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Onsager symmetry from mesoscopic time reversibility and the hydrodynamic dispersion tensor for coarse-grained systems

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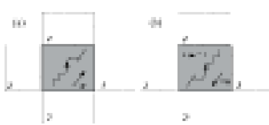
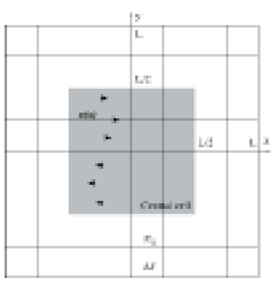
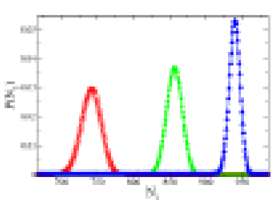
ABSTRACT

Onsager reciprocity relations derive from the fundamental time reversibility of the underlying microscopic equations of motion. This gives rise to a large set of symmetric cross-coupling phenomena. We here demonstrate that different reciprocity relations may arise from the notion of mesoscopic time reversibility, i.e., reversibility of intrinsically coarse-grained equations of motion. We use Brownian dynamics as an example of such a dynamical description and show how it gives rise to reciprocity in the hydrodynamic dispersion tensor as long as the background flow velocity is reversed as well.



- 
- 
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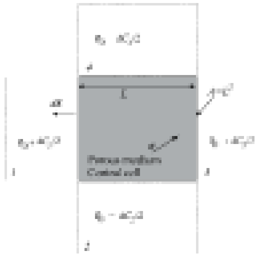

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Physics Subject Headings (PhySH)

1. Research Areas

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Statistical Physics

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ARTICLE TEXT

I. INTRODUCTION

Onsager reciprocity or symmetry relations [1,2] describe a wide range of cross-coupling phenomena. Even though they were most intensely studied in the 1940s to 1960s—see Ref. [3] for an excellent review—their relevance is still strong in many fields, and they play the role as a foundation of irreversible thermodynamics [4]. Well studied cross-coupling phenomena include the thermomechanical effect (piezoelectrical elements), the thermoelectric effect, electrokinetic phenomena, multispecies molecular diffusion, transference in electrolytic solutions, and thermomagnetism [3]. More recently, the statistical mechanical arguments of Onsager have also been applied in a hydrodynamic context [5,6].

Historically, the diffusion of heat in anisotropic solids and the symmetry of the thermal conductivity tensor have played a key role. These symmetries were observed as early as 1893 by Soret [7,8] and, at the time, partly explained by geometrical arguments pertaining to the symmetries of crystal lattices. But only with the general theory of Onsager, who also used heat diffusion as a starting point, were the wide range of cross-coupling phenomena given a common and fundamental theoretical basis.

Classical Onsager theory as given by de Groot [4] and by Onsager himself is based on the notion of the fundamental time reversibility of the underlying microdynamics. The time-reversal symmetry is attributed to the microscopic equations that describe individual particles. In this paper we demonstrate that the time-reversal symmetry does not have to be attributed to the microdynamics but may just as well be attributed to a mesoscopic description in between the microlevel and that of the linear laws with its transport coefficients and in this case too Onsager reciprocity relations for the macroscale transport coefficients results. This enlarges the scope of irreversible thermodynamics by opening for the application of the same analysis to new systems, and therefore the class of reciprocity relations that results will also be enlarged.

This is exemplified here by a case of flow of two miscible fluids in a complex medium. This flow is described by a hydrodynamic dispersion tensor which becomes symmetric under hydrodynamic flow reversal by virtue of Onsager reciprocity. This is shown by a mesoscopic approach where Brownian dynamics is taken as the mesoscopic and lowest level description. The Brownian particles are simply random walkers that move along on the hydrodynamic background field u. This means that we are dealing with three separate length scales:

- (i) the mean free path of the particles,
- (ii) the hydrodynamic scale on which the particle motion may be averaged into velocity and density fields ρ and u, and
- (iii) the porous-continuum scale on which averaging over the geometric heterogeneities and flow field of the porous medium makes sense.

These different scales are assumed to be sufficiently far apart.

The end result, which pertains to the porous-continuum scale show that the tensor, relating the concentration gradients in the spatial direction i to the diffusive flux in direction j satisfies the symmetry relation,

$$D_{ij}(u)=D_{ji}(-u). \tag{1}$$

In doing so we make contact with the results of Auriault *et al.* [9] who showed these relations, albeit on the basis of continuum mechanics and only in the small Péclet (Pe) number limit.

The structure of the derivation proceeds from the equations of motion of the Brownian particles and the equivalent Fokker-Planck equation. Then a small numerical simulation is used to show that particle number fluctuations behave as in an equilibrium situation, even though our system is not in equilibrium but in a driven steady state. The standard Onsager theory may then be applied as soon as the fluxes and forces governing the entropy production are identified. The Gibbs expression for the entropy [10,11] allows this identification in a straightforward way. The end result of Eq. (1), which belongs on the largest scale, is thus connected to the time reversibility on the smallest scale (i).

II. RECIPROCITY DERIVED FROM THE MESOSCOPIC LEVEL

III. THE FOKKER-PLANCK EQUATION AND THE CONTINUUM DESCRIPTION

IV. GIBBS ENTROPY AND THE ENTROPY PRODUCTION

V. FROM THE PORE LEVEL TO THE COARSE-GRAINED POROUS-CONTINUUM LEVEL

VI. CONCLUSIONS

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