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Technical Notes

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Statistical Mechanical Derivation of Cattaneo's Heat Flux Law

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Nomenclature

$A(t)$ = dynamical variable
c_v = specific heat capacity
D = self-diffusion constant
d = diameter of a single particle
$\mathrm{d}\boldsymbol{a}$ = differential element of area
E = total kinetic energy
$\hat{e}_l$ = unit vector
$f(\boldsymbol{v}, \boldsymbol{r}, t)$ = nonequilibrium distribution function
$f_L(\boldsymbol{v}, \boldsymbol{r}, t)$ = local equilibrium Maxwellian for a monoatomic gas:

$$n(\boldsymbol{r}, t)\left[\frac{m\beta(\boldsymbol{r}, t)}{2\pi}\right]^{\frac{3}{2}} \exp\left\{-\frac{m\beta(\boldsymbol{r}, t)}{2}[\boldsymbol{v} - \boldsymbol{u}(\boldsymbol{r}, t)]^2\right\}$$

$g(v)$ = general velocity dependent function
$\boldsymbol{J}(t)$ = heat flux
k_B = Boltzmann constant
ℓ = mean free path
m = particle's mass
N = total number of particles, pN_A
N_A = Avogadro's number
n = number density of particles
$\hat{\boldsymbol{n}}$ = unit vector
p = any integer
$\boldsymbol{r}$ = position vector
S = total surface of a right circular cylinder
S_1, S_2 = two equal circular cross sections of S
S_3 = curved surface of S
T = temperature
t = time
$\boldsymbol{u}$ = average velocity vector, $\langle \boldsymbol{v} \rangle$
$\boldsymbol{v}$ = particle's velocity
$\boldsymbol{v}_j$ = velocity of the jth particle
α = dimensionless number, $m(\delta v)^2/3k_B T$
β = $1/k_B T$
β^* = Eucken number, $3(1 - \alpha)$
γ = physical constant, $(1 - \alpha)\langle E \rangle/\Delta a$
Δ = variable's nonequilibrium instantaneous departure from its equilibrium value
$\Delta \boldsymbol{a}$ = total area, $\int_{S_1} \mathrm{d}\boldsymbol{a}$
δ = fluctuation in a variable
∂_t = derivative with respect to time, $\partial/\partial t$
ϵ = perturbation
θ = time as an integration variable
λ = thermal conductivity, $\beta^* \langle E \rangle u/2T\,\Delta a$
τ = relaxation time
$\langle\,\rangle_e$ = equilibrium ensemble average
$\langle\,\rangle$ = nonequilibrium ensemble average

Introduction

THE Fourier heat flux equation gives a parabolic energy equation that implies an infinite speed of heat propagation, and an infinite speed of heat propagation is physically unrealistic. The problem of finding a hyperbolic heat equation that yields a finite speed of heat propagation was first investigated by Cattaneo and later by Vernotte, as was discussed by Fulks and Guenther.[1] The parabolic and the hyperbolic heat equations have been widely discussed.[2] Cattaneo proposed a heat flux equation that relates the heat flux and its time derivative to the gradient of temperature. This proposition allowed him to derive a hyperbolic heat equation with finite signal speed. Cattaneo, however, did not present a proof of his heat flux equation, which one must have to obtain an equation that is physically plausible, namely, the hyperbolic heat equation. The hyperbolic heat equation was investigated by many others, for example, Fulks and Guenther,[1] Roetman,[3] Glass et al.,[4] and Glass and McRae.[5] The first attempt to investigate the derivation of Cattaneo's hyperbolic heat equation was due to Müller.[6] Later, the branch of thermodynamics called extended thermodynamics[7] was developed by Müller and Ruggeri. Their approach was axiomatic.

Another derivation of Cattaneo's hyperbolic heat equation is presented here. In deriving Cattaneo's heat flux equation, nonequilibrium statistical mechanics is applied. Such an approach is necessary because it presents a nonaxiomatic approach and demonstrates the process of heat propagation on a microscopic level. Because a near equilibrium state was assumed, the nonequilibrium distribution function used was local Maxwellian. Note that in this Note the calculations were done for a monoatomic gas and the Eucken number obtained was 2.547. The Eucken number obtained by the Chapman and Enskog equation (see Ref. 8) for a monoatomic gas is 2.5, which is close to the value obtained here. Experimentally, the Eucken number shows some dependence on temperature[9]; however, for inert gases it is close to the Chapman and Enskog number. For diatomic gases the Eucken number is smaller in value.[10]

Derivation of Cattaneo's Heat Flux

The Onsager hypothesis, which follows, will prove important in our derivation of Cattaneo's heat flux equation.[11] The relaxation of macroscopic nonequilibrium disturbances is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium system. The Onsager hypothesis is true for systems in near equilibrium. A system is said to be near equilibrium if the system's deviations from equilibrium are linearly related to the perturbations that remove the system from equilibrium.[11] In all of our calculations the system is assumed to be near equilibrium or in a local equilibrium state. A quantitative statement of the Onsager hypothesis would be as follows: Given $\langle A(t) \rangle$, $\delta A = A(t) - \langle A \rangle_e$, and $\langle \Delta A(t) \rangle = \langle A(t) \rangle - \langle A \rangle_e$, then $\langle \Delta A(t) \rangle = (\epsilon/k_B T)\langle \delta A(0)\delta A(t) \rangle_e$. When applied to the heat flux $\boldsymbol{J}(t)$, the preceding definitions will be $\langle \Delta \boldsymbol{J}(t) \rangle = \langle \boldsymbol{J}(t) \rangle - \langle \boldsymbol{J} \rangle_e$, with a perturbation $\epsilon \propto \nabla T$. Also, the fluctuations in $\boldsymbol{J}(t)$ will be given by $\delta \boldsymbol{J}(t) = \boldsymbol{J}(t) - \langle \boldsymbol{J} \rangle_e = (mv^2/2)\boldsymbol{v}$, and $\langle \boldsymbol{J} \rangle_e = 0$. Therefore,

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$$\langle \delta \boldsymbol{J}(0)\cdot \delta \boldsymbol{J}(t)\rangle_e = \left\langle \frac{mv(0)^2}{2}\boldsymbol{v}(0)\cdot \frac{mv(t)^2}{2}\boldsymbol{v}(t)\right\rangle_e$$

$$= \left(\frac{m}{2}\right)^2 \sum_{i=1}^{3}\left\langle v_i(0)^3 v_i(t)^3\right\rangle_e \leq \left(\frac{m}{2}\right)^2 \sum_{i}\langle v_i(0)v_i(t)\rangle_e^3$$

where isotropic correlations are assumed. Therefore, the corresponding equation for the Onsager hypothesis in the case of heat flux is

$$\langle \Delta \boldsymbol{J}(t)\rangle = \langle \boldsymbol{J}(t)\rangle = \beta\epsilon \sum_{l=1}^{3}\langle \delta \boldsymbol{J}(0)\cdot \delta \boldsymbol{J}(t)\rangle_e \frac{\hat{e}_l}{3}$$

$$\leq \beta\epsilon\left(\frac{m}{2}\right)^2 \sum_{l=1}^{3}\sum_{i=1}^{3}\langle v_i(0)v_i(t)\rangle_e^3 \frac{\hat{e}_l}{3} \tag{1}$$

which is true $\forall t$. Here $\lim_{t\to\infty}\langle v_i(0)v_i(t)\rangle_e = 0$ (Ref. 11), and for long times the behavior is given by $\langle v_i(0)v_i(t)\rangle_e \to (1/t)^{3/2}$; in other words, $\langle J\rangle$ decays to zero as time goes to infinity,[12] which is consistent with the time dependence of the temperature in the hyperbolic heat equation.

Now consider the following conservation of energy equation:

$$\int_0^t \mathrm{d}\theta \oint_S \boldsymbol{J}(\boldsymbol{v},\theta)\cdot \mathrm{d}\boldsymbol{a} = -E(v) \tag{2}$$

with $v = |\boldsymbol{v}|$. The theorem in Eq. (2) applies to an arbitrary surface; therefore, any surface can be chosen to apply the theorem [Eq. (2)] to it. Therefore, if $S = S_1 + S_2 + S_3$, then

$$\oint_S \boldsymbol{J}(\boldsymbol{v},\theta)\cdot \mathrm{d}\boldsymbol{a} = \int_{S_1}\boldsymbol{J}(\boldsymbol{v},\theta)\cdot \mathrm{d}\boldsymbol{a} + \int_{S_2}\boldsymbol{J}(\boldsymbol{v},\theta)\cdot \mathrm{d}\boldsymbol{a} + \int_{S_3}\boldsymbol{J}(\boldsymbol{v},\theta)\cdot \mathrm{d}\boldsymbol{a}$$

Choose $\boldsymbol{J} \perp \boldsymbol{S}_3$, so that the third integral vanishes. Also it is assumed that the N particles enclosed by S absorb all of the heat flux and exhibit it as kinetic energy. Therefore, what comes out of the surface S_2 is negligible; hence, we can let the second integral vanish. This result can also be achieved by considering an infinitely long cylinder. Then

$$\oint_S \boldsymbol{J}(\boldsymbol{v},\theta)\cdot \mathrm{d}\boldsymbol{a} = \int_{S_1}\boldsymbol{J}(\boldsymbol{v},\theta)\cdot \mathrm{d}\boldsymbol{a}$$

and because $\boldsymbol{J}$ is a function of $\boldsymbol{v}$ and θ, the conservation of energy equation is written as

$$\int_0^t \mathrm{d}\theta \boldsymbol{J}(\boldsymbol{v},\theta)\cdot \Delta\boldsymbol{a} = -E(v) \tag{3}$$

To be able to study the dynamics of the system of particles enclosed by the cylinder under consideration one must follow the time development of every particle, which is practically impossible. Therefore, statistical averages must be computed. For a general $g = g(v)$, the ensemble average is given by $\langle g(\boldsymbol{r},t)\rangle = \int d^3v g(v) f(\boldsymbol{v},\boldsymbol{r},t)/n(\boldsymbol{r},t)$. Taking the ensemble average of Eq. (3) will give

$$\int_0^t \mathrm{d}\theta \int d^3v \boldsymbol{J}(\boldsymbol{v},\theta) f(\boldsymbol{v},\boldsymbol{r},t)\cdot \frac{\Delta\boldsymbol{a}}{n}(\boldsymbol{r},t)$$

$$= -\int d^3v E(v)\frac{f(\boldsymbol{v},\boldsymbol{r},t)}{n(\boldsymbol{r},t)}$$

or

$$\int_0^t \mathrm{d}\theta \langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle \cdot \Delta\boldsymbol{a} = -\langle E(\boldsymbol{r},t)\rangle \tag{4}$$

Taking ∂_t of Eq. (4) will lead to

$$\int_0^t \mathrm{d}\theta\, \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle \cdot \Delta\boldsymbol{a} + \langle \boldsymbol{J}(\boldsymbol{r},t,t)\rangle \cdot \Delta\boldsymbol{a} = -\partial_t\langle E(\boldsymbol{r},t)\rangle \tag{5}$$

Now choose $t \ni$:

$$\int_t^\tau \mathrm{d}\theta\, \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle \ll \int_0^\tau \mathrm{d}\theta\, \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle \tag{6}$$

where $\tau = \beta m D$ (Ref. 11). For water molecules at 10°C the relaxation time is calculated to be $\tau = 765$ ps. The physical meaning of τ represents the time it takes for the diffusional regime to be reached and it is also the time it takes to reach equilibrium from a nonequilibrium state.[11] Equation (1) and the paper by Stillinger and Rahman[13] are used to justify the inequality in Eq. (6). The plot referred to in this Note is for water molecules at the temperature of 10°C (Ref. 13). The normalized velocity autocorrelation decays to 0.02 at about 1 ps. Because of Eq. (1), the same statement can be made about the heat flux. By squaring the normalized velocity autocorrelation, multiplying it by its time derivative, and integrating the product from 0.02 ps to 1 ps, we obtain the value −0.32. The same integration starting at 0.68 ps would give the value -3.3×10^{-7} for that integral. For any time after 0.68 ps, as the initial point of integration the value of the integral would be of the order 10^{-7}. Now, by observing the time integral of the time derivative of both sides of the inequality in Eq. (1), we can immediately see the justification of the approximation in Eq. (6). Also, the time t in Eq. (6) can be chosen to be in the neighborhood of 0.68 ps or any time after that. For higher temperatures, for example, above 200°C (Ref. 13), the normalized velocity autocorrelation decays even faster. Therefore, the inequality in Eq. (6) applies to gaseous states as well. The left-hand side in Eq. (5) is then written as

$$\left(\int_0^\tau \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle\,\mathrm{d}\theta - \int_t^\tau \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle\,\mathrm{d}\theta + \langle \boldsymbol{J}(\boldsymbol{r},t,t)\rangle\right)\cdot \Delta\boldsymbol{a}$$

$$= -\partial_t\langle E(\boldsymbol{r},t)\rangle \tag{7}$$

where

$$\int_0^\tau \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle\,\mathrm{d}\theta = \int_0^t \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle\,\mathrm{d}\theta + \int_t^\tau \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle\,\mathrm{d}\theta$$

By the use of the inequality in Eq. (6), Eq. (7) can be written as

$$\left(\int_0^\tau \partial_t\langle \boldsymbol{J}(\boldsymbol{r},\theta,t)\rangle\,\mathrm{d}\theta + \langle \boldsymbol{J}(\boldsymbol{r},t,t)\rangle\right)\cdot \Delta\boldsymbol{a} = -\partial_t\langle E(\boldsymbol{r},t)\rangle \tag{8}$$

Because near-equilibrium gaseous state is being assumed, we can evaluate the right-hand side using $f_L(\boldsymbol{v},\boldsymbol{r},t)$ (Ref. 8). Therefore, by the taking of the average using $f_L(\boldsymbol{v},\boldsymbol{r},t)$ and the taking of the time derivative of the average, the right-hand side of Eq. (8) will become

$$\partial_t\langle E(\boldsymbol{r},t)\rangle = \left\langle E(v)\tfrac{3}{2}(m/2\pi)(2\pi/m\beta)\partial_t\beta\right\rangle$$

$$+ \langle \beta m E(v)[\boldsymbol{v}-\boldsymbol{u}(\boldsymbol{r},t)]\partial_t\boldsymbol{u}\rangle - \langle E(v)(m/2)[\boldsymbol{v}-\boldsymbol{u}(\boldsymbol{r},t)]^2\partial_t\beta\rangle \tag{9}$$

However, at local equilibrium Euler equations hold[8] and the Euler equation for the evolution of the temperature T is given by $\partial_t T = -\boldsymbol{u}\cdot\nabla T - 2T(\nabla\cdot\boldsymbol{u})/3$, which will give us

$$\partial_t\beta = \left(1/k_B T^2\right)\boldsymbol{u}\cdot\nabla T + \left(1/k_B T^2\right)\tfrac{2}{3}T\nabla\cdot\boldsymbol{u} \tag{10}$$

A direct substitution of Eq. (10) into Eq. (9) would give

$$\partial_t\langle E(\boldsymbol{r},t)\rangle = \left\langle E(v)\frac{3}{2}\frac{\boldsymbol{u}\cdot\nabla T}{T} + E(v)\nabla\cdot\boldsymbol{u}\right\rangle$$

$$+ \frac{m}{k_B T}\langle E(v)\,[\boldsymbol{v}-\boldsymbol{u}(\boldsymbol{r},t)]\rangle(\partial_t\boldsymbol{u})$$

$$- \frac{m}{2k_B T^2}\langle E(v)\,[\boldsymbol{v}-\boldsymbol{u}(\boldsymbol{r},t)]^2\rangle\left(\boldsymbol{u}\cdot\nabla T + \frac{2}{3}T\nabla\cdot\boldsymbol{u}\right) \tag{11}$$