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Derivation of Heat-Flux Dependence on Pressure Gradient

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Nomenclature

$E(\mathbf{r}, t)$	=	total energy
$f(\mathbf{r}, \mathbf{v}, t)$	=	local equilibrium Maxwellian
$\mathbf{J}_E(\mathbf{r}, t)$	=	average heat-flux vector
k_B	=	Boltzmann constant
$P^{(\tilde{N})}$	=	\tilde{N} particle specific distribution function
$p(\mathbf{r}, t)$	=	pressure
\mathbf{r}	=	position vector
$T(\mathbf{r}, t)$	=	temperature
t	=	time
\mathbf{v}	=	microscopic velocity
Δa	=	an element of area
$\rho(\mathbf{r}, t)$	=	mass density

Introduction

IN the derivation of Cattaneo's heat-flux law that was presented before,^{1–3} some steps were approximations, which were done for the purpose of demonstrating the salient feature of the heat-flux law that results from energy dynamics considerations. For example, the equalities $\langle E\mathbf{v} \rangle = \langle E \rangle \langle \mathbf{v} \rangle$ and $\langle E v^2 \rangle = \langle E \rangle \langle v^2 \rangle$ were used, and the extra terms on the right-hand side of the preceding equalities were not included in the final result. Moreover, the distribution function needed to be the constant $[1 - (8/3\pi)]$ multiplied by the local Maxwellian in order for the Eucken number to be close to the value 2.5, and the gas needed to have an overall speed that is higher than the sonic speed. The purpose of this Note is to show that when the extra terms are included then one would recover the preceding result with an additional term, which is the pressure gradient. Also, the consistency of the energy equation presented before¹ with the energy equation in transport phenomenon is explained here. It is shown that under certain conditions the heat-flux law will depend simultaneously on temperature and pressure gradients. The heat flow dependence on pressure gradient was suggested by Truesdell and Toupin

and Chapman and Cowling, as was discussed by Roetman.⁴ This dependence helps deriving a hyperbolic heat equation, which is the needed equation for heat conduction with finite signal time.

Statistical Mechanical Derivation of the Pressure Gradient Term

To derive the constitutive heat-flux law, which includes the relaxation time from the principles of energy transport, one needs to consider the following relations:

$$\mathbf{J}_E(\mathbf{r}, t) = \frac{1}{2} \rho(\mathbf{r}, t) \langle v^2 \mathbf{v} \rangle = \frac{1}{2} \rho(\mathbf{r}, t) \frac{\int d^3 v f(\mathbf{r}, \mathbf{v}, t) v^2 \mathbf{v}}{n(\mathbf{r}, t)} \quad (1)$$

$$\rho_E(\mathbf{r}, t) = \frac{1}{2} \rho(\mathbf{r}, t) \langle v^2 \rangle = \frac{1}{2} \rho(\mathbf{r}, t) \frac{\int d^3 v f(\mathbf{r}, \mathbf{v}, t) v^2}{n(\mathbf{r}, t)} \quad (2)$$

where $\rho(\mathbf{r}, t) = mn(\mathbf{r}, t)$, $n(\mathbf{r}, t) = \int d^3 v f(\mathbf{r}, \mathbf{v}, t)$ is the number density and m is the mass of the microscopic particle. In the absence of external forces and when there are no interactions between the particles of the gas, as in point particles, the energy conservation law in a fixed frame is given by⁵

$$\frac{\partial \rho_E(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{J}_E(\mathbf{r}, t) \quad (3)$$

which when Eqs. (1) and (2) are substituted into will give

$$\begin{aligned} \int d^3 v \left\{ \frac{\rho(\mathbf{r}, t) v^2}{2} \frac{\partial}{\partial t} \left[\frac{f(\mathbf{r}, \mathbf{v}, t)}{n(\mathbf{r}, t)} \right] + \frac{\rho(\mathbf{r}, t) v^2}{2} \mathbf{v} \cdot \nabla \left[\frac{f(\mathbf{r}, \mathbf{v}, t)}{n(\mathbf{r}, t)} \right] \right\} \\ + \int d^3 v \frac{f(\mathbf{r}, \mathbf{v}, t)}{n(\mathbf{r}, t)} \frac{\partial}{\partial t} \left[\frac{\rho(\mathbf{r}, t) v^2}{2} \right] \\ = - \int d^3 v \frac{f(\mathbf{r}, \mathbf{v}, t)}{n(\mathbf{r}, t)} \nabla \cdot \left[\frac{\rho(\mathbf{r}, t) v^2 \mathbf{v}}{2} \right] \end{aligned} \quad (4)$$

The Liouville equation is given by⁵

$$\frac{\partial P^{(\tilde{N})}}{\partial t} + \mathbf{V} \cdot \nabla P^{(\tilde{N})} = 0 \quad (5)$$

where $\mathbf{V} = (\dot{\mathbf{r}}_1, \dot{\mathbf{r}}_2, \dots, \dot{\mathbf{r}}_{\tilde{N}}; \dot{\mathbf{p}}_1, \dot{\mathbf{p}}_2, \dots, \dot{\mathbf{p}}_{\tilde{N}})$ is the phase space velocity. Integrating Eq. (5) with respect to all of the phase space coordinates except the position \mathbf{r}_1 and the momentum \mathbf{p}_1 and assuming the absence of both pair potentials responsible for internal forces and the one particle potentials responsible for external forces will give

$$\frac{\partial P^{(1)}}{\partial t} + \mathbf{V} \cdot \nabla P^{(1)} = 0 \quad (6)$$

where $P^{(1)} = P^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t)$. But $P^{(1)} = f^{(1)}/\tilde{N}$, with $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$ being the generic distribution function.⁶ The replacement of the distribution function in phase space by the distribution function in coordinate-velocity space in Eq. (6) will lead to

$$\frac{\partial}{\partial t} \left(\frac{f}{\tilde{N}} \right) + \mathbf{v} \cdot \nabla \left(\frac{f}{\tilde{N}} \right) = 0 \quad (7)$$

If one is to consider averaging over a finite volume element δV , then that would correspond to reducing the sample space over which the averaging is done. Moreover, δV can be chosen small enough such that $f(\mathbf{r}, \mathbf{v}, t)$ is constant over δV . Hence, Eq. (7) must be true only for the total number of particles in δV , in which case avoiding overcounting can be accomplished by dividing f by the total number of particles in δV only. The volume δV should be chosen such that it is a very large volume for molecular dimensions yet a very small volume for the macroscopic dimensions of the gas. Now $\tilde{N} = \int_V d^3 r \int d^3 v f(\mathbf{r}, \mathbf{v}, t) = \int_V d^3 r n(\mathbf{r}, t)$ is the total number of particles in the entire gas. Therefore,

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$N = \int_{\delta V} d^3r n(\mathbf{r}, t) = \delta V n(\mathbf{r}, t)$ is the total number of particles in δV , which along with Eq. (7) will give

$$\frac{\partial}{\partial t} \left(\frac{f}{N} \right) + \mathbf{v} \cdot \nabla \left(\frac{f}{N} \right) = \frac{1}{\delta V} \frac{\partial}{\partial t} \left(\frac{f}{n} \right) + \frac{1}{\delta V} \mathbf{v} \cdot \nabla \left(\frac{f}{n} \right) = 0 \quad (8)$$

or

$$\frac{\partial}{\partial t} \left(\frac{f}{n} \right) + \mathbf{v} \cdot \nabla \left(\frac{f}{n} \right) = 0 \quad (9)$$

Equation (9) will reduce Eq. (4) to

$$\int d^3v \left(\frac{f}{n} \right) \frac{\partial}{\partial t} \left[\frac{\rho(\mathbf{r}, t) v^2}{2} \right] = - \int d^3v \left(\frac{f}{n} \right) \nabla \cdot \left[\frac{\rho(\mathbf{r}, t) v^2 \mathbf{v}}{2} \right] \quad (10)$$

Assuming the validity of the equation

$$\frac{\partial}{\partial t} \left[\frac{\rho(\mathbf{r}, t) v^2}{2} \right] = - \nabla \cdot \left[\frac{\rho(\mathbf{r}, t) v^2 \mathbf{v}}{2} \right] \quad (11)$$

does not contradict any physical statement. By multiplying Eq. (11) by (f/n) and integrating over all values of \mathbf{v} , one will get Eq. (10), which is a physical equation that results from the conservation of energy law. Moreover, if all of the particles have only one value of \mathbf{v} then Eq. (11) will follow. There is nothing that overrules that assumption; however, if that state did exist then it will be for an instant because particle collisions will redistribute the velocities among the particles. Therefore, we are saying that among all of the possible states that the particles in δV can have the one state that corresponds to all particles having equal velocities satisfies Eq. (11). Integrating Eq. (11) over the local volume δV will give

$$\int d^3r \nabla \cdot \mathcal{J}_E = - \int d^3r \frac{\partial \mathcal{Q}_E}{\partial t} = - \frac{d}{dt} \int d^3r \mathcal{Q}_E \quad (12)$$

where $\mathcal{J}_E = (1/2) \rho v^2 \mathbf{v}$ and $\mathcal{Q}_E = (1/2) \rho v^2$. Using the divergence theorem in Eq. (12) will lead to

$$\oint \mathcal{J}_E(\mathbf{r}, \mathbf{v}, t) \cdot d\mathbf{a} = - \frac{d}{dt} \mathcal{E}(\mathbf{v}, t) \quad (13)$$

where $\mathcal{E}(\mathbf{v}, t) = \int d^3r \mathcal{Q}_E(\mathbf{r}, \mathbf{v}, t) = \int d^3r (1/2) \rho v^2$. Assume δV to be a cylinder and use its symmetry¹ to write Eq. (13) in the form

$$\mathcal{E}(\mathbf{v}, t) = - \int_0^t d\theta \int_{S_i} \mathcal{J}_E(\mathbf{r}, \mathbf{v}, \theta) \cdot d\mathbf{a} = - \int_0^t d\theta \mathcal{J}_E(\mathbf{v}, \theta) \cdot \Delta \mathbf{a} \quad (14)$$

where on the surface S_i it is assumed that $\mathcal{J}_E(\mathbf{r}, \mathbf{v}, \theta) = \mathcal{J}_E(\mathbf{v}, \theta)$ only. Equation (14) was the starting point in the earlier work, which was an application of statistical mechanics and the conservation of energy principle to derive Cattaneo's heat-flux law.¹ Taking the ensemble average of Eq. (14) will give

$$\frac{\int d^3v \mathcal{E}(\mathbf{v}, t) f(\mathbf{r}, \mathbf{v}, t)}{n(\mathbf{r}, t)} = - \int_0^t d\theta \frac{\int d^3v \mathcal{J}_E(\mathbf{v}, \theta) f(\mathbf{r}, \mathbf{v}, t)}{n(\mathbf{r}, t)} \cdot \Delta \mathbf{a} \quad (15)$$

Because local averages are taken, the integrand can be assumed constant over the volume integral; hence,

$$\langle \mathcal{E}(\mathbf{v}, t) \rangle = \delta V \frac{\int d^3v \frac{1}{2} \rho v^2 f(\mathbf{r}, \mathbf{v}, t)}{n(\mathbf{r}, t)} = \delta V \rho_E(\mathbf{r}, t) = E(\mathbf{r}, t) \quad (16)$$

where $E(\mathbf{r}, t)$ is the total energy in δV . With Eq. (16) one can write Eq. (15) as

$$E(\mathbf{r}, t) = - \int_0^t d\theta \mathcal{J}_E(\mathbf{r}, \theta, t) \cdot \Delta \mathbf{a} \quad (17)$$

which is a local equation that holds for the local volume δV . To be able to study the dynamics of heat flow, one must take the time derivative of Eq. (17), which is

$$\left[\int_0^t d\theta \frac{\partial \mathcal{J}_E(\mathbf{r}, \theta, t)}{\partial t} + \mathcal{J}_E(\mathbf{r}, t, t) \right] \cdot \Delta \mathbf{a} = - \frac{d}{dt} E(\mathbf{r}, t) \quad (18)$$

When evaluated, the right-hand side of Eq. (18) will become

$$\begin{aligned} \frac{d}{dt} E(\mathbf{r}, t) &= \left\langle \frac{\partial \mathcal{E}(\mathbf{v}, t)}{\partial t} \right\rangle + \frac{3}{2} \frac{1}{\beta} \left\langle \frac{\partial \beta}{\partial t} \right\rangle \langle \mathcal{E} \rangle \\ &\quad - \frac{m}{2} \left\langle \frac{\partial \beta}{\partial t} \right\rangle [\langle \mathcal{E} v^2 \rangle + \langle \mathcal{E} \rangle \langle v^2 \rangle - 2 \langle \mathcal{E} \mathbf{v} \rangle \cdot \langle \mathbf{v} \rangle] \\ &\quad - m \beta \left\langle \mathcal{E} \mathbf{v} \cdot \frac{\partial \mathbf{v}}{\partial t} \right\rangle + m \beta \langle \mathcal{E} \mathbf{C} \rangle \cdot \frac{\partial \mathbf{u}}{\partial t} + m \beta \mathbf{u} \cdot \left\langle \mathcal{E} \frac{\partial \mathbf{v}}{\partial t} \right\rangle \end{aligned} \quad (19)$$

where $\mathbf{C}(\mathbf{r}, t) = \mathbf{v} - \mathbf{u}(\mathbf{r}, t)$ is the microscopic velocity relative to the frame of the moving gas, $\mathbf{u} = \langle \mathbf{v} \rangle$, $\beta = 1/k_B T$, and where use has been made of the relation

$$\langle \mathcal{E} \mathbf{v} \rangle = \langle \mathcal{E} \rangle \langle \mathbf{v} \rangle + \langle \mathcal{E} \mathbf{C} \rangle \quad (20)$$

Also, because the distribution function is the local Maxwellian a direct evaluation of the averages would reveal that

$$\langle \mathcal{E} v^2 \rangle = \langle \mathcal{E} \rangle \langle v^2 \rangle + N k_B T (\langle v^2 \rangle + \langle v \rangle^2) \quad (21)$$

where the same direct evaluation will indicate that $\langle \mathcal{E} \mathbf{C} \rangle = N k_B T \langle \mathbf{v} \rangle$, which when substituted, along with Eqs. (20) and (21), into Eq. (19) will give

$$\begin{aligned} \frac{d}{dt} E(\mathbf{r}, t) &= \left\langle \frac{\partial \mathcal{E}(\mathbf{v}, t)}{\partial t} \right\rangle - \frac{3}{2} N k_B T \frac{1}{\beta} \left\langle \frac{\partial \beta}{\partial t} \right\rangle - m \beta \left\langle \mathcal{E} \mathbf{v} \cdot \frac{\partial \mathbf{v}}{\partial t} \right\rangle \\ &\quad + m \beta \mathbf{u} \cdot \left\langle \mathcal{E} \frac{\partial \mathbf{v}}{\partial t} \right\rangle + M \mathbf{u} \cdot \frac{\partial \mathbf{u}}{\partial t} \end{aligned} \quad (22)$$

where $M = Nm$ is the total mass within δV . Because the collisionless Boltzmann equation is being considered and because the distribution function is the generic one, one can assume that within the infinitesimal time δt the net change in the velocity is zero. In other words, set $\partial \mathbf{v} / \partial t = 0$. Then Eq. (22) will become

$$\frac{d}{dt} E(\mathbf{r}, t) = \left\langle \frac{1}{2} \frac{\partial M}{\partial t} v^2 \right\rangle - \frac{3}{2} N k_B T \frac{1}{\beta} \left\langle \frac{\partial \beta}{\partial t} \right\rangle + M \mathbf{u} \cdot \frac{\partial \mathbf{u}}{\partial t} \quad (23)$$

The first term on the right-hand side of Eq. (23) is the change of energy caused by the flow of matter into δV . When neglecting convective transport,⁴ this term will be equal to $-(\delta V/2) \langle v^2 \rangle \rho \nabla \cdot \mathbf{u}$, which when substituted, together with the relation

$$\frac{\partial \beta}{\partial t} = \frac{1}{k_B T^2} \mathbf{u} \cdot \nabla T + \frac{1}{k_B T^2} \frac{2}{3} T \nabla \cdot \mathbf{u} \quad (24)$$

into Eq. (23) will give

$$\frac{d}{dt} E(\mathbf{r}, t) = - \frac{3}{2} N k_B T \frac{\mathbf{u}}{T} \cdot \nabla T - \delta V \mathbf{u} \cdot \nabla p - \frac{5}{2} N k_B T \nabla \cdot \mathbf{u} \quad (25)$$

where in getting Eq. (25) use has been made of the Euler equation $\rho(\partial \mathbf{u} / \partial t) + \rho \mathbf{u} \cdot \nabla \mathbf{u} = - \nabla p$ and terms with \mathbf{u} to a third order have been neglected, which is similar to neglecting convective energy current.⁷ Putting Eq. (25) into Eq. (18) leads to

$$\begin{aligned} \left[\int_0^t d\theta \frac{\partial \mathcal{J}_E(\mathbf{r}, \theta, t)}{\partial t} + \mathcal{J}_E(\mathbf{r}, t, t) \right] \cdot \Delta \mathbf{a} &= \frac{3}{2} N k_B T \frac{\mathbf{u}}{T} \cdot \nabla T \\ &\quad + \delta V \mathbf{u} \cdot \nabla p + \frac{5}{2} N k_B T \nabla \cdot \mathbf{u} \end{aligned} \quad (26)$$

If the overall motion of the gas is along the heat flow, then $\mathbf{u} = u\hat{n}$, and $\Delta\mathbf{a} = -\Delta a\hat{n}$, which will help writing Eq. (26) as

$$\int_0^t d\theta \frac{\partial \mathbf{J}_E(\mathbf{r}, \theta, t)}{\partial t} + \mathbf{J}_E(\mathbf{r}, t, t) = -\lambda \nabla T - \lambda' \nabla p + \tilde{\lambda}(\nabla \cdot \mathbf{u})\hat{n} \quad (27)$$

where $\lambda = (3/2)Nk_B T u / \Delta a T$, $\lambda' = \delta V u / \Delta a$, and $\tilde{\lambda} = (5/2)Nk_B T / \Delta a$. With the application of linear response theory, the Application of the inequality in Eq. (A1) given in the Appendix, and the Ergodic Theory,¹ the left-hand side of Eq. (27) can be written in the form

$$\tau \frac{\partial \mathbf{J}_E(\mathbf{r}, t)}{\partial t} + \mathbf{J}_E(\mathbf{r}, t, t) = -\lambda \nabla T - \lambda' \nabla p + \tilde{\lambda}(\nabla \cdot \mathbf{u})\hat{n} \quad (28)$$

Equation (28) says that if the relaxation time τ is small enough to make that term in the equation negligible then one would still get a finite signal time for heat conduction because of the presence of the pressure gradient.⁴ If, however, the pressure gradient is negligible compared to the other terms appearing in the heat-flux equation, then in order to have heat flow with finite speed of propagation one must have a finite value for the relaxation time τ . Therefore, for constant densities the Fourier heat flux law is recovered only if both the pressure gradient and the relaxation time have small contributions to the heat-flux law.

Conclusion

When one considers heat flow in a monoatomic ideal gas at the local equilibrium state then the heat flux's direct proportionality to the pressure gradient becomes an inherent property of the system.

Appendix: Proof of the Inequality

To be able to get Eq. (28), one needs the inequality

$$\langle [v_i(0)v_i(t)]^3 \rangle \leq \langle [v_i(0)v_i(t)] \rangle^3 \quad (A1)$$

To show the preceding inequality, let $Y = [v_i(0)v_i(t)]^2$ and $X = v_i(0)v_i(t)$, then the Schwartz inequality will allow one to write

$$\langle [v_i(0)v_i(t)]^3 \rangle = \langle X^3 \rangle = \langle YX \rangle \leq \sqrt{\langle Y^2 \rangle \langle X^2 \rangle} \quad (A2)$$

The functions X^2 and Y^2 are convex functions; therefore, the functions $-X^2$ and $-Y^2$ are concave functions. Hence, by applying the Jensen's inequality twice to the right-hand side of Eq. (A2) one gets

$$\begin{aligned} \sqrt{\langle Y^2 \rangle \langle X^2 \rangle} &= \sqrt{\langle -Y^2 \rangle \langle -X^2 \rangle} \leq \sqrt{-\langle Y \rangle^2 \langle -X^2 \rangle} \\ &\leq \sqrt{(-\langle Y \rangle^2)(-\langle X \rangle^2)} = \sqrt{\langle Y \rangle^2 \langle X \rangle^2} \end{aligned} \quad (A3)$$

While realizing the fact that $Y = X^2$, apply the Jensen's inequality twice to the last equality in Eq. (A3):

$$\begin{aligned} \sqrt{\langle Y \rangle^2 \langle X \rangle^2} &= \sqrt{(-\langle Y \rangle)(-\langle Y \rangle) \langle X \rangle^2} = \sqrt{(-\langle X^2 \rangle)(-\langle X^2 \rangle) \langle X \rangle^2} \\ &= \sqrt{\langle -X^2 \rangle \langle -X^2 \rangle \langle X \rangle^2} \leq \sqrt{\langle X \rangle^2 \langle X \rangle^2 \langle X \rangle^2} = \langle X \rangle^3 \end{aligned} \quad (A4)$$

Therefore, from Eqs. (A2–A4)

$$\langle X^3 \rangle \leq \langle X \rangle^3 \quad (A5)$$

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