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Heat fluctuation distribution from non-equilibrium states

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Abstract. A non-equilibrium state is described by parameters $\alpha_j = \langle A_j \rangle$ which are ensemble averages of dynamical phase functions $A_j(\Gamma)$. By using a projection operator technique of Zwanzig, one can derive from the classical Liouville equation an integro-differential equation for $g(\{v_j\})$, the amplitude for the probability that the A_j have respective values v_j. These previously derived results are applied to the heat flux $\boldsymbol{A}_J$ in a fluid and an approximate differential equation derived for $g(\boldsymbol{v}-\boldsymbol{J})$, where $\boldsymbol{J} = \langle \boldsymbol{A}_J \rangle$. The first moment of this equation yields the Cattaneo–Vernotte equation with a set of auxiliary assumptions which are also employed in solving the equation for g. We obtain $g = g^{(0)}[1 + G(\boldsymbol{v}-\boldsymbol{J})]$, where $g^{(0)} = (\kappa/\pi\mu)^{3/2} \exp[-\mu(\boldsymbol{v}-\boldsymbol{J})^2/\kappa]$ is the Einstein distribution, and G is a sum of products of scalar combinations of $\boldsymbol{J}$, $\boldsymbol{v}-\boldsymbol{J}$, and ∇T and Laguerre polynomials $L_n^{(1/2)}(z^2)$, where $\boldsymbol{z} \equiv (\mu/\kappa)^{1/2}(\boldsymbol{v}-\boldsymbol{J})$. The Einstein distribution $g^{(0)}$ gives correctly $\langle v^2 \rangle$ to $\mathrm{O}(J^2)$ when $\nabla T = 0$ but not in the presence of a temperature gradient.

1. Introduction

It was shown by Zwanzig (1960, 1961) that by operating with a projection operator on f, the phase space distribution which obeys the classical Liouville equation, one can obtain a distribution function for values of a set $\{A_j(x)\}$ of dynamical functions whose averages $\alpha_j = \int f A_j(x)\,\mathrm{d}x$ are the macroscopic variables appropriate to a given non-equilibrium thermodynamic description. Thus if

$$W(A) \equiv \int \delta(A(x') - A(x))\,\mathrm{d}x' \tag{1a}$$

$$\delta(A' - A) \equiv \prod_j \delta(A'_j - A_j) \tag{1b}$$

$$Pf \equiv W(A)^{-1} \int f(x')\delta(A(x) - A(x'))\,\mathrm{d}x' \tag{1c}$$

then

$$g(v) = W(v)Pf|_{A=v} \tag{2}$$

gives the amplitude for the probability that the set A has values within dv of v. An equation for g can be derived by operating with P on the Liouville equation, and from the first moments of the equation for g one gets the macroscopic phenomenological equations of non-equilibrium thermodynamics obeyed by the set $\{\alpha_j\}$, with coefficients which, at least in the linear case, exhibit Onsager–Casimir symmetry. By relaxing an approximation of Zwanzig (1961) who took g to be perfectly sharp, it was possible (Nettleton 1964) to extend these results to the case where the variables include

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$\dot{A}_j \equiv \mathrm{i}LA_j$, with L the self-adjoint Liouville operator, so that the phenomenological equations exhibit inertial terms and, in particular, to include the case where the heat flux, $\boldsymbol{J}$, is one of the thermodynamic state variables. In the present paper, our aim is to specialise these earlier results to derive the equation obeyed by the distribution g of fluctuations in the heat flux about the average value $\boldsymbol{J}$ in a non-equilibrium ensemble. By solving this equation, we can show that the Einstein expression, $g \sim \exp \delta^2 S/\kappa$, where $\delta^2 S$ is the second-order fluctuation of the entropy and κ = Boltzmann's constant, should give the heat flux correlation in the absence of a temperature gradient. When $\nabla T \neq 0$, as in a steady, non-equilibrium state, the Einstein function does not give the non-equilibrium corrections to the correlation function. This conclusion agrees with a calculation (Jou and Careta 1982) based on a kinetic theory Boltzmann equation.

To derive an equation for g, we first specify the system to be a cube of side $l \sim 10^{-4}$ cm immersed in an infinite fluid. The thermodynamic state variables can be taken to be mass density ρ, temperature T, and heat flux $\boldsymbol{J}$. The latter obeys (Cattaneo 1958, Vernotte 1958)

$$\partial \boldsymbol{J}/\partial t = -2\mu L\boldsymbol{J} - \gamma \nabla T \tag{3}$$

where L is a phenomenological coefficient, and the entropy $S = S_0(\rho, T) - \mu J^2$. μ, γ, and L are functions of ρ and T. Equation (3) expresses the flux $\partial \boldsymbol{J}/\partial t$ in terms of the thermodynamic forces, $-2\mu\boldsymbol{J}$ and $-T^{-1}\nabla T$, conjugate to $\dot{\boldsymbol{J}}$ and $\boldsymbol{J}$, respectively (Nettleton 1960). The relaxation described by the first term on the right in equation (3) is very rapid (Jou *et al* 1981), and this should be calculable from a model assuming a closed system, since it arises from irreversible processes within the system. We can thus calculate the contribution of these processes to the equation for g from a model appropriate to a closed system (Zwanzig 1961, Nettleton 1964). The fluid surrounding the cube of volume l^3, selected for discussion, constitutes a heat bath coupled to the system by a term which, in the first approximation, is linear in ∇T. This term, if held constant, produces an eventual steady state with $\boldsymbol{J} = -\lambda \nabla T$.

We shall suppose that ρ, T are known with high precision and calculate the distribution $g(\boldsymbol{v})$ for fluctuations in the dynamical heat flux operator $\boldsymbol{A}_J(P, Q)$ which is a function of the particle coordinates and momenta, given that the ensemble average of $\boldsymbol{A}_J$ is $\boldsymbol{J}$, i.e.

$$\boldsymbol{J} = \int f\boldsymbol{A}_J \, \mathrm{d}\Gamma = \int g(\boldsymbol{v})\boldsymbol{v} \, \mathrm{d}\boldsymbol{v}. \tag{4}$$

Thus $\delta(\boldsymbol{A}_J - \boldsymbol{v})$ is the only Dirac delta used in defining the projection operator P in equations (1), (2). Operating with this projection operator, P, on the Liouville equation, we have (Zwanzig 1961, equations (27) and (31), Nettleton 1964, equations (8) and (31)) the Fokker–Planck-type equation:

$$\partial g/\partial t = -\nabla_{\boldsymbol{v}} \cdot (\boldsymbol{q}g) + \int_0^t \mathrm{d}s \, \nabla_{\boldsymbol{v}} \cdot \{W(\boldsymbol{v})D(\boldsymbol{v}, s)\nabla_{\boldsymbol{v}}[g(v, t-s)\, W(v)^{-1}]\} + \gamma \nabla_{\boldsymbol{v}} g \cdot \nabla T \tag{5}$$

where (cf Grabert 1982)

$$\boldsymbol{q} \equiv W(v)^{-1} \int \dot{\boldsymbol{A}}_J \delta(\boldsymbol{A}_J - \boldsymbol{v}) \, \mathrm{d}\Gamma \tag{6a}$$

$$D_{\alpha\beta} = D\delta_{\alpha\beta} = W(\boldsymbol{v})^{-1} \int \delta(\boldsymbol{A}_J - \boldsymbol{v})(\dot{\boldsymbol{A}}_J - \boldsymbol{q})_\alpha \, \mathrm{e}^{-\mathrm{i}sL}(\dot{\boldsymbol{A}}_J - \boldsymbol{q})_\beta \, \mathrm{d}\Gamma \tag{6b}$$

the integrals being taken over phase space. The first three terms in equation (5), on multiplication by $\boldsymbol{v}$ and integration over $\boldsymbol{v}$-space, give rise to the first two terms in equation (3) (Nettleton 1964, equation (16)), and the last term in equation (5), which arises from coupling the system to the surrounding fluid acting as a set of heat reservoirs, leads to the term $-\gamma\nabla T$ in equation (3). A detailed discussion of this coupling, for the case of a gas, with evaluation of γ, is given in the appendix.

To obtain the phenomenological equation (3) of extended irreversible thermodynamics, certain additional assumptions (Nettleton 1964) were required to extract these results.

(1) Terms of third or higher order in A or $\dot{A}$ are neglected in comparison with second-order terms. This was invoked to justify the dropping of contributions from $\boldsymbol{q}$. For the case of a heat flux, we shall show in § 2 that $\boldsymbol{q}=0$.

(2) $\nabla_v \kappa \ln W = -2\mu\boldsymbol{v}$. This assumption is in the spirit of the Zwanzig approach in which Dirac deltas represent distributions which, in practice, would not be perfectly sharp. Thus $\kappa \ln W$, which is the entropy of a system microcanonically distributed in a shell defined by $\boldsymbol{A}_J=\boldsymbol{v}$, should be approximately the entropy when $\boldsymbol{A}_J$ can fluctuate narrowly.

(3) $g=g^{(0)}\,[1+G(\boldsymbol{v}-\boldsymbol{J})]$ where $g^{(0)}$ is $\exp(\delta^2 S/\kappa)$ is the Einstein approximation with $\delta^2 S = \mathrm{O}((\boldsymbol{v}-\boldsymbol{J})^2)$, and $G(\boldsymbol{v}-\boldsymbol{J})$ is of second order or higher in its arguments. In the present paper, we calculate G in the presence of an externally imposed temperature gradient, which was absent in the earlier work (Nettleton 1964) which referred to a closed system. This is done by solving equation (5) in a perturbation expansion which starts with $g^{(0)}$, for consistency with the earlier derivation of the phenomenological equations.

(4) We make a Markovian approximation and replace $g(t-s)\to g(t)$ in equation (5). Otherwise, we should have to introduce higher-order time derivatives as independent variables or, alternatively, replace equation (3) with an integro-differential equation.

(5) We set $L\equiv \kappa^{-1}\int_0^t \mathrm{d}s \int \mathrm{d}\boldsymbol{v}\, g^{(0)}\, D(\boldsymbol{v},s) \cong \kappa^{-1}\int_0^t \mathrm{d}s D(\boldsymbol{v},s) = \text{constant}$.

Thus there is assumed to be a time t sufficiently short so that the inertial term in equation (3) is significant yet sufficiently long so that the correlation function defining D may be taken to be time independent. The explicit $\boldsymbol{v}$-dependence of D may be neglected in the first approximation if $g^{(0)}$ is very sharply peaked about $\boldsymbol{v}=0$ (μ very large).

Applying the last two of these assumptions to equation (5), we reduce it in § 2 to a solvable differential equation for $g(\boldsymbol{v})$. This is solved in § 3 with an ansatz corresponding to assumption (3) and use of assumption (2). The solution depends on ∇T in such a way that when we calculate $\langle v^2\rangle$ in § 4, we get terms in the temperature gradient which are not predicted by the Einstein function, $g^{(0)}$. The latter, therefore, does not give the non-equilibrium contributions to the correlation functions when the system is coupled to external reservoirs and, in particular, when the fluctuations are defined with respect to a steady state.

2. Fokker–Planck equation for $g(\boldsymbol{v})$

To reduce equation (5) to a solvable form, we must evaluate $\boldsymbol{q}$ and investigate the

$\boldsymbol{v}$-dependence of $D(\boldsymbol{v}, s)$. For the discussion of q, we use

$$l^3\boldsymbol{A}_J = \sum_i \frac{p_i^2}{2m}\frac{\boldsymbol{p}_i}{m} + \tfrac{1}{2}\sum_{i\neq j}(\phi_{ij}\boldsymbol{\delta} + \boldsymbol{r}_{ij}\boldsymbol{F}_{ij})\cdot\frac{\boldsymbol{p}_i}{m} - h\sum_i\frac{\boldsymbol{p}_i}{m} \tag{7}$$

where ϕ_{ij} is pairwise potential for the interaction of particles at $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ with separation $\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$, $\boldsymbol{F}_{ij} = -\nabla_{ri}\phi_{ij}$ and h is the enthalpy per particle. $\boldsymbol{\delta}$ is the unit tensor. From $\boldsymbol{A}_J$, we compute

$$\begin{aligned} l^3\dot{\boldsymbol{A}}_J &= -l^3\sum_i\left(\dot{\boldsymbol{p}}_i\cdot\nabla_{\boldsymbol{p}_i}\boldsymbol{A}_J + \frac{\boldsymbol{p}_i}{m}\cdot\nabla_{\boldsymbol{r}_i}\boldsymbol{A}_J\right) \\ &= -\sum_{k\neq i}\boldsymbol{F}_{ik}\cdot\left(m^{-2}\boldsymbol{p}_i\boldsymbol{p}_i + [(p_i^2/2m^2) - h]\boldsymbol{\delta} + (2m)^{-1}\sum_{j\neq i}[\phi_{ij}\boldsymbol{\delta} + \boldsymbol{r}_{ij}\boldsymbol{F}_{ij}]\right) \\ &\quad + (4m^2)^{-1}\sum_{j\neq i}(\boldsymbol{p}_i - \boldsymbol{p}_j)\cdot\left(\boldsymbol{F}_{ij}\boldsymbol{\delta} + \boldsymbol{\delta}\boldsymbol{F}_{ij} + \boldsymbol{r}_{ij}\cdot\frac{\delta}{\delta\boldsymbol{r}_{ij}}\boldsymbol{F}_{ij}\right)\cdot(\boldsymbol{p}_i + \boldsymbol{p}_j). \end{aligned} \tag{8}$$

From equation (7) we see that $\boldsymbol{A}_J$ is invariant under interchange of any pair $\boldsymbol{r}_i \leftrightarrow \boldsymbol{r}_j$, whereas for each term in $\dot{\boldsymbol{A}}_J$ there is a pair whose interchange produces a change of sign. Since the configuration coordinates are integration variables in equation (6*a*), the integral will vanish if the integrand is odd with respect to interchange of a pair, and so $\boldsymbol{q} = 0$.

Similar reasoning may be used to evaluate $\nabla_{\boldsymbol{v}}[W\int_0^t D\,\mathrm{d}s]$ in equation (5). We have

$$\begin{aligned} \sum_\alpha\frac{\partial}{\partial v_\alpha}\left[W\int_0^t D_{\alpha\beta}\,\mathrm{d}s\right] &= -\int_0^t \mathrm{i}L\delta(\boldsymbol{A}_J - \boldsymbol{v})\,\mathrm{e}^{-\mathrm{i}sL}\dot{\boldsymbol{A}}_{J\beta}\,\mathrm{d}\Gamma \\ &= \int_0^t \mathrm{d}s\frac{\partial}{\partial s}\int\delta(\boldsymbol{A}_J - \boldsymbol{v})\,\mathrm{e}^{-\mathrm{i}sL}\,\dot{\boldsymbol{A}}_{J\beta}\,\mathrm{d}\Gamma \\ &= -Wq_\beta + \int\delta(\boldsymbol{A}_J - \boldsymbol{v})\,\mathrm{e}^{-\mathrm{i}sL}\dot{\boldsymbol{A}}_{J\beta}\,\mathrm{d}\Gamma \\ &= \int\delta(\boldsymbol{A}_J(\Gamma) - \boldsymbol{v})\dot{\boldsymbol{A}}_{J\beta}(\Gamma_{-t})\,\mathrm{d}\Gamma \end{aligned} \tag{9}$$

where Γ_{-t} is the phase at $-t$ which evolves into Γ at $t = 0$. Now if we interchange labels $i \leftrightarrow j$ in a configuration coordinate pair at $t = 0$, leaving all other coordinates and all momenta unchanged, this will interchange the same pair of configuration coordinates at $-t$ and thus the sign $\dot{\boldsymbol{A}}_J$. Accordingly the integral in equation (9) vanishes like the integral defining $\boldsymbol{q}$.

With the foregoing results and assumption (5) of the preceding section, we reduce equation (5) to the form:

$$\partial g/\partial t = \kappa LW(\boldsymbol{v})\nabla_v^2(g/W) + \gamma\nabla_v g\cdot\nabla T. \tag{10}$$

We seek a solution to this equation of the form

$$g(\boldsymbol{z}) = g^{(0)}(1 + G(\boldsymbol{z})) \tag{11a}$$

$$g^{(0)}(\boldsymbol{z}) = \pi^{-3/2}\exp(-z^2) \tag{11b}$$

where $\boldsymbol{z} \equiv (\mu/\kappa)^{1/2}(\boldsymbol{v}-\boldsymbol{J})$, and

$$\int g^{(0)} G \, \mathrm{d}\boldsymbol{z} = 0 = g^{(0)} \boldsymbol{z} G \, \mathrm{d}\boldsymbol{z}. \tag{12}$$

This form of $g^{(0)}$ is chosen (Nettleton 1964) to yield the phenomenological equation (3) from the first moment of equation (5), and the conditions (12) preserve the normalisation and the requirement that $\langle A_J \rangle = \boldsymbol{J}$.

3. Solution for the distribution function

We can solve equation (10) with an ansatz, consistent with equations (11) and (12), of the form:

$$\begin{aligned} G(\boldsymbol{z}) = {} & a_2 J^2 L_2^{(1/2)}(z^2) + a_3 \boldsymbol{J} \cdot \boldsymbol{z} L_2^{(1/2)}(z^2) + b_1 (\nabla T)^2 L_1^{(1/2)}(z^2) \\ & + b_2 \boldsymbol{J} \cdot \nabla T L_1^{(1/2)}(z^2) + b_3 \boldsymbol{z} \cdot \nabla T L_2^{(1/2)}(z^2) + \ldots . \end{aligned} \tag{13}$$

Here the $L_i^{(1/2)}(x)$ are generalised Laguerre polynomials of degree i in x, defined by

$$L_n^{(\alpha)}(x) = \sum_{m=0}^{n} (-x)^m \binom{n+\alpha}{n-m} (m!)^{-1}. \tag{14}$$

The polynomials appearing in equation (13) are the lowest order for which the constant coefficients, a_j and b_j, can be determined uniquely from equation (10). The ellipsis signifies additional terms involving Laguerre polynomials of higher order. This choice of polynomials automatically satisfies equation (12).

If we substitute the ansatz determined by equations (11*a*, *b*) and (13) into equation (10) and use equation (3) to calculate $\partial \boldsymbol{J}/\partial t$, we have:

$$\begin{aligned} \partial g/\partial t = {} & \tfrac{3}{2}\gamma g (\nabla T)^2 [\tfrac{5}{4}(\mu/\kappa)^{1/2} b_3 - b_2] \\ & + \tfrac{3}{2} g \boldsymbol{J} \cdot \nabla T [\mu L (\tfrac{5}{2} b_3 \sqrt{\mu/\kappa} - 2 b_2) + \tfrac{5}{4}\gamma (a_3 \sqrt{\mu/\kappa} - 2 a_2)] \\ & - \gamma g \boldsymbol{z} \cdot \nabla T [2(\mu/\kappa)^{1/2} + \tfrac{15}{8} a_3] + \ldots . \end{aligned} \tag{15}$$

This expression is to be compared term-by-term with a result of similar form obtained by substituting the ansatz (13) into the right-hand member of equation (10). To evaluate the latter, we need assumption (2) listed in § 1 to give the explicit $\boldsymbol{v}$-dependence of ln W. Comparing in turn the coefficients of $\boldsymbol{J} \cdot \nabla T$, $\boldsymbol{z} \cdot \nabla T$, and $(\nabla T)^2$, we get, respectively:

$$\tfrac{5}{4}\gamma a_2 - \mu L b_2 - \tfrac{5}{4}\mu L (\mu/\kappa)^{1/2} b_3 = 0 \tag{16a}$$

$$b_3 = \tfrac{3}{40}(\gamma/\mu L) a_3 \qquad b_1 = \tfrac{1}{4}(\gamma/\mu L) b_2. \tag{16b, c}$$

These equations determine the b_i in terms of a_2 and a_3. By equating coefficients of J^2 and $\boldsymbol{J} \cdot \boldsymbol{z}$ in $\partial g/\partial t$ and in $\kappa L W \nabla_v^2 (g/W)$, we obtain

$$a_2 = \tfrac{2792}{4335} \mu/\kappa \qquad a_3 = \tfrac{16}{85} (\mu/\kappa)^{1/2}. \tag{17}$$

Substitution into equations (16) yields

$$b_2 = \tfrac{116059}{147390} \gamma/L\kappa \qquad b_3 = \tfrac{6}{425}(\gamma/\mu L)(\mu/\kappa)^{1/2}. \tag{18}$$

These coefficients are affected by the truncation to Laguerre polynomials of lowest order and we should expect their numerical values to be altered in a higher approximation.

4. Discussion and calculation of correlation functions

The calculation of the preceding section illustrates the fact that the Einstein function $g^{(0)}$ does not solve equation (10) to $O(v^2)$, even when $\nabla T = 0$. However, since $L_2^{(1/2)}(z^2)$ is orthogonal to z^2, we find that $g^{(0)}$ gives correctly the correlation function $\langle v^2 \rangle = (\kappa/\mu)\langle z^2 \rangle + J^2$ in the absence of a coupling of the system to external reservoirs represented by the temperature gradient in the present problem. When $\nabla T \neq 0$, there are corrections proportional to $(\nabla T)^2$ and $\boldsymbol{J} \cdot \nabla T$ which apply, in particular, to fluctuations from a non-equilibrium steady state in which $\boldsymbol{J} = -\lambda \nabla T$.

To obtain these corrections explicitly, we compute:

$$\begin{aligned}\langle v^2 \rangle &= J^2 + \frac{4\kappa}{\pi^{1/2}\mu} \int_0^\infty \mathrm{e}^{-z^2} z^4 \,\mathrm{d}z [1 + b_1 (\nabla T)^2 L_1^{(1/2)}(z^2) + b_2 \boldsymbol{J} \cdot \nabla T L_1^{(1/2)}(z^2)] \\ &= J^2 + 3\kappa/\mu - (3\kappa/2\mu)[b_1(\nabla T)^2 + b_2 \boldsymbol{J} \cdot \nabla T]. \qquad (19)\end{aligned}$$

In the steady state, $\boldsymbol{J} = -(\gamma/2\mu L)\nabla T$, so that

$$\begin{aligned}\langle (\boldsymbol{v} - \boldsymbol{J})^2 \rangle &= 3\kappa/\mu - (3\kappa/2\mu)(\nabla T)^2 [b_1 - (b_2\gamma/2\mu L)] \\ &= 3\kappa/\mu + \tfrac{3}{8}(\gamma/\mu L)^2 [\tfrac{698}{867} - \tfrac{3}{170}](\nabla T)^2. \qquad (20)\end{aligned}$$

In this way, we have been able to predict that the Einstein distribution, $\exp \delta^2 S/\kappa$, should be useful to describe fluctuations from a non-equilibrium state in a closed system but that it becomes inadequate when reservoirs are coupled which tend to induce a steady, non-equilibrium state. The distribution, $g(\boldsymbol{v})$ and correlations calculated from it will depend on variables, e.g. ∇T, which characterise the reservoirs and do not appear in the free energy (Lebon 1980). Because of the truncation which has restricted us to Laguerre polynomials of lowest order, the present approach will probably require considerable elaboration before it can yield reliable numerical values for correlation functions. Equation (20) should be expected to agree only as to sign and rough order-of-magnitude with expressions calculated by alternative methods (cf Jou and Careta 1982).

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Appendix

Having proposed the ∇T-term in equation (5) on the basis that it yields correctly the last term in equation (3), we proceed to derive this term for a moderately dilute gas for which $l^3 A_J = \Sigma_i [(p_i^2 p_{ix}/2m^2) - hp_{ix} m^{-1}]$, limiting ourselves for simplicity to heat flow in the x-direction. The fluid outside the system, for $\frac{1}{2}l < x < -\frac{1}{2}l$, is replaced by heat reservoirs at temperatures $T(\pm\frac{1}{2}l)$, where $T(x)$, the macroscopic temperature, is a continuous, differentiable function of x. Within the system, the temperature T is the mean kinetic energy of all the particles and does not vary microscopically from place to place.

On this model, the contribution to the equation for $g = W(v)Pf$ from the force $F(\boldsymbol{r}_i)$ on a gas particle at $\boldsymbol{r}_i$, caused by interaction with the reservoirs, is:

$$-\sum_i \int \delta(A_J - v)\nabla_{p_i} f \cdot \boldsymbol{F}(\boldsymbol{r}_i)\,\mathrm{d}\Gamma. \tag{A1}$$

In the absence of mass flow, we shall take the integral of f over all configuration coordinates save $\boldsymbol{r}_i$ to be independent of $\boldsymbol{r}_i$, i.e. $\bar{f}(P)$ which depends only on momenta. The integrand in equation (A1) is zero except when $\boldsymbol{r}_i$ is adjacent to a reservoir boundary. If there are n particles per unit volume adjacent to the boundary, $nF_x\,\mathrm{d}\boldsymbol{r} = \mp P_\pm \mathrm{d}\sigma$, where the upper sign refers to the reservoir at $x = \frac{1}{2}l$ and the lower to that at $x = -\frac{1}{2}l$, P being the pressure in the reservoir and $\mathrm{d}\sigma$ an element of area of the boundary. The integral in equation (A1) becomes after partial integration:

$$\pm\frac{1}{n}\frac{\partial}{\partial v}\sum_i \int \delta(A_J - v)\frac{\partial A_J}{\partial p_{ix}}\bar{f}P_\pm\,\mathrm{d}\boldsymbol{P}\,\mathrm{d}\sigma$$

$$= \pm\frac{1}{nl^3m}\frac{\partial}{\partial v}\int \delta(A_J - v)\left[\sum_i \frac{5}{6}\frac{p_i^2}{m} - Nh\right]\cdot \bar{f}P_\pm\,\mathrm{d}\boldsymbol{P}\,\mathrm{d}\sigma. \tag{A2}$$

In the first approximation, we propose to neglect fluctuations in kinetic energy and confine our attention to those in A_J. The integral in equation (A2) becomes

$$\pm(\tfrac{5}{2}\kappa T - h)(ml^3)^{-1}(\partial g/\partial v)P_\pm l^2. \tag{A3}$$

Combining the contributions from the two reservoirs, we obtain

$$(ml^3)^{-1}(\tfrac{5}{2}\kappa T - h)(\partial g/\partial v)[P(l/2) - P(-l/2)] = m^{-1}(\tfrac{5}{2}\kappa T - h)(\partial g/\partial v)(\partial P/\partial T)\partial T/\partial x. \tag{A4}$$

On generalisation to three dimensions, equation (A4) has the form of the ∇T-term in equation (5).

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