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Onsager Relations for Transport in Inhomogeneous Media

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The nonlinear equations that describe transport in inhomogeneous media cannot be obtained by a straightforward extension of the known phenomenological equations for homogeneous media. One cannot therefore assert *a priori* that the Onsager reciprocity relations remain valid. Previously the correct equations have been obtained for three special models using kinetic theory. It is here shown that in these models the Onsager relations do indeed hold, provided that they are formulated with care.

KEY WORDS: Onsager relations; inhomogeneous media; nonlinear transport.

1. ONSAGER RELATIONS FOR DISCRETE SYSTEMS

The Onsager relations(1) appear in their conceptually simplest form when they are applied to the transport of matter and energy between two vessels *I* and *II*. Either vessel contains a gas in equilibrium and the two temperatures and chemical potentials must be sufficiently close to each other for the rate of transport to be linear in their difference. The transport equations then have the form

$$\dot{\alpha}_i = \sum_k L_{ik} X_k \tag{1}$$

The α_i denote the transported quantities, in this case energy α_0 and mass α_1. More precisely, they are the excess of energy and mass contained in vessel *I* over and above its rightful share in the overall equilibrium of both vessels. Hence the total entropy

$$S(\alpha) = S^I(\alpha) + S^{II}(-\alpha)$$

has a maximum at $\alpha_i = 0$.

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Apart from the conserved extensive quantities α_i one defines for each vessel the corresponding intensive quantities

$$\zeta_i^I = \frac{\partial S^I}{\partial \alpha_i}, \qquad \zeta_i^{II} = -\frac{\partial S^{II}}{\partial \alpha_i} \tag{2}$$

The thermodynamic forces or affinities X_i are defined as $\zeta_i^I - \zeta_i^{II}$, or rather by the linear terms thereof:

$$X_i = \sum_j \left(\frac{\partial^2 S^I}{\partial \alpha_i \, \partial \alpha_j} + \frac{\partial^2 S^{II}}{\partial \alpha_i \, \partial \alpha_j} \right) \alpha_j = \sum_j \frac{\partial^2 S}{\partial \alpha_i \, \partial \alpha_j} \alpha_j$$

The derivatives are taken at $\alpha_i = 0$. In our case of one gas in two vessels one has for each vessel

$$\zeta_0 = \frac{1}{T}, \qquad \zeta_1 = -\frac{\mu}{T} \tag{3}$$

μ is the chemical potential. Hence

$$X_0 = \Delta \left(\frac{1}{T} \right) = -\frac{\Delta T}{T^2}, \qquad X_1 = \Delta \left(\frac{-\mu}{T} \right) = \frac{-\Delta \mu}{T} + \frac{\mu}{T^2} \Delta T$$

where Δ denotes the difference between the vessels I and II.

For our purpose it is necessary to include, as an additional feature, a given external potential field V, which is constant inside each vessel, but may differ between them. Again this difference ΔV must be small enough to be treated only in linear approximation. For d-dimensional ideal gases one then has in each vessel

$$\mu = -\frac{d}{2} T \log T + T \log n + V \tag{4}$$

where n is the density. As is well known, Boltzmann's constant equals unity.

The Onsager relations state $L_{ik} = L_{ki}$. The transport coefficients L_{ik} are in general functions of the intensive quantities ζ, but thanks to the linear approximation it is not necessary to specify whether these are the ζ of the one vessel or of the other, or for instance the mean. This is one reason why the restriction to the linear approximation is indispensable. Without it the right-hand side of (1) would have to be replaced by some function of the state variables of both vessels,

$$\dot{\alpha}_i = f_i(\zeta_k^I, \zeta_k^{II})$$

It is not known how a generalization of Onsager's relation for this case could be formulated.[2]

2. ONSAGER RELATIONS FOR EXTENDED SYSTEMS

It is easy to extend the consideration of the previous section to a chain of vessels *I*, *II*, *III*,..., in which every two successive ones are linked according to (1). In each vessel the α_i vary due to transport to both the preceding vessel and the succeeding one. It is convenient to regard these two terms as the flows J_i through each of the links. The L_{ik} of each link depend on the ζ, for which one may take the value of either vessel because the ζ vary little between two successive ones. However, the values of ζ along the whole chain may vary considerably. As a consequence the local values of ζ may also vary considerably in the course of the time evolution. If initially one end of the chain is much hotter than the other, the colder end will heat up, so that $\zeta_0 = 1/T$ cannot be treated as a constant. Hence the L_{ik} are no longer constant and their dependence on the evolving $\zeta(t)$ must be taken seriously. The chain of equations (1) constitute therefore a set of nonlinear differential equations.

To summarize, the flows J_i are still proportional to the *local* differences $\Delta\zeta$ of the ζ, but the proportionality factors $L_{ik}(\zeta)$ vary in the course of time through their dependence on the *global* variations of the ζ in the extended system.

It is not necessary that the L_{ik} of the successive links are all the same function of the local ζ. Their dependence on ζ may change along the chain, which means that the system is inhomogeneous. This has nothing to do with the linearity or nonlinearity of the evolution equations.

This chain of vessels may seem contrived, but it describes precisely what happens in a continuous medium. Consider a one-dimensional pipe containing a fluid, which is locally in equilibrium. Let $\alpha_i(x)$ denote the various conserved quantities per unit length and $J_i(x)$ their flows along the pipe. The intensive variables ζ_k are defined as in (2) through the local entropy density $s(x)$ by

$$\zeta_k(x) = \frac{\partial s}{\partial \alpha_k} = \sum_j \frac{\partial^2 s}{\partial \alpha_k \, \partial \alpha_j} \alpha_j \tag{5}$$

This relation involves only equilibrium properties. Transport is described by the flows $J_i(x)$; they are proportional to the differences of the ζ_k in adjacent elements

$$J_i(x) = \sum_k L_{ik}[\zeta(x))] \frac{d\zeta_k}{dx} \tag{6}$$

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[2] A previous attempt^(2) was unsuccessful, because on second thought it appeared much more restricted than originally realized and presumably applies exclusively to a Knudsen gas.

Hence the evolution of the α_i is given by

$$\dot{\alpha}_i(x) = -\frac{dJ_i(x)}{dx} = -\sum_k \frac{d}{dx} L_{ik}(\zeta) \frac{d\zeta_k}{dx} \tag{7}$$

Together with the linear relations (5), this is a closed set of nonlinear equations.

The extension to three dimensions is merely a matter of notation, but it is not needed for our purpose. Moreover, we restrict ourselves to the simple fluid, having only an energy flow J_0 and a mass flow J_1. According to (3), the flow equations (6) take the form

$$J_0 = L_{00} \frac{d}{dx} \frac{1}{T} + L_{01} \frac{d}{dx} \frac{-\mu}{T}$$

$$J_1 = L_{10} \frac{d}{dx} \frac{1}{T} + L_{11} \frac{d}{dx} \frac{-\mu}{T}$$

If the fluid consists of noninteracting particles, each with d degrees of freedom, one may use (4) to express μ in terms of the density n. One then gets equations of the more familiar form

$$\begin{aligned} J_0 &= -A \frac{dT}{dx} - B\left(\frac{dn}{dx} + \frac{n}{T}\frac{dV}{dx}\right) \\ J_1 &= -C \frac{dT}{dx} - D\left(\frac{dn}{dx} + \frac{n}{T}\frac{dV}{dx}\right) \end{aligned} \tag{8}$$

in which the phenomenological coefficients A, B, C, D are given by

$$A = \frac{L_{00}}{T^2} - \left(\frac{d}{2T} + \frac{V}{T^2}\right) L_{01}, \qquad B = \frac{L_{01}}{n}$$

$$C = \frac{L_{10}}{T^2} - \left(\frac{d}{2T} + \frac{V}{T^2}\right) L_{11}, \qquad D = \frac{L_{11}}{n}$$

In terms of these coefficients the Onsager relation $L_{01} = L_{10}$ reads

$$nB = T^2 C + \left(\frac{d}{2} T + V\right) nD \tag{9}$$

3. WHY IS THERE A PROBLEM?

The equation (7) for the particle density is

$$\frac{\partial n}{\partial t} = -\frac{\partial J_1}{\partial x} = \frac{\partial}{\partial x}\left[D \frac{\partial n}{\partial x} + \frac{D}{T} V'(x) n + CT'(x)\right] \tag{10}$$

where the primes denote derivatives. This is only one of two coupled equations, but suppose that by some external means the temperature $T(x)$ at each point x is kept fixed. Then (10) represents a generalized diffusion equation for the particle density $n(x)$ alone. The coefficients depend on x through $T(x)$ and may have an additional x dependence for inhomogeneous systems.

The problem of diffusion in an inhomogeneous medium with inhomogeneous temperature has been studied by a number of authors, mainly in connection with semiconductors.(3,4) It gives rise to some interesting phenomena.(5,6) The reason why it is a problem is the following. The familiar phenomenological derivation used above yields a transport equation (10) in which the transport coefficients are the same ones as occur in the linear transport equations. The only reason why they depend on x is that the linear transport coefficients have to be taken at the local values of the thermodynamic variables $T(x)$, $\mu(x)$. The assumption of local equilibrium is indispensable for deriving (10). However, this assumption is dubious, because strict local equilibrium is incompatible with transport. As a consequence the phenomenological approach is not precise enough to find the correct form of the transport equations. There is no unique prescription for relating the coefficients in the nonlinear equations of inhomogeneous systems to the familiar coefficients known from measurements in homogeneous systems. Various similar, but not identical, equations seem equally plausible.(7)

To clarify the problem, a number of kinetic models have been investigated.(3,6–10) They gave rise to generalized diffusion equations, which could not be guessed phenomenologically. It is therefore also not clear *a priori* that in these cases the Onsager relations survive. The purpose of the present article is to verify that they do for the three kinetic models for which the diffusion equation has been derived previously.(6,9,10)

In each case the particles diffuse independently, so that our present density $n(x, t)$ may be identified with the probability density $P(x, t)$ in the previous treatments. On identifying the diffusion equation for P with the present phenomenological equation (10), we obtain the explicit form of D and C for each of the three models. In order to verify the Onsager relation, it is necessary to compute the energy flow J_0 as well. These computations are relegated to appendices, because they are somewhat involved and rely heavily on previous publications. The result will be that in each case Onsager is obeyed.

For practical use we cast the condition (9) in yet another form. The energy flow J_0 often appears in the form

$$J_0 = \varphi J_1 + \psi \frac{dT}{dx} \tag{11}$$

where φ and ψ are functions of n and T. The factor φ may be regarded as the average energy carried by each transferred particle. One then has $B=\varphi D$ and the Onsager relation (9) becomes

$$(\varphi-(d/2)T-V)D=(T^2/n)C \tag{12}$$

4. FIRST MODEL: LANDAUER'S PIPE

A Knudsen gas is enclosed in a thin pipe$^{(8)}$ of radius ε. The wall is kept at a fixed temperature $T(x)$, where x is the coordinate along the pipe. Molecules impinging on the wall are returned with the Maxwell distribution corresponding to the local $T(x)$. There is also a potential field $V(x)$. It has been proved$^{(9)}$ that to first order in ε the density $n(x, t)$ obeys a diffusion equation; the diffusion flow is

$$J_1=-\frac{8\varepsilon}{3(2\pi)^{1/2}}\left[\frac{\partial}{\partial x}T^{1/2}n+T^{-1/2}V'n\right]$$

Comparison with (8) shows that, omitting the numeral prefactor,

$$D=T^{1/2}, \qquad C=\tfrac{1}{2}nT^{-1/2}$$

The energy flow is computed in Appendix A, with the result

$$J_0=(V+2T)J_1-\frac{4\varepsilon}{3(2\pi)^{1/2}}T^{1/2}n\frac{dT}{dx}$$

Thus (11) applies with $\varphi=V+2T$. Hence it is convenient to verify the Onsager relation in the form (12). For the present model it reduces to

$$(V+2T-(3/2)T-V)T^{1/2}=(T^2/n)\,\tfrac{1}{2}nT^{-1/2}$$

which is manifestly satisfied.

5. SECOND MODEL: BROWNIAN PARTICLE

A heavy particle is embedded in a fluid, which is responsible for a friction force and a random Langevin force. The joint probability distribution $R(x, v)$ of its position and velocity obeys the Kramers equation$^{(11)}$

$$\frac{\partial R}{\partial t}=-v\frac{\partial R}{\partial x}+V'(x)\frac{\partial R}{\partial v}+\gamma(x)\frac{\partial}{\partial v}\left[vR+T(x)\frac{\partial R}{\partial v}\right] \tag{13}$$

We have taken one dimension; $V(x)$ is an external field. $T(x)$ is the local temperature of the fluid and $\gamma(x)$ is proportional to its density. We allow

γ to depend on x, so that not only the temperature, but also the system itself may be inhomogeneous. Recently an extension of (13) has been given which includes a thermophoretic force,$^{(12)}$ but I have not been able to verify the Onsager relation for that case.

Kramers' equation determines the evolution of the distribution in phase space. In the limit of large γ, however, the velocity distribution is practically a Maxwellian, corresponding to the local temperature $T(x)$. As a consequence, the spatial density $n(x, t)$ obeys an equation by itself from which the velocity has been eliminated. It can be obtained in the same way as for constant γ and T.$^{(11,13)}$ The diffusion flow is then found to be$^{(6)}$

$$J_1 = -\frac{1}{\gamma(x)}\left[\frac{\partial}{\partial x} T(x)n + V'(x)n\right] \tag{14}$$

This has the form (8) with

$$D(x) = \frac{T(x)}{\gamma(x)}, \qquad C(x) = \frac{n(x)}{\gamma(x)}$$

The energy flow is computed in Appendix B, with the result

$$J_0 = \left(\frac{3}{2}T + V\right)J_1 - \frac{Tn}{2\gamma}\frac{dT}{dx} \tag{15}$$

That shows that $\varphi = \frac{3}{2}T + V$ and the Onsager relation (12) takes the form

$$\left(\frac{3}{2}T + V - \frac{1}{2}T - V\right)\frac{T}{\gamma} = \frac{T^2}{n}\frac{n}{\gamma}$$

which is satisfied.

6. THIRD MODEL: TRANSPORT BY HOPPING

A particle moves in a one-dimensional medium containing traps in the form of potential pits of depth Φ. The particle resides in a trap until it happens to collect from the heat motion of the medium the escape energy Φ. For a particle trapped at x' the probability per unit time to escape is

$$c\exp[-\Phi/T(x')] \tag{16}$$

where $T(x')$ is the local temperature of the medium. It then travels until it is caught by another trap; the traveling time is negligible compared to the time spent inside traps. The density of traps is $\Omega\sigma(x)$, where Ω serves as a parameter to scale up the density and thereby reduce the average length of the hops. The probability for the traveling particle to be caught in a trap between x and $x+dx$ is

$$\alpha\Omega\sigma(x)\,dx$$

where α is the probability to get stuck on passing a trap.

When there is an external potential field $V(x)$ the same excitation probability (16) is still valid for a hop in the direction of lower V. In the direction of increasing V, however, the probability per second for a particle, trapped at x', to undergo an excitation that allows it to travel to x is

$$c\exp\{-[\Phi+V(x)-V(x')]/T(x')\}$$

This defines our hopping model for transfer in the presence of an external field and an inhomogeneous temperature; the medium itself is inhomogeneous because σ depends on x. The model need not be realized in nature; all that matters is that it could exist—that is, that it does not violate any physical laws.

It has been shown$^{(10)}$ that for large Ω the transport of particles is described in first approximation by a diffusion equation. The particle flow is

$$J_1=-\frac{2c}{\alpha^2\Omega^2}\left(\frac{1}{\sigma}\frac{d}{dx}e^{-\Phi/T}\frac{n}{\sigma}+\frac{V'}{T\sigma}e^{-\Phi/T}\frac{n}{\sigma}\right) \tag{17}$$

The energy flow is computed in Appendix C, with the result

$$J_0=VJ_1 \tag{18}$$

In order to confront these equations with Onsager we have to develop the thermodynamics of particles hopping around in a medium. First, they have no kinetic energy, but a potential energy $V(x)-\Phi$ per particle at x. The internal energy per unit volume is

$$u(x)=[V(x)-\Phi]\,n(x)+u_0(x)$$

where $u_0(x)$ is the energy density of the static medium. A particle has no other freedom than the choice of a site among the $\Omega\sigma(x)$ traps in each unit volume; hence each trap is occupied with probability $n(x)/\Omega\sigma(x)$ and the entropy per unit volume is

$$s(x)=-n(x)\log\frac{n(x)}{\Omega\sigma(x)}+s_0(x)$$

s_0 refers to the medium, so that $T\,ds_0 = du_0$. Standard thermodynamics now readily yields

$$\mu = T \log \frac{n}{\Omega\sigma} + V - \Phi$$

This replaces (4). One now has

$$J_1 = [L_{10} - (V - \Phi) L_{11}] \frac{d}{dx}\frac{1}{T} - L_{11}\left(\frac{d}{dx}\log\frac{n}{\sigma} + \frac{1}{T}\frac{dV}{dx}\right)$$

On the other hand, it has been shown$^{(10)}$ that for large Ω the transport of particles is described in lowest order by a diffusion equation. The particle flow is

$$J_1 = -\frac{2c}{\alpha^2\Omega^2}\left(\frac{1}{\sigma}\frac{d}{dx} e^{-\Phi/T}\frac{n}{\sigma} + \frac{n}{T\sigma^2} e^{-\Phi/T}\frac{dV}{dx}\right)$$

Comparison of both expressions shows that, omitting the numerical prefactor,

$$L_{11} = \frac{n}{\sigma^2} e^{-\Phi/T}, \qquad L_{10} = \frac{n}{\sigma^2} V e^{-\Phi/T}$$

It follows from (18) that $L_{01} = VL_{11}$ and this is, indeed, equal to L_{10}. Hence Onsager is again obeyed.

APPENDIX A

In cylindrical coordinates x, $\varepsilon\rho$ $(0 \leqslant \rho \leqslant 1)$ the azimuth disappears because of symmetry. Let the velocity component along the x axis be u, in the radial direction p, and in the tangential direction $\rho\kappa$. For the probability density in the one-particle phase space I write$^{(9)}$

$$(\varepsilon\rho)^{-2} F(x, \rho; u, p, \kappa; t)$$

The spatial density is

$$n(x, t) = \int_0^1 d\rho \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} d\kappa\, F(x, \rho; u, p, \kappa; t)$$

The particle flow is

$$J_1(x, t) = \int_0^1 d\rho \int_{-\infty}^{\infty} u\, du\, dp\, d\kappa\, F \tag{19}$$

and the energy flow

$$J_0(x,t)=\int_0^1 d\rho \int_{-\infty}^{\infty} \left[\tfrac{1}{2}(u^2+p^2+\rho^2\kappa^2)+V\right]u\,du\,dp\,d\kappa\,F$$

In the limit $\varepsilon \to 0$ the distribution becomes the local Maxwell distribution

$$F^{(0)}=2(2\pi T)^{-3/2}\rho^2 e^{-(u^2+p^2+\rho^2\kappa^2)/2T}n(x)$$

To obtain the flows one needs the next order, which according to the method for eliminating fast variables$^{(14)}$ is

$$\varepsilon F^{(1)}=-\varepsilon\mathscr{L}_0^{-1}\mathscr{L}_1 F^{(0)} \tag{20}$$

The operators $\mathscr{L}_0$ and $\mathscr{L}_1$ are

$$\mathscr{L}_0=-p\frac{\partial}{\partial\rho}-\rho\kappa^2\frac{\partial}{\partial p}+2\frac{p}{\rho}\frac{\partial}{\partial\kappa}\kappa$$

$$\mathscr{L}_1=-u\frac{\partial}{\partial x}+V'(x)\frac{\partial}{\partial u}$$

To evaluate (20), we first notice

$$\mathscr{L}_1 F^{(0)}=-\left(\frac{\partial}{\partial x}+\frac{V'}{T}\right)uF^{(0)}$$

Since $\mathscr{L}_0$ does not involve x, one now has to determine $\mathscr{L}_0^{-1}uF^{(0)}\equiv G(x,\rho;u,p,\kappa)$ by solving the equation $\mathscr{L}_0 G=uF^{(0)}$. A somewhat subtle argument involving the boundary conditions gives

$$G=-\frac{u}{p^2+\rho^2\kappa^2}\left[\rho p+(p^2+\rho^2\kappa^2-\rho^4\kappa^2)^{1/2}\right]F^{(0)}$$

Substitution in (19) gives

$$\begin{aligned}
J_1&=-\varepsilon\left(\frac{\partial}{\partial x}+\frac{V'}{T}\right)\int_0^1 d\rho\int_{-\infty}^{\infty}\frac{\rho p+(p^2+\rho^2\kappa^2-\rho^4\kappa^2)^{1/2}}{p^2+\rho^2\kappa^2}\,dp\,d\kappa\\
&\quad\times\int_{-\infty}^{\infty}u^2F^{(0)}\,du\\
&=-\varepsilon\left(\frac{\partial}{\partial x}+\frac{V'}{T}\right)\frac{1}{\pi}\int_0^1\rho\,d\rho\int_{-\infty}^{\infty}\frac{[p^2+(1-\rho^2)\lambda^2]^{1/2}}{p^2+\lambda^2}\\
&\quad\times e^{-(p^2+\lambda^2)/2T}\,dp\,d\lambda\cdot n(x)\\
&=-\varepsilon\left(\frac{\partial}{\partial x}+\frac{V'}{T}\right)\frac{8}{3}\left(\frac{T}{2\pi}\right)^{1/2}n(x)
\end{aligned}$$

This is the old result.[9] For the energy flow we now find

$$J_0 = VJ_1 + \frac{\varepsilon}{2}\left(\frac{\partial}{\partial x} + \frac{V'}{T}\right) \int_0^1 d\rho \int_{-\infty}^{\infty} (u^2 + p^2 + \rho^2\kappa^2) G\, u\, du\, dp\, d\kappa$$

The term u^2 under the integral differs from the expression for J_1 merely by this extra factor u^2, which is easily seen to contribute $\frac{3}{2}T$. Hence

$$J_0 = \left(V + \frac{3}{2}T\right) J_1 - \frac{\varepsilon}{2}\left(\frac{\partial}{\partial x} + \frac{V'}{T}\right)$$

$$\times \int_0^1 d\rho \int_{-\infty}^{\infty} (p^2 + \rho^2\kappa^2 - \rho^4\kappa^2)^{1/2}\, dp\, d\kappa \int_{-\infty}^{\infty} u^2 F^{(0)}\, du$$

The integral can again be evaluated to give

$$\frac{1}{\pi}\int_0^1 \rho^2\, d\rho \int_{-\infty}^{\infty} (p^2 + \rho^2\kappa^2 - \rho^4\kappa^2)^{1/2}\, e^{-(p^2 + \rho^2\kappa^2)/2T}\, dp\, d\rho \cdot n = \frac{8}{3(2\pi)^{1/2}}\, T^{3/2} n$$

Collecting results, one obtains

$$J_0 = \left(V + \frac{3}{2}T\right) J_1 - \frac{4\varepsilon}{3(2\pi)^{1/2}}\left(\frac{\partial}{\partial x} + \frac{V'}{T}\right) T^{3/2} n$$

$$= (V + 2T) J_1 - \frac{4\varepsilon}{3(2\pi)^{1/2}}\, T^{1/2} n \frac{dT}{dx}$$

which was used in Section 4.

APPENDIX B

In order to find a solution of (13) for large γ one utilizes again the method for eliminating fast variables. In ref. 6 it was found that the first two orders are

$$R(x, v, t) = e^{-v^2/2T(x)} \left\{ f(x) + \frac{1}{\gamma(x)}\, g(x, t) \right.$$

$$\left. - \frac{1}{\gamma(x)} \left[\frac{v^3}{6} \frac{f}{T^2} \frac{dT}{dx} + v \left(\frac{f}{T} \frac{dV}{dx} + \frac{f}{T} \frac{dT}{dx} + \frac{df}{dx} \right) \right] \right\}$$

f is an arbitrary function of x and we do not need to know $g(x, t)$. Integrating on v, one sees

$$n(x, t) = [2\pi T(x)]^{1/2}\, [f(x) + \mathcal{O}(\gamma^{-1})] \tag{21}$$

The particle flow is

$$J_1(x,t)=\int vR(x,v,t)\,dv$$
$$=-\frac{1}{\gamma}(2\pi T)^{1/2}\left(fV'+\frac{3}{2}fT'+Tf'\right)$$

With the aid of (21) this reduces to (14). The energy flow can be computed in the same way,

$$J_0(x,t)=\int \left(\tfrac{1}{2}v^2+V\right)vR(x,v,t)\,dv$$
$$=VJ_1-\frac{1}{2\gamma}(2\pi T)^{1/2}\left(3fTV'+\frac{11}{2}fTT'+3T^2f'\right)$$

With the aid of (21) it reduces to (15).

APPENDIX C

Suppose $V'(x)>0$. The flow of particles consists of particles going from right to left and therefore downhill, and particles going to the right and therefore uphill. Each particle starts at a point x' and ends up in x. To describe the first contribution, take $x<x'$. The probability per unit time for a particle at x' to jump to x is

$$W(x\,|\,x')=c\{\exp[-\beta(x')\Phi]\}\;\alpha\Omega\sigma(x)\exp\left[-\alpha\Omega\int_x^{x'}\sigma(x'')\,dx''\right]\tag{22}$$

where $\beta(x)=1/T(x)$. For the second contribution one has $x>x'$ and

$$W(x\,|\,x')=c\exp\{-\beta(x')[\Phi+V(x)-V(x')]\}$$
$$\times\,\alpha\Omega\sigma(x)\exp\left[-\alpha\Omega\int_{x'}^{x}\sigma(x'')\,dx''\right]\tag{23}$$

The flow of particles past a given point x_0 is

$$J_1(x_0)=-\int_{x_0}^{\infty}dx'\int_{-\infty}^{x_0}dx\;W(x\,|\,x')\,n(x')$$
$$+\int_{-\infty}^{x_0}dx'\int_{x_0}^{\infty}dx\;W(x\,|\,x')\,n(x')\tag{24}$$

In the first integral, substitute (22), introduce the integration variables r, r' by setting $x' = x_0 + r'/\Omega$, $x = x_0 - r/\Omega$, and expand in $1/\Omega$:

$$-\frac{\alpha c}{\Omega}\int_0^\infty dr' \int_0^\infty dr\, e^{-\beta\Phi}\left(1-\frac{r'}{\Omega}\beta'\Phi\right)\left(\sigma-\frac{r}{\Omega}\sigma'\right)e^{-\alpha\sigma(r+r')}$$
$$\times\left(1-\alpha\sigma'\frac{r'^2-r^2}{2\Omega}\right)\left(n+\frac{r'}{\Omega}n'\right) \tag{25}$$

Here the argument of all functions is x_0. The result is

$$-\frac{c}{\Omega}e^{\beta\Phi}\left(\frac{n}{\alpha\sigma}-\frac{\beta'\Phi}{\alpha^2\Omega}\frac{n}{\sigma^2}-\frac{\sigma'}{\alpha^2\Omega}\frac{n}{\sigma^3}+\frac{n'}{\alpha^2\Omega\sigma^2}\right) \tag{26}$$

The second integral of (24) involves the transition probability (23) rather than (22). As a result there appears a new factor in (25), viz.

$$1-\frac{\beta}{\Omega}V'\cdot(r+r')$$

Accordingly, one obtains for the flow of particles moving to the right

$$+\frac{c}{\Omega}e^{-\beta\Phi}\left(\frac{n}{\alpha\sigma}+\frac{\beta'\Phi}{\alpha^2\Omega}\frac{n}{\sigma^2}-2\frac{\beta n}{\alpha^2\Omega\sigma^2}V'+\frac{n\sigma'}{\alpha^2\Omega\sigma^3}-\frac{n'}{\alpha^2\Omega\sigma^2}\right) \tag{27}$$

The net result is

$$J_1=\frac{2c}{\alpha^2\Omega^2}e^{-\beta\Phi}\left(\frac{n\Phi}{\sigma^2}\beta'-\frac{n\beta}{\sigma^2}V'-\frac{1}{\sigma}\frac{d}{dx}\frac{n}{\sigma}\right)$$

This is the same as (17): we have rederived the result of ref. 10 in a different manner.

To compute the energy flow, we note that a particle excited at x' and hopping to $x < x'$ carries the energy $V(x')$. Hence the energy flow represented by the particles that hop to the left is

$$-\int_{x_0}^\infty dx' \int_{-\infty}^{x_0} dx\, W(x\,|\,x')\,n(x')\,V(x')$$

As a consequence, one obtains (25) supplemented with a new factor

$$V(x_0)+\frac{r'}{\Omega}V'(x_0)$$

That has the effect on (26) that it is multiplied with $V(x_0)$ and, moreover, a new term is added

$$-\frac{c}{\alpha^2\Omega^2} e^{-\beta\Phi} \frac{n}{\sigma^2} V'(x_0) \tag{28}$$

A particle, however, that hops from x' to $x > x'$ has collected the energy $V(x)$. Hence the particles moving to the right contribute to the energy flow at x_0,

$$+\int_{-\infty}^{x_0} dx' \int_{x_0}^{\infty} dx\, W(x|x')\, n(x')\, V(x)$$

Again it has the effect of multiplying (27) with the factor $V(x_0)$ and adding a new term

$$+\frac{c}{\alpha^2\Omega^2} e^{-\beta\Phi} \frac{n}{\sigma^2} V'(x_0)$$

This cancels the contribution (28), so that the total energy flow is precisely equal to the particle flow times $V(x_0)$,as announced in (18).

It may be objected that a particle that is excited out of its pit does not acquire the exact amount of energy needed, but may have any amount larger than this threshold value. The average excess energy is known from the barometric formula to be $(d/2)T$. One thus finds, rather than (18),

$$J_0 = \left(V + \frac{d}{2} T\right) J_1 \tag{29}$$

However, one then also has to add to μ a kinetic energy term as in (4). With these two modifications one finds again that Onsager is obeyed.

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