the boundary conditions used in this section are different from those that will be used in section 4 in which convective turbulence is considered. In these cases the boundary conditions for the temperature must be modified (for instance in Rayleigh–Bénard convection is usual to use a constant temperature at the boundaries).

The equation of the variables T^{2n} is also derived from equation (4), multiplying it now by T^{2n-1}

$$\frac{\partial T^{2n}}{\partial t} + v \cdot \nabla T^{2n} = k\nabla T^{2n} - 2nk(2n-1)T^{2n-2}(\nabla T)^2 + 2nHT^{2n-1}\Delta c. \tag{7}$$

The next step is to introduce the normalized temperature $X = T/Q^{1/2}$. The equation for X^{2n} is easily derived

$$\frac{\partial X^{2n}}{\partial t} - 2nX^{2n}Q^{-1}\langle k(\nabla T)^2 + H(\nabla T)\cdot(\nabla c)\rangle + v \cdot \nabla X^{2n}$$
$$= k\Delta X^{2n} - 2nk(2n-1)X^{2n-2}Q^{-1}(\nabla T)^2 + 2nHX^{2n-1}Q^{-1/2}\Delta c. \tag{8}$$

Averaging the last equation spatially, we obtain in the stationary state

$$Q^{-1}\langle X^{2n}\langle k(\nabla T)^2 + H(\nabla T)\cdot(\nabla c)\rangle\rangle$$
$$= (2n-1)kQ^{-1}\langle X^{2n-2}(\nabla T)^2\rangle - HQ^{-1/2}\langle X^{2n-1}\Delta c\rangle. \tag{9}$$

The right-hand side of the last equation can easily be transformed using the relation

$$\langle X^{2n-1}\Delta c\rangle = \langle\nabla(X^{2n-1}\nabla c)\rangle - \langle\nabla X^{2n-1}\cdot\nabla c\rangle$$
$$= -(2n-1)\langle X^{2n-2}(\nabla X)\cdot(\nabla c)\rangle$$
$$= -(2n-1)Q^{-1/2}\langle X^{2n-2}(\nabla T)\cdot(\nabla c)\rangle. \tag{10}$$

Then, equation (9) becomes

$$\langle X^{2n}\langle k(\nabla T)^2 + H(\nabla T)\cdot(\nabla c)\rangle\rangle = (2n-1)\langle X^{2n-2}(k(\nabla T)^2 + H(\nabla T)\cdot(\nabla c))\rangle. \tag{11}$$

This is equivalent to

$$\langle X^{2n}\rangle = (2n-1)\langle X^{2n-2}Z/\langle Z\rangle\rangle \tag{12}$$

where

$$Z = k(\nabla T)^2 + H(\nabla T)\cdot(\nabla c) \tag{13}$$

$\langle Z\rangle$ is, in accordance with equation (6), the mean dissipation rate of the fluctuations of the temperature scalar field.

Equations (11) and (12) are the generalization of the fluctuation–dissipation relation to binary mixtures. An important property of the above expressions is that all moments of the X variable can be determined from the correlations of X^{2n} with the variable Z.

When the Dufour effect is neglected, $H = 0$, we recover the usual relation in one-component systems

$$\langle X^{2n}\rangle = (2n-1)\langle X^{2n-2}(\nabla T)^2/\langle(\nabla T)^2\rangle\rangle. \tag{14}$$

Equation (12) expresses the moments of the variable X in terms of the conditional expectation value of the normalized scalar dissipation rate. These equations can be written directly in terms of the fluctuation fluxes. If we denote the heat flux by $\boldsymbol{J}_Q = \boldsymbol{J}_{QT} + \boldsymbol{J}_{Qc}$, with $\boldsymbol{J}_{QT} = -k\nabla T$ the direct term, and $\boldsymbol{J}_{Qc} = -H\nabla c$ the crossed one, Z is

$$Z = k^{-1}(\boldsymbol{J}_{QT}^2 + \boldsymbol{J}_{QT}\cdot\boldsymbol{J}_{Qc}). \tag{15}$$

An important difference between one-component systems and binary mixtures emerges from the above analysis. In the case of single fluids the dissipation rate only depends on $(\nabla T)^2$, whereas in mixtures the dissipation rate is also a function of $(\nabla T)\cdot(\nabla c)$; in binary mixtures the local gradients of concentration fluctuations can modify the dissipation rate of the temperature fluctuations. In one-component systems these local fluctuation concentration gradients do not induce changes on the dissipation rate of the temperature fluctuations.

The fluctuation–dissipation relation for the concentration can be derived following the same steps of the temperature case. If $Y^* = c/\langle c^2\rangle^{1/2}$, we have

$$\langle Y^{2n}\rangle = (2n-1)\langle Y^{(2n-2)}Z^*/\langle Z^*\rangle\rangle \tag{16}$$

where

$$Z^* = D(\nabla c)^2 + S(\nabla T)\cdot(\nabla c) = D^{-1}(\boldsymbol{J}_{Mc}^2 + \boldsymbol{J}_{Mc}\cdot\boldsymbol{J}_{MT}) \tag{17}$$

with the matter flux given by $\boldsymbol{J}_M = \boldsymbol{J}_{Mc} + \boldsymbol{J}_{MT}$. The subscripts Mc and MT refer to the direct term and the Soret component.

The physical interpretation of equations (16) and (17) is similar to the interpretation of equations (12) and (13).

Note that Z and Z^*, the two scalar dissipation rates, depend on the gradients of the two scalar fluctuations. Consequently, the two sets of fluctuation–dissipation relations are coupled relations and not independent relations as it is the case in one-component systems. These statistical correlations reflect at the statistical level the crossed effects present in the dynamics of the system.

3. Probability density functions of decaying fluctuations

In the previous section we obtained the fluctuation–dissipation relations in binary mixtures. Now, we must study the PDFs that can be derived from these relations. As the fluctuation–dissipation relations above derived only hold for passive fluctuations, the PDFs that we shall obtain in this section will also be only valid for decaying fluctuations. The fluctuation–dissipation relations constitute an infinite set of moment relations. Instead of this complicated mathematical picture we want to express the probability densities as functions of only two statistical variables. We begin by writing the fluctuation–dissipation relations in a more compact form; $\langle X^{2n}\rangle = (2n-1)\langle X^{2n-2}(u^2 + U)\rangle$ and $\langle Y^{2n}\rangle = (2n-1)\langle Y^{2n-2}(w^2 + W)\rangle$ where $u^2 = k(\nabla T)^2/\langle Z\rangle$, $w^2 = D(\nabla c)^2/\langle Z^*\rangle$, $U = H(\nabla T)\cdot(\nabla c)/\langle Z\rangle$ and $W = S(\nabla T)\cdot(\nabla c)/\langle Z^*\rangle$. U, u, w and W are the new variables of the problem. Assuming that volume averaging is equivalent to ensemble averaging we introduce the stationary probability density P. Because of the dynamic coupling between the scalar fluctuations due to the crossed effects, the probability density will read as $P = P(X, u, U, Y, w, W)$. In other words, the probability density cannot be factored in the form $P = P_x(X, u, U)P_y(Y, w, W)$, as it is the case in one-component systems.

Introducing the joint probability distribution P in equation (12), the fluctuation–dissipation relation for the temperature can be written as follows

$$\int X^{2n}P\,\mathrm{d}X\,\mathrm{d}u\,\mathrm{d}U\,\mathrm{d}Y\,\mathrm{d}w\,\mathrm{d}W = \int (X^{2n-1})'(u^2 + U)P\,\mathrm{d}X\,\mathrm{d}u\,\mathrm{d}U\,\mathrm{d}Y\,\mathrm{d}w\,\mathrm{d}W \tag{18}$$

where the prime denotes the X derivative of the variable considered. Now we introduce q_x, the conditional probability of the variables u, U, Y, w and W for a given value of the variable X, $P(X, u, U, Y, w, W) = P_x(X)q_x(u, U, Y, w, W; X)$. Using this new expression for the joint probability equation (18) becomes

$$\int X^{2n}P_x(X)\,\mathrm{d}X = \int (X^{2n-1})'P_x(X)(q_{xu} + q_{xU})\,\mathrm{d}X. \tag{19}$$

To obtain equation (19) we used the normalization condition $\int q_x\,\mathrm{d}u\,\mathrm{d}U\,\mathrm{d}Y\,\mathrm{d}w\,\mathrm{d}W = 1$. The new functions

$$q_{xu}(X) = \int q_x(u, U, Y, w, W; X)u^2\,\mathrm{d}u\,\mathrm{d}U\,\mathrm{d}Y\,\mathrm{d}w\,\mathrm{d}W \tag{20}$$

and

$$q_{xU}(X) = \int q_x(u, U, Y, w, W; X)U \, \mathrm{d}u \, \mathrm{d}U \, \mathrm{d}Y \, \mathrm{d}w \, \mathrm{d}W \qquad (21)$$

are the expectation values of u^2 and U for a given value of X. After simple manipulations equation (19) becomes

$$\int X^{2n-1} \left(XP_x - \frac{\partial P_x}{\partial X}(q_{xu} + q_{xU}) - P_x \frac{\partial(q_{xu} + q_{xU})}{\partial X} \right) \mathrm{d}X = 0. \qquad (22)$$

Equation (22) is satisfied for an arbitrary n only when the expression in the square brackets of the integrand in (22) is equal to zero. This gives the differential equation for P_x with the solution

$$P_x(X) = \frac{C}{q_{xu}(X) + q_{xU}(X)} \exp\left(-\int_0^X \frac{z \, \mathrm{d}z}{q_{xu}(z) + q_{xU}(z)} \right) \qquad (23)$$

where C is the normalization constant.

Equation (23) gives the probability density defined by two variables only, q_{xu} and q_{xU}, instead of the infinite set of moment relations provided by the fluctuation–dissipation relations. To make further progress we need an expression for the expectation values. One way to obtain this expression is to derive it experimentally or via numerical simulation. However, up to now, there have not been studies about binary mixtures in any of the two fields. Then, we must propose an expression of the q's based only on analytical considerations. In particular, we shall follow the approach of Sinai and Yakhot [4]. These authors proposed for the one-component systems an expression of the form $q_1(X) = 1 + k^* X^2$ with k^* a constant and $q_1 = q_u$ (when the crossed effects are neglected). Using these expression they obtained a PDF for the problem that reproduced quite well the data of a numerical simulation. In the case of binary mixtures, as the crossed effects are small in comparison with the direct ones, we can expect a rather similar expression. To obtain the actual form of these expressions we must remark on a property that differentiates the one- and two-component dynamics. The one-component dynamics is invariant under the change of sign of the temperature, $T \to -T$, because $-T$ is also a solution of equation (1). If the dynamics is invariant under these changes we must expect that the expectation values, that are only statistical properties of the underlying dynamics, will also be invariant under the change $X \to -X$ (provided that we are considering an isotropic problem). Then, the expectation values of an isotropic problem of a one-component system are restricted by the condition of being a series of even powers of X. We now consider the case of two-component systems. In binary systems the dynamics is not invariant under the change $T \to -T$ (the dynamics is invariant under the simultaneous changes $T \to -T$ and $c \to -c$). Therefore, if the underlying dynamics is not invariant we cannot expect the expectation values to be invariant under the change $X \to -X$. The expectation values are not, in general, symmetric under these changes and now we can have odd powers of X.

At this point we are in a position to write an expression for the expectation values in a binary mixture. Taking into account that the crossed effects are small and that now we can have odd powers of X we propose the following expression

$$q_{xu}(X) + q_{xU}(X) = 1 + dX + EX^2 \qquad (24)$$

where d and E are two new coefficients.

Substituting this expression into (23) and resolving simple integrals we obtain the PDFs. We must consider two different cases.

(A) $r = 4E - d^2 < 0$

$$P_x(X) = C(1 + dX + EX^2)^{-[1+(2E)^{-1}]} \left(\frac{1 + M_- X}{1 + M_+ X} \right)^M \tag{25}$$

where $M_\pm = 2E/(d \pm [-r]^{1/2})$ and $M = d/2E(-r)^{1/2}$.
   (B) $r = 4E - d^2 > 0$

$$P_x(X) = C'(1 + dX + EX^2)^{-[1+(2E)^{-1}]} \exp \left(\frac{d}{Er^{1/2}} \left(\text{tg} \frac{2EX + d}{r^{1/2}} \right)^{-1} \right) \tag{26}$$

where $C' = C \exp(-d[Er^{1/2} \, \text{tg}(dr^{-1/2})]^{-1})$.

   We must study the sign of $d^2 - 4E$ for every particular binary mixture. When the sign is positive we must use equation (25) and when is negative we must use equation (26). In any of the two cases the probability distribution will not be symmetric $P_x(-X) \neq P_x(X)$. This is a property that can, in principle, differentiate one-component systems and binary mixtures.

   We remark that equation (24) is an assumption independent of the general theory presented and expressed by equations (20), (21) and (23). An experimental study of the PDFs would also be a test of the validity of equation (24).

   Note that the symmetries of equation (1) under the change of sign of temperature, and equations (4) and (5) under simultaneous changes of sign of temperature and concentration are only valid when the viscous dissipation is neglected. When the viscous term is taken into account in equations (1) and (4) all the terms change the sign under the change of sign of the temperature, except the viscous term that remains unchanged [11, 12] (this term can depend on the temperature through the shear viscosity coefficient, but this dependence is not linear). Then, these symmetries are not exact and are only valid in the approximation of negligible viscous dissipation effects.

   One can introduce the functions $P_y(Y), q_y \ldots$ just in the same way as $P_x(X), q_x \ldots$ and one expects the existence of symmetry relations between the functions q_y and $q_x \ldots$. A possible way to study these relations is based on the symmetries of the basic equations. Instead of the symmetry under the change of sign of temperature and concentration we shall consider now another symmetry. Equations (4) and (5) are invariant under the simultaneous changes $c \leftrightarrow T$, $D \leftrightarrow k$ and $S \leftrightarrow H$. From this symmetry it is clear that all the statistical properties referred to variables X and Y must have the same analytical form. The difference between both types of expressions is given by the different values of the transport coefficients (in a dimensionless form of the equations). In particular, the expression for equation (24) in the case of the variable Y is $q_{Yw}(Y) + q_{YW}(Y) = 1 + d'Y + E'Y^2$. It is not simple to obtain an evaluation of the relation between the numerical values of the two expressions using only the symmetry properties. We only expect that they will be different because of the different values of the transport coefficients.

4. Probability density functions in convective turbulence

In the previous two sections we considered the fluctuation–dissipation relations and the PDFs of not forced scalar fluctuations. In this section we want to extend these results to convective turbulence. In the case of one-component systems Ching proposed in an interesting work [7], that a similar fluctuation–dissipation relation $\langle X^{2n} \rangle = (2n - 1)\langle X^{2n-2} R^2 \rangle$ is also valid in convective turbulence if we use $R = (\partial T/\partial t)/\langle (\partial T/\partial t)^2 \rangle^{1/2}$, the normalized temperature derivative. The q's become in this approach $q(x) = \langle (\partial T/\partial t)^2 \rangle_{X=x}/\langle (\partial T/\partial t)^2 \rangle$. The

subscripts $X = x$ indicate that the mean square is to be calculated at a given value, x, of the normalized fluctuation X. The PDFs obtained in this way agree quite well with the experimental data (except in the case of very large fluctuations for very short time separations), justifying the assumption made in the generalization of the fluctuation–dissipation relations.

Following the proposal of Ching, in the case of binary convective turbulence we suppose that equation (12) is valid if we substitute Z by

$$\frac{\mathrm{D}T}{\mathrm{D}t} = k \left(\frac{\partial T}{\partial t}\right)^2 + H \frac{\partial T}{\partial t} \frac{\partial c}{\partial t}. \tag{27}$$

Just in the same way, we assume that equation (16) is valid if we substitute Z^* by

$$\frac{\mathrm{D}c}{\mathrm{D}t} = D \left(\frac{\partial c}{\partial t}\right)^2 + S \frac{\partial c}{\partial t} \frac{\partial T}{\partial t}. \tag{28}$$

These assumptions in situations where the system is forced are not obvious and might be justified by considerations of universality of fluctuations in turbulence and by the good results of the similar proposal in one-component systems.

The PDFs of the temperature are given by the expression

$$P_x(X) = \frac{C}{q_x(X)} \exp\left(-\int_0^X \frac{z\,\mathrm{d}z}{q_x(z)}\right) \tag{29}$$

where the q's are now given by

$$q_x(x) = \frac{\langle (\mathrm{D}T/\mathrm{D}t)^2\rangle_{X=x}}{\langle (\mathrm{D}T/\mathrm{D}t)^2\rangle}. \tag{30}$$

A similar expression holds for the concentration fluctuations. Equations (29) and (30) explicitly relate the PDFs of temperature fluctuations to the statistics of the temperature and concentration derivatives. The discussion of the physical meaning of these equations follows closely those presented in sections 2 and 3. One needs only to refer to derivatives instead of gradients of the magnitude. This point can be justified by the fact that both, gradients and derivatives, have similar statistics when a mean flow exists and Taylor's frozen flow hypothesis is valid. We recover the results of one-component systems when we disregard the crossed effects ($H = S = 0$). Note, finally, that the above results are independent of any assumption about the existence in two-component systems of the two different turbulent regimes, soft and hard turbulence, observed in one-component systems. One can expect, based on the universality of turbulence, that these two regimes will also be present in binary mixtures.

5. Discussion

In this paper we have presented a theory of fluctuations of scalars in binary mixtures. The most important result of this paper is the existence of a dynamic coupling between temperature and concentration fluctuations induced by the Soret and Dufour effects. In one-component systems these fluctuations are statistically independent (one can observe some correlations induced by the fact that both passive fluctuations are generated by the same random velocity field; however, we do not refer to this kind of correlation). The first effect derived from these couplings is the fact that in binary mixtures the dissipation rates must depend on the two fluctuating fields. For instance, the local gradients of concentration fluctuations can enhance or diminish the dissipation rate of temperature fluctuations. This effect does not have a counterpart in one-component systems.

To our knowledge, this is the first time that the fluctuation–dissipation relations for binary mixtures have been presented in the literature. The fluctuation–dissipation relations for the variables X and Y are not independent. The correlations between X, Y and the gradients of T and c imply that the moments of the variable $X(Y)$ are not entirely determined by the correlations of $X^{2n}(Y^{2n})$ with the single variable $(\nabla T)^2((\nabla c)^2)$.

We have also obtained closed expressions for the PDFs in the stationary limit of decaying fluctuations. An important consequence of the coupling between the two fields of scalar fluctuations is that, in general, the conditional probabilities and expectation values are not symmetric functions of $X(Y)$. An immediate consequence of the last result is the loss of symmetry of the probability distributions, that is, $P_x(-X) \neq P_x(X)$ and $P_y(-Y) \neq P_y(Y)$.

The most important shortcoming of the analysis is the absence of a numerical estimation of the coefficients d and E. The estimation could be done relating these parameters to the turbulent scales of the problem. However, we do not have experimental or numerical information about the fundamental turbulent scales of binary mixtures. Finally, we have extended the above results to convective turbulence.

Besides the intrinsic interest of the fluctuation–dissipation relations and the PDFs the results of this paper are useful as a possible guide to design tests on the existence and relative importance of crossed effects in turbulence. The first possible test is based on the dissipation rates. Let us only consider the case of temperature fluctuations. The mean dissipation rate, $\langle k(\nabla T)^2 + H(\nabla T) \cdot (\nabla c) \rangle$, can be measured at different times. We can also measure the mean direct dissipation rate $\langle k(\nabla T)^2 \rangle$ and the scalar covariance of the temperature fluctuations Q. Then, using equation (6) we can determine whether the correct variation of the scalar covariance is given by $\langle Z \rangle$ or by the mean direct dissipation rate. A second possibility is to consider directly the PDFs. The loss of the $X, -X(Y, -Y)$ symmetry of the probability distributions would be a clear mark of the crossed effects. As remarked at the end of section 3, the corroboration of equations (25) and (26) would also be a validation of the hypotheses given by equation (24). A third possibility is the study of convective turbulence. The advantage of this approach is the simplicity of the experiments. There is an important experimental experience on the field (in one-component systems) and in the techniques of analysis of the data [1, 9, 12]. Moreover, it is simple to reach a very wide range of Reynolds numbers.

From all the experiments considered in the previous paragraph, only those based on convective turbulence seem to be realizable in a simple way. This fact suggests the possibility to explore numerically the other alternatives. As a matter of fact, the numerical simulation is the method used to validate the PDFs of single fluids derived in [4]. The extension of this type of simulation to binary mixtures seems to be simple. The numerical evaluation of the dissipation rates would follow a procedure similar to those of the PDFs. The most important difficulty to implement these numerical simulations is, as remarked earlier, the lack of information about the turbulent scales of binary mixtures. A previous exploration of this point would be necessary to develop these numerical simulations.

We expect that the magnitude of the turbulent crossed effects will be small, especially in nonconvective situations. In the nonturbulent regime it is possible to measure the magnitude of the nonconvective crossed effects despite their smallness [11]. Invoking again the results of [10] we have that the ratio between the direct and crossed components is of the same order of magnitude in the turbulent and nonturbulent regimes and, consequently, we expect that in nonconvective turbulence the crossed effects will also be measurable. On the other hand, in the case of nonturbulent convective problems we have effects associated with the crossed terms that are detected experimentally in a simpler way than in the nonconvective

case [8]. We expect that the crossed effects in convective turbulence could be determined experimentally with less difficulties than in nonconvective problems.

Acknowledgments

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