

Extended irreversible thermodynamics and the quality of temperature and pressure

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Abstract. It is reiterated that without a Gibbs–Duhem equation no thermodynamic description of irreversible and reversible processes exists. It is shown with the help of Gibbs–Duhem equation of extended irreversible thermodynamics that the physical contents of intensive quantities, the temperature and the pressure, do not change in going from reversible to irreversible processes. This confirms well with the earlier demonstrations of $\bar{E}u$ and García–Colín.

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1. Introduction

The extended irreversible thermodynamics (EIT) [1–7] attempts to cover those nonequilibrium situations which are supposed as not covered by local equilibrium assumption. However, the past two decades of research has generated an unfortunate debate about the meaning of entropy and temperature in nonequilibrium [8–15]. Recently it has been demonstrated [16] that the temperature concept retains the same physical meaning whether the system is in equilibrium or not. That is, it is the absolute temperature which appears in the thermodynamic description of a system in equilibrium or in nonequilibrium. Their demonstration [16] is based on general thermodynamic considerations, kinetic theory aspects and a few other phenomenological considerations. On the other hand we have reached the same conclusion by considering the act of temperature measurement in the case of both equilibrium and nonequilibrium [17].

We have earlier stressed [17,18] that without the existence of a corresponding Gibbs–Duhem equation no thermodynamic description exists including those for irreversible processes. However, almost in all irreversible thermodynamic descriptions no adequate attention appears to have been paid to the role of corresponding Gibbs–Duhem equation. Hence it is no wonder that in the above mentioned demonstrations a deduction based on the requirements of the Gibbs–Duhem equation is not found. Therefore, we present below a purely thermodynamic proof, based on the requirements of the Gibbs–Duhem equation of EIT, about the quality of temperature and pressure in nonequilibrium which elegantly

substantiates the above stated deductions. It also establishes that the same will remain true even if one is required to go for a more general extended thermodynamic space.

2. Some of the foundational aspects of EIT

Recall that the equilibrium thermodynamics establishes that entropy of an equilibrium state is a function of internal energy, volume and composition variables [19,20]. The classical irreversible thermodynamics (CIT) or the linear irreversible thermodynamics (LIT) of Onsager–Prigogine–Meixner–de Groot [21–30] is based on the local equilibrium assumption and hence the same functional dependence of entropy remains valid in this domain too. In the past 6 decades or so we have seen that LIT covers very large number of irreversible processes [21–31]. However, at the same time there are substantially large number of nonequilibrium situations which do not get accommodated in LIT or CIT which lead us to believe that the local equilibrium assumption breaks down in these cases. Therefore, a need was felt to go beyond the scope of LIT. This is achieved in EIT by enlarging the space of fundamental independent variables by introducing certain nonequilibrium variables, such as the dissipative fluxes, say the heat flux density, dissipative stress tensor etc. The independent character of these fluxes has been demonstrated in various ways. Perhaps the oldest demonstration, one which is frequently cited in EIT, is that of Reynolds [6,32]. The experiment of Reynolds is as follows. He filled a leather bag with marble pieces, topped it with water and then gently twisted it, thereby inducing a shear. The water level drops because the close packing of the marbles is disrupted as layers of them slide apart each other. As a result the marbles are farther apart on the average creating spaces that the water has to fill. This of course implies that the total density decreases when the system under consideration is subjected to shear at constant temperature and pressure. Therefore, the local equilibrium assumption of LIT gets violated since the density is no longer a function only of the pressure and temperature, it depends also on the rate of shear (twisting). A similar phenomena of shear thinning, that is the decrease of coefficient of viscosity with the rate of shear has been pointed out by Burnett [33]. In this category we also have the dissipative processes which have very short relaxation times (of the order of nanoseconds or so), the non-Fickian diffusion, the phenomena of second sound and stress waves [1–7]. The reader will find more examples in ref. [1–7] which necessitate the consideration of dissipative fluxes as independent variables.

The microscopic theories also provide the necessary justification of EIT. For example, consider the methods of Enskog–Chapman [34] and Grad [35] in which the equilibrium kinetic theory is appropriately augmented for dealing with the nonequilibrium situations especially those originating from the existence of spatial inhomogeneities. The space of this paper does not allow us to describe the details of these methods and of their thermodynamic implications, however the reader may consult the references [1–7], [14–16], [21] and [36–44] cited in this paper. In the nutshell these theories demonstrate that if the second and higher order terms, in the expansion of entropy function about the given local equilibrium value, are negligibly small then the time dependent entropy function, computed using the nonequilibrium distribution function, depends only on internal energy, volume and composition variables [21,38], which is therefore taken as the case of local equilibrium in thermodynamic sense. On the other hand, if the higher order terms in the expansion of entropy cannot be ignored then it becomes obvious that the local equilibrium assumption crumbles

down and hence entropy would depend on the additional independent variables having their origin in the existing nonequilibrium. The nonequilibrium distribution function is obtained by solving the Boltzmann integro-differential equation both in Grad and Enskog–Chapman methods. When the entropy is computed using the nonequilibrium distribution function so obtained, the result in the first approximation is that the above mentioned dissipative fluxes serve as the additional thermodynamic variables [1–7,14–16,36–44].

Precisely this is the premise with which EIT starts and builds its framework. Thus it is obvious that EIT is a legitimate extension of LIT/CIT because the latter framework gets smoothly recovered from the former one in the linear region of the thermodynamic domain.

3. The EIT framework

Consider the following extended Gibbs relation of EIT [1–7], namely :

$$d_t s = \theta^{-1} d_t u + \theta^{-1} \pi d_t v - \alpha_{\mathbf{q}} \mathbf{q} \cdot d_t \mathbf{q} - \alpha_{\Pi} \Pi : d_t \Pi \quad (1)$$

where s is the per unit mass entropy, θ is the so-called nonequilibrium temperature, u is the per unit mass internal energy, π is the so-called nonequilibrium pressure, $v (= \rho^{-1})$ is the specific volume, ρ is the mass density, \mathbf{q} is the heat flux density, Π is the dissipative stress tensor, $\alpha_{\mathbf{q}}$ and α_{Π} are the respective coefficients and t is time. For the sake of simplicity we have not included in eq. (1) the terms corresponding to the viscous pressure (which takes care of the volume viscosity [45], the result of an additional dissipative process other than those which culminate into the observance of shear viscosity) and the chemical potentials (or mass fractions of the components, albiet we have considered a single component system). Since in eq. (1) we have θ and π instead of T and p (the temperature and pressure respectively) some authors use η in place of s and call it a generalized entropy or an entropy like function.

From (1) we have the following equations of state, namely:

$$\theta^{-1} = \left(\frac{\partial s}{\partial u} \right)_{v, \mathbf{q}, \Pi}, \quad (2)$$

$$\pi \theta^{-1} = \left(\frac{\partial s}{\partial v} \right)_{u, \mathbf{q}, \Pi}, \quad (3)$$

$$-\alpha_{\mathbf{q}} \mathbf{q} = \left(\frac{\partial s}{\partial \mathbf{q}} \right)_{u, v, \Pi}, \quad (4)$$

$$-\alpha_{\Pi} \Pi = \left(\frac{\partial s}{\partial \Pi} \right)_{u, v, \mathbf{q}}. \quad (5)$$

In EIT one integrates eqs (4) and (5) which gives

$$s = s^0 - \frac{1}{2} \alpha_{\mathbf{q}} \mathbf{q}^2 - \frac{1}{2} \alpha_{\Pi} \Pi^2 \quad (6)$$

with

$$s = s(u, v, \mathbf{q}, \Pi), \quad (7)$$

$$s^0 = s^0(u, v), \quad (8)$$

where s^0 is the reference entropy when \mathbf{q} and Π are equal to zero at the same u and v of the nonequilibrium state. The second law of thermodynamics demands that the entropy of an equilibrium state is always higher than that of the corresponding nonequilibrium states (a consequence of the stability of equilibrium [19]) and hence in eq. (6) we have

$$s^0 > s \quad (9)$$

and

$$\alpha_{\mathbf{q}} > 0, \quad \alpha_{\Pi} > 0. \quad (10)$$

Notice that eqs (2) to (5) are the prescriptions for a nonequilibrium state and eqs (4) and (5) do produce the respective nonequilibrium quantities. Perhaps because of this in several versions of EIT θ and π are termed respectively as the nonequilibrium temperature and the nonequilibrium pressure with an understanding that they are distinctly different in quality than the corresponding quantities in equilibrium. In EIT this distinction is further elaborated as follows. The partial derivatives of eqs (2) and (3) are evaluated using eq. (6) keeping in view the functional dependences of eqs (7) and (8) and thus one is led to

$$\left(\frac{\partial s}{\partial u}\right)_{v, \mathbf{q}, \Pi} = \left(\frac{\partial s^0}{\partial u}\right)_v - \frac{1}{2}\mathbf{q}^2 \left(\frac{\partial \alpha_{\mathbf{q}}}{\partial u}\right)_{v, \mathbf{q}, \Pi} - \frac{1}{2}\Pi^2 \left(\frac{\partial \alpha_{\Pi}}{\partial u}\right)_{v, \mathbf{q}, \Pi}, \quad (11)$$

$$\left(\frac{\partial s}{\partial v}\right)_{u, \mathbf{q}, \Pi} = \left(\frac{\partial s^0}{\partial v}\right)_u - \frac{1}{2}\mathbf{q}^2 \left(\frac{\partial \alpha_{\mathbf{q}}}{\partial v}\right)_{u, \mathbf{q}, \Pi} - \frac{1}{2}\Pi^2 \left(\frac{\partial \alpha_{\Pi}}{\partial v}\right)_{u, \mathbf{q}, \Pi}. \quad (12)$$

Now on adopting the equilibrium thermodynamic expressions for T and p [19,20], namely:

$$T^{-1} = \left(\frac{\partial s^0}{\partial u}\right)_v, \quad pT^{-1} = \left(\frac{\partial s^0}{\partial v}\right)_u \quad (13)$$

and using (2) and (3), eqs (11) and (12) are reexpressed as

$$\theta^{-1} = T^{-1} - \frac{1}{2}\mathbf{q}^2 \left(\frac{\partial \alpha_{\mathbf{q}}}{\partial u}\right)_{v, \mathbf{q}, \Pi} - \frac{1}{2}\Pi^2 \left(\frac{\partial \alpha_{\Pi}}{\partial u}\right)_{v, \mathbf{q}, \Pi}, \quad (14)$$

$$\pi\theta^{-1} = pT^{-1} - \frac{1}{2}\mathbf{q}^2 \left(\frac{\partial \alpha_{\mathbf{q}}}{\partial v}\right)_{u, \mathbf{q}, \Pi} - \frac{1}{2}\Pi^2 \left(\frac{\partial \alpha_{\Pi}}{\partial v}\right)_{u, \mathbf{q}, \Pi}. \quad (15)$$

If the above distinctions are to be accepted then they should be self-consistent. That is, they should remain unimpaired on further thermodynamic manipulations. Indeed, precisely this basic aspect remained uninvestigated so far. The self-consistency test can be easily performed because as stated above any thermodynamic description inherently follows its Gibbs–Duhem equation. This test we perform in the next section.

4. The Gibbs–Duhem equation regulations

The companion Gibbs–Duhem equation to eq. (1) is (c.f. Appendix A eq. (A7)):

$$\mathbf{q}^2 d\alpha_{\mathbf{q}} + \Pi^2 d\alpha_{\Pi} = 0. \quad (\text{A7})$$

Hence eqs (11) and (12) or eqs (14) and (15) gives,

$$\theta^{-1} = \left(\frac{\partial s}{\partial u} \right)_{v, \mathbf{q}, \Pi} = \left(\frac{\partial s^0}{\partial u} \right)_v = T^{-1}, \quad (\text{16})$$

$$\pi \theta^{-1} = \left(\frac{\partial s}{\partial v} \right)_{u, \mathbf{q}, \Pi} = \left(\frac{\partial s^0}{\partial v} \right)_u = p T^{-1} \quad (\text{17})$$

and hence we do have

$$\theta = T, \quad \pi = p \quad (\text{18})$$

both in magnitude and in their physical contents that is in quality, because the nonequilibrium contributions to θ and π appearing on the right hand side of eqs (14) and (15) vanish identically due to the operation of the companion Gibbs–Duhem equation. Therefore, the temperature and pressure appearing in the extended Gibbs relation, eq. (1), are indeed the absolute temperature on the Kelvin scale and the hydrostatic pressure respectively. The correct version, therefore, of eq. (1) is

$$d_t s = T^{-1} d_t u + T^{-1} p d_t v - \alpha_{\mathbf{q}} \mathbf{q} \cdot d_t \mathbf{q} - \alpha_{\Pi} \Pi : d_t \Pi. \quad (\text{19})$$

Further, on using the EIT expressions of $\alpha_{\mathbf{q}}$ and α_{Π} namely:

$$\alpha_{\mathbf{q}} = \frac{v\tau_1}{\lambda T^2}, \quad \alpha_{\Pi} = \frac{v\tau_2}{2\eta T}, \quad (\text{20})$$

where τ_1 and τ_2 are the relaxation times, λ is the heat conductivity and η is the shear viscosity, in eq. (A7) we obtain

$$\begin{aligned} & (\mathbf{q}^2 \alpha_{\mathbf{q}} + \Pi^2 \alpha_{\Pi}) \frac{dv}{v} + \mathbf{q}^2 \alpha_{\mathbf{q}} \frac{d\tau_1}{\tau_1} + \Pi^2 \alpha_{\Pi} \frac{d\tau_2}{\tau_2} \\ & = \mathbf{q}^2 \alpha_{\mathbf{q}} \frac{d\lambda}{\lambda} + \Pi^2 \alpha_{\Pi} \frac{d\eta}{\eta} + (2\mathbf{q}^2 \alpha_{\mathbf{q}} + \Pi^2 \alpha_{\Pi}) \frac{dT}{T}. \end{aligned} \quad (\text{21})$$

Now for a constant volume process (say in liquids and solids) τ_1 and τ_2 are much smaller than T and η [1] and hence eq. (21) reduces to

$$\mathbf{q}^2 \alpha_{\mathbf{q}} \frac{T}{\lambda} \frac{\partial \lambda}{\partial T} + \Pi^2 \alpha_{\Pi} \frac{T}{\eta} \frac{\partial \eta}{\partial T} = -(2\mathbf{q}^2 \alpha_{\mathbf{q}} + \Pi^2 \alpha_{\Pi}) < 0. \quad (\text{22})$$

Thus as expected the increase in temperature makes λ and η to decrease and if one of them increases then the other will decrease sufficiently to maintain the negative sign of eq. (22). However, if one considers the individual processes we have

$$\left(\frac{\partial \lambda}{\partial T}\right)_{v, \tau_1} = -\frac{2\lambda}{T}, \quad \left(\frac{\partial \eta}{\partial T}\right)_{v, \tau_2} = -\frac{\eta}{T}. \quad (23)$$

Thus each quotient of eq. (23) as expected is very small in magnitude in view of the fact $\lambda, \eta \ll T$ [1] unless one is very close to the absolute zero of temperature.

The present paper has two important results. Firstly, we conclude that from the thermodynamic point of view the nonequilibrium temperature and pressure have identically the same physical contents as they have in equilibrium as is established by eqs (16) and (17). Secondly, for a single component non-uniform system if we write a more general extended Gibbs relation, say,

$$d_t s = T^{-1} d_t u + T^{-1} p d_t v - \sum_j \beta_j \odot d_t \alpha_j, \quad (24)$$

where α_j and β_j are the conjugate pairs of the additional thermodynamic variables extensive and intensive respectively and \odot denotes the scalar product, then the following operative Gibbs–Duhem equation accompanies it, namely:

$$\sum_j \alpha_j \odot d_t \beta_j = 0 \quad (25)$$

and hence the corresponding analogues of eqs (16) and (17) are guaranteed justifying the use of T and p in eq. (24). Finally, we stress that the role of the relevant Gibbs–Duhem equation in an irreversible thermodynamic description is as important as thermodynamic laws in thermodynamics. That is the Gibbs–Duhem equation is the backbone of any thermodynamic description both reversible and irreversible ones.

Appendix A

To understand the basis of eq. (A7) of the main text let us recall the equilibrium thermodynamic expression for the local equilibrium entropy s^0 , namely :

$$s^0 = T^{-1}(u + pv - \mu^0), \quad (A1)$$

where μ^0 is the local equilibrium chemical potential (a single component system is assumed). The differentiation of eq. (A1) gives

$$ds^0 = T^{-1} du + pT^{-1} dv \quad (A2)$$

and the corresponding Gibbs–Duhem equation, namely :

$$s^0 dT - v dp + d\mu^0 = 0. \quad (A3)$$

Similarly, the differentiation of eq. (6) of the main text and then using eq. (A1) gives

$$ds = T^{-1} du + T^{-1} p dv - \alpha_q \mathbf{q} \cdot d\mathbf{q} - \alpha_\Pi \Pi : d\Pi \quad (A4)$$

and the corresponding Gibbs–Duhem equation, namely :

$$s^0 dT - v dp + d\mu^0 + \frac{1}{2} T \mathbf{q}^2 d\alpha_q + \frac{1}{2} T \Pi^2 d\alpha_\Pi = 0. \quad (A5)$$

Notice that no θ and π can be introduced in eq. (A1) because this equation corresponds to the reference equilibrium state and hence eqs (A4) and (A5) contain T and p . But the condition of (A3) reduces (A5) to

$$\frac{1}{2}T\mathbf{q}^2d\alpha_{\mathbf{q}} + \frac{1}{2}T\Pi^2d\alpha_{\Pi} = 0 \quad (\text{A6})$$

or simply

$$\mathbf{q}^2d\alpha_{\mathbf{q}} + \Pi^2d\alpha_{\Pi} = 0 \quad (\text{A7})$$

which is the operative Gibbs–Duhem equation in nonequilibrium. This is the rigorous proof of the validity of (A7) and this derivation in turn establishes the validity of eqs (16) and (17) of the main text.

Recall that s^0 is the entropy of the reference equilibrium state having the same values of u and v as that in the nonequilibrium state in question, its physical reality can be established as follows. Let the tiny volume element, δV , (large enough from the microscopic point of view containing in it a very large number of molecules) be instantly isolated and allowed to evolve in a rigid enclosure. Then by design u and v of this tiny volume element, δV , remain constant during its isolated state evolution. T and p will also remain constant if the tiny volume element consists of a monatomic gas. During this evolution the fluxes \mathbf{q} and Π ultimately die out and s finally attains an equilibrium value s^0 . On the other hand one may have an objection that during an irreversible evolution of a system (that is when the tiny volume element is a part of a global nonequilibrium system) the Gibbs–Duhem equations namely eqs (A3) and (A5) may not be valid simultaneously. Recall, however, that when a system traverses an irreversible trajectory it passes through a succession of nonequilibrium states and hence as described above one easily identifies a unique succession of the corresponding equilibrium states. Thus when a system irreversibly traverses a succession of nonequilibrium states it is accompanied by an unidirectional passage through the succession of the corresponding reference equilibrium states and hence both (A3) and (A5) are followed simultaneously. This simultaneous validity of (A3) and (A5) during an irreversible passage of a system is akin to a description in the thermodynamics of equilibrium states [19,20]. For example, in equilibrium thermodynamics the Gibbs free energy, G , is given by

$$G = G^{\ominus} + nRT \ln a, \quad (\text{A8})$$

where \ominus denotes the chosen standard reference state, n is the number of moles (a single component system assumed), R is the universal gas constant and a is the activity. However, in terms of Gibbs–Duhem equation we do have,

$$SdT - Vdp + nd\mu = 0, \quad (\text{A9})$$

$$S^{\ominus}dT - V^{\ominus}dp + nd\mu^{\ominus} = 0, \quad (\text{A10})$$

where S is the entropy, V is the volume and μ is the chemical potential per mole.

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References

- [1] D Jou, J Casas-Vázquez and G Lebon, *Extended irreversible thermodynamics* (Springer-Verlag, Berlin, 1993, 1996)
- [2] P Salamon and S Sieniutycz (eds), *Extended thermodynamic systems* (Taylor and Francis, New York, 1992)
- [3] I Müller and T Ruggeri, *Extended thermodynamics* (Springer-Verlag, Berlin, 1993)
- [4] B C Eu, *Kinetic theory and irreversible thermodynamics* (John Wiley, New York, 1992)
- [5] D Jou, J Casas-Vázquez and G Lebon, *Rep. Prog. Phys.* **51**, 1105 (1988)
- [6] L S García-Colín, *Rev. Mex. Fís.* **34**, 344 (1988) (in english)
- [7] R E Nettleton and S L Sobolev, *J. Non-Equilib. Thermodyn.* **20**, 205, 297 (1995); **21**, 1 (1996)
- [8] D Jou and J Casas-Vázquez, *Phys. Rev.* **E45**, 8371 (1992)
- [9] R E Nettleton, *Can. J. Phys.* **72**, 106 (1994)
- [10] D Jou and J Casas-Vázquez, *Phys. Rev.* **E48**, 3201 (1993)
- [11] W G Hoover, B L Holian and H A Posch, *Phys. Rev.* **E48**, 3196 (1993)
- [12] K Henjes, *Phys. Rev.* **E48**, 3199 (1993)
- [13] D Jou and J Casas-Vázquez, *Phys. Rev.* **E49**, 1040 (1994)
- [14] L S García-Colín and V Micenmacher, *Mol. Phys.* **88**, 399 (1996)
- [15] L S García-Colín, *Mol. Phys.* **86**, 697 (1995)
- [16] B C Eu and L S García-Colín, *Phys. Rev.* **E54**, 2501 (1996)
- [17] A A Bhalekar and L S García-Colín, *Pramana – J. Phys.* **50**, 295 (1998)
- [18] A A Bhalekar, *Pramana – J. Phys.* **50**, 281 (1998)
- [19] H B Callen, *Thermodynamics* (Wiley, New York, 1962)
- [20] E A Guggenheim, *Thermodynamics: An advanced treatment for chemists and physicists* (North-Holland, Amsterdam, 1954)
- [21] S R de Groot and P Mazur, *Nonequilibrium thermodynamics* (North-Holland, Amsterdam, 1962)
- [22] D D Fitts, *Nonequilibrium thermodynamics* (McGraw-Hill, New York, 1962)
- [23] A Katchalsky and P Curran, *Nonequilibrium thermodynamics in biophysics* (Harvard University Press, Cambridge, M.A., 1965)
- [24] I Prigogine, *Introduction to thermodynamics of irreversible processes* (Wiley-Interscience, New York, 1967)
- [25] R Haase, *Thermodynamics of irreversible processes* (Addison-Wesley, Reading, M.A., 1969)
- [26] I Gyarmati, *Nonequilibrium thermodynamics* (Springer-Verlag, Berlin, 1970)
- [27] K G Denbigh, *The thermodynamics of the steady state* (Methuen, London, 1951)
- [28] S Wisneiwski, B Staniszewski and R Szymanik, *Thermodynamics of nonequilibrium processes* (D Reidel, Dordrecht, 1976)
- [29] Y L Yao, *Irreversible thermodynamics* (Science Press, Beijing and distributors Van Nostrand Reinhold, New York, 1981)
- [30] L S García-Colín, *Termodinámica de Procesos Irreversibles* (in spanish, Colección CBI, UAM-Iztapalapa, México D.F., 1989)
- [31] P Glansdorff and I Prigogine, *Thermodynamic theory of structure, stability and fluctuations* (Wiley-Interscience, London, 1971)
- [32] O Reynolds, *Philos. Mag. (London)* **20**, 469 (1885)
- [33] D Burnett, *Proc. London Math. Soc.* **40**, 382 (1935)
- [34] S Chapman and T G Cowling, *The mathematical theory of non-uniform gases* (Cambridge University Press, Cambridge, 1970)
- [35] H Grad, Principles of Kinetic Theory of Gases in *Handbuch der Physik*, edited by S Flügge, (Springer-Verlag, Berlin, 1958) vol. 12

- [36] L S García-Colín, M Lopez de Haro, R F Rodriguez, J Casas-Vázquez and D Jou, *J. Stat. Phys.* **37**, 465 (1984)
- [37] L S García-Colín, *Acta Phys. Hungarica* **67**, 79 (1989)
- [38] L S García-Colín, *Teoría Cinética de Los Gases* (in spanish, Colección CBI, UAM-Iztapalapa, México D. F., 1990)
- [39] R E Nettleton, *J. Chem. Phys.* **93**, 8247 (1990)
- [40] L S García-Colín and F J Uribe, *J. Non-Equilib. Thermodyn.* **16**, 89 (1991)
- [41] R M Velasco and L S García-Colín, *Stat. Phys.* **69**, 217 (1992)
- [42] R E Nettleton, *Ann. Phys.* **2**, 490 (1993)
- [43] R M Velasco and L S García-Colín, *J. Non- Equilib. Thermodyn.* **18**, 157 (1993)
- [44] L S García-Colín and A A Bhalekar, *Proc. Pakistan Acad. Sci.* **34**, 35 (1997)
- [45] G K Batchelor, *An introduction to fluid dynamics* (Cambridge University Press, Cambridge, 1967)