

Pressure vs. Energy:

A Mathematical Treatment of the Thermal Energy Equation

Christopher Winfield

MAST

We derive the Thermal Energy Equation

$$\frac{\partial P}{\partial t} + \mathbf{u} \cdot \nabla P = \frac{\Gamma_1 P}{\rho} \left(\frac{\partial \rho}{\partial t} + \mathbf{u} \cdot \nabla \rho \right). \quad (1)$$

To avoid the ad-hoc approaches of various references, let us derive energy/pressure relationships for ideal (classical) and photon gases systematically by using the following formula for pressure P

$$P = - \left(\frac{\partial U}{\partial V} \right)_{s,N,T} \quad (\text{Ideal gas}); \quad P = - \left(\frac{\partial U}{\partial V} \right)_{s,T} \quad (\text{Photon gas}).$$

Here U is the internal energy, V is the volume, N is the number of particles (where appropriate), T is the temperature, and s is the entropy of the ensemble (here σ , N and T are fixed in the definition of pressure p).

We can apply this formula as we use implicit differentiation on the entropy formula of each model. Let us start with the photon gas: Here photon number is not conserved, but we count quantum states according to Plank distribution (cf. Chapt 9 of Reed and Roy): We will show that

$$s = \Phi(U V^{1/3}) \quad (2)$$

for some strictly increasing, differentiable function Φ . We will supply details since the reference is out of print and since we would prefer additional rigorous arguments to ensure differentiability. If we find the internal energy as a function of T , we apply the thermal identity $(dU)_V = T ds$

$$s = \int_0^U \frac{1}{T(\zeta)} d\zeta$$

to find formula for s . Here U_0 is the internal energy. We arrive at such a formula for T by the Plank distribution

$$U = \frac{E}{e^{E/T} - 1}$$

Where $E = \hbar\omega$ is the energy of a single photon mode. We find s to be given by an improper integral which we check:

$$\begin{aligned} \frac{1}{T} &= \frac{1}{E} \ln \left[1 + \frac{E}{U} \right] \\ s &= \frac{1}{E} \int_0^U \ln \left[1 + \frac{E}{\zeta} \right] d\zeta \end{aligned} \quad (3)$$

Antideriv = Integrate[Log[1 + (E / x)] / E, x] /. x -> U

Limit[Antideriv, U -> 0]

$$\frac{E \text{Log}[U + E] + U \text{Log}\left[\frac{U+E}{U}\right]}{E}$$

Log[E]

We obtain

$$s = \ln[U + E] + \frac{U}{E} \ln\left[\frac{U+E}{U}\right] - \ln E = \left[1 + \frac{U}{E}\right] \ln\left[1 + \frac{U}{E}\right].$$

Photon Pressure vs. Volume: The Bohr-Sommerfeld Quantization Rule

We begin with the formal (semi-classical) Hamiltonian for a photon:

$$\mathcal{H} = c p$$

where $p = |\vec{p}|$, \vec{p} is a photon's momentum and c is the (constant) speed of light in a vacuum. We note that the Hamiltonian does not depend on the generalized coordinates \vec{p} , so that contours of constant energy in phase space will lie in regions of the form $\mathcal{B} \times \mathcal{S}_r$ where \mathcal{S}_r denotes a sphere of radius \tilde{p} in momentum space, ie. $\mathcal{S}_r = \{\vec{p} : |\vec{p}| = \tilde{p}\}$. We therefore choose to use spherical coordinates (r, ϕ, θ) with position and momentum variables \vec{q}, \vec{p} given by

$$\vec{q} = (r_{\vec{q}}, \phi_{\vec{q}}, \theta_{\vec{q}}), \vec{p} = (r_{\vec{p}}, \phi_{\vec{p}}, \theta_{\vec{p}}), r_{\vec{q}} \equiv |\vec{q}|, r_{\vec{p}} \equiv |\vec{p}|$$

where the θ 's and ϕ 's are the respective azimuthal and polar angles for arbitrary but fixed axes. Standard volume forms in the position and momentum spaces are (up to orientation)

$$dV = dr_{\vec{p}} \wedge r_{\vec{p}} \sin \phi_{\vec{p}} d\theta_{\vec{p}} \wedge r_{\vec{p}} d\phi_{\vec{p}} = r_{\vec{p}}^2 \sin \phi_{\vec{p}} dr_{\vec{p}} \wedge d\theta_{\vec{p}} \wedge d\phi_{\vec{p}}$$

$$d\mathcal{V} = dr_{\vec{q}} \wedge r_{\vec{q}} \sin \phi_{\vec{q}} d\theta_{\vec{q}} \wedge r_{\vec{q}} d\phi_{\vec{q}} = r_{\vec{q}}^2 \sin \phi_{\vec{q}} dr_{\vec{q}} \wedge d\theta_{\vec{q}} \wedge d\phi_{\vec{q}}$$

The various components of \vec{p} and \vec{q} are now considered to be conjugate variables which are coupled along contours in phase space as we apply the Bohr-Sommerfeld Rule along with Stoke's Theorem (cf. Landau, Lifshitz Vol. 3, § 45). We parametrize contour curves $C_a : a = 1, 2, 3$, using spherical components (q_r, q_ϕ, q_θ) and (p_r, p_ϕ, p_θ) , along with 1 forms accordingly:

$$C_1(r_{\vec{q}}, r_{\vec{p}}, \theta_{\vec{q}}, \theta_{\vec{p}}) = \left\{ (r_{\vec{q}}, \phi_{\vec{q}}, \theta_{\vec{q}}) \times (r_{\vec{p}}, \phi_{\vec{p}}, \theta_{\vec{p}}) : 0 \leq \phi \leq \pi \right\}, d p_\phi = r_{\vec{p}} d \phi_{\vec{p}}, d q_\phi = r_{\vec{q}} d \phi_{\vec{q}};$$

$$C_2(r_{\vec{q}}, r_{\vec{p}}, \phi_{\vec{q}}, \phi_{\vec{p}}) = \left\{ (r_{\vec{q}}, \phi_{\vec{q}}, \theta_{\vec{q}}) \times (r_{\vec{p}}, \phi_{\vec{p}}, \theta_{\vec{p}}) : 0 \leq \theta \leq 2\pi \right\}, d p_\theta = r_{\vec{p}} \sin \phi_{\vec{p}} d \theta_{\vec{p}}, d q_\theta = r_{\vec{q}} \sin \phi_{\vec{q}} d \theta_{\vec{q}};$$

$$\mathcal{J}_1(r_{\vec{q}}, r_{\vec{p}}) \equiv \oint_{C_1(r_{\vec{q}}, \theta_{\vec{q}})} p_\phi d q_\phi = 2\pi(N_1(r_{\vec{q}}, r_{\vec{p}}) + 1/2)\hbar = \int_0^\pi \int_0^\pi r_{\vec{q}} r_{\vec{p}} d \phi_{\vec{q}} d \phi_{\vec{p}}$$

$$\mathcal{J}_2(r_{\vec{q}}, r_{\vec{p}}, \phi_{\vec{q}}, \phi_{\vec{p}}) \equiv \oint_{C_2(r_{\vec{q}}, r_{\vec{p}}, \phi_{\vec{q}}, \phi_{\vec{p}})} p_\theta d q_\theta = 2\pi(N_2(r_{\vec{q}}, r_{\vec{p}}, \phi_{\vec{q}}, \phi_{\vec{p}}) + 1/2)\hbar = \int_0^{2\pi} \int_0^{2\pi} r_{\vec{q}} r_{\vec{p}} \sin \phi_{\vec{q}} \sin \phi_{\vec{p}} d \theta_{\vec{q}} d \theta_{\vec{p}}$$

$$\mathcal{J}_3(R, \tilde{p}) \equiv \oint_{C_3(R, \tilde{p})} p_r d q_r = 2\pi(N_3(R, \tilde{p}) + 1/2)\hbar = \int_0^{\tilde{p}} \int_0^R dr_{\vec{q}} dr_{\vec{p}}$$

The value of the countour integrals depend on the indicated variables as do the integer values N_1, N_2, N_3 which have finitely many jump discontinuities as functions of these variables. We will suppose, for simplicity, that \mathcal{J}_3 is continuous at (\tilde{p}, R) .

We choose open intervals $I_{a,b}$

$$r_{\vec{p}} \in I_{1,i}, r_{\vec{q}} \in I_{2,j}, \phi_{\vec{p}} \in I_{3,k}, \phi_{\vec{q}} \in I_{4,l},$$

indices i, j, k, l running from 1 to some $M_1, M_2, M_3, M_4 \in \mathbb{N}$, respectively, on which both \mathcal{J}_1 and \mathcal{J}_2 are constant where $N_1(r_{\vec{q}}, r_{\vec{p}}) = N_{1,i,j}$ and $N_2(r_{\vec{q}}, r_{\vec{p}}, \phi_{\vec{q}}, \phi_{\vec{p}}) = N_{2,i,j,k,l}$. For each a , the intervals $I_{a,b}$ are disjoint, where $\bigcup_{b=1}^{M_b} \bar{I}_{a,b} = [0, R], [0, \tilde{p}], [0, \pi], [0, \pi]$ for $a = 1, 2, 3, 4$, respectively (\bar{I} denotes closure).

$$\text{Vol}(\mathcal{B}_R) \cdot \text{Vol}(\mathcal{B}_{\tilde{p}}) = \sum_{i,j,k,l} \int_{I_{1,i}} \int_{I_{2,j}} \left[\int_0^{2\pi} \int_0^{2\pi} \left[\int_{I_{3,k}} \int_{I_{4,l}} r_{\vec{q}} r_{\vec{p}} \sin \phi_{\vec{q}} \sin \phi_{\vec{p}} d \phi_{\vec{q}} d \phi_{\vec{p}} \right] r_{\vec{q}} r_{\vec{p}} d \theta_{\vec{q}} d \theta_{\vec{p}} \right] dr_{\vec{q}} dr_{\vec{p}}$$

$$\begin{aligned}
&= 8 b (N_3 + 1/2) \left(\sum_{i,j,k,l} b(N_{1,i,j} + 1/2) \cdot b(N_{2,j,k,l} + 1/2) \right) \\
&= N b^3 / 2
\end{aligned}$$

for some positive integer N . We will replace \tilde{p} by p to find

$$\frac{4}{3} \pi R^3 \cdot \frac{4}{3} \pi p^3 = N b^3 / 2$$

Therefore there is a positive constant C such that

$$p^3 = C/V \tag{4}$$

We finish this section with some comments on the interpretation of our results in regards to pressure. From §12 LL Statistical Physics I (page 42) that pressure is determined by external parameters in the sense that thermal quantities involving pressure and volume do not depend on the canonical variables used to compute (5) - the implied force is averaged out over the entire surface $\text{bdy}(V)$. Moreover, applying Pascal's Law, pressure may be measured in an outward normal direction on a spherical surface where differential changes in spatial volume result from a differential change dR over a fixed differential solid angle Ω . We therefore write

$$dV = \frac{\partial V}{\partial R} dR = \Omega R^2 dR, \tag{5}$$

whereby the derivative is well defined at any point of our surface. We may adjust the constant C of equation so that (3) holds on any volume element of the form (5) so that we have a clear relationships among P , V and p and their various differentials.

Pressure of a Photon Gas

It is now clear that $p \propto V^{-1/3}$ in this model. Furthermore, since $E = \epsilon p$ for a photon, it is clear also that $E \propto V^{-1/3}$ so that there is a constant K so that $\frac{U}{E} = K U V^{1/3}$. For our purposes, we only needed to know that the integral (3) converges as a smooth function of U/E and to ensure that (2) holds. We obtain from the chain rule

$$0 = \Phi'(U V^{1/3}) \left(\frac{1}{3} V^{-2/3} U + \left(\frac{\partial U}{\partial V} \right)_{s,T} V^{1/3} \right).$$

Since $\Phi' > 0$, we have

$$\frac{1}{3} V^{-2/3} U + \left(\frac{\partial U}{\partial V} \right)_{s,T} V^{1/3} = 0$$

$$\frac{1}{3} V^{-2/3} U = P V^{1/3}$$

so that $P = U/(3V)$

Pressure of an Ideal Gas

Let us find a U, T, V relationship for the ideal gas by similar means: By 6-34 of Kittel, Kroemer (a form of the Sackur-Tetrode equation), the entropy can be written in the form

$$s = \frac{3}{2} N \log(U) + N \log(V) + f(N, T)$$

for some function f depending only on N and T . By the chain rule we obtain

$$0 = \frac{3N}{2U} \left(\frac{\partial U}{\partial V} \right)_{s,N,T} + \frac{N}{V} = \frac{-3NP}{2U} + \frac{N}{V}$$

so that $P = 2U/(3V)$.

The total energy U is determined by the well – known ideal gas law and the Stefan – Boltzmann law so that we obtain

$$U = \frac{3}{2} k T + c V T^4$$

$$P = \frac{k N T}{V} + c T^4$$

The Adiabatic Exponent

For a gas with both photon and classical properties we compute

$$\Gamma_1 = (d \ln P / d \ln \rho)_s = \frac{-V}{P} \left(\frac{d P}{d V} \right)_s \quad (6)$$

in terms of heat capacities C_p and C_V . Here we will show that

$$\Gamma_1 = \chi \left(\frac{C_p}{C_V} \right) \quad (7)$$

where $\chi = \left(\frac{d \ln p}{d \ln \rho} \right)_T = - \frac{V}{P} \left(\frac{d P}{d V} \right)_T$. We note that for fixed N , we see that $U = U(T, V)$ and $P = P(T, V)$ with independent variables T and V . We use the thermodynamic identity (with constant N) which we treat as a 1-form defined on \mathbb{R}^2

$$d Q = T d s = d U + P d V = (\partial_V U + P) d V + (\partial_T U) d T.$$

To compute $C_p = (d Q / d T)_p$ we have to consider a submanifold of \mathbb{R}^2 where $P = \text{constant}$ as we treat V as a function of T and restrict our 1-forms as indicated by subscript. (Partial symbols with subscript denote standard partial derivatives.)

$$C_p = (d Q / d T)_p$$

$$(d Q)_p = ((\partial_V U + P) (d V)_p + (\partial_T U)) (d T)_p$$

On such a submanifold we can compute $(d V)_p$ by using $(d P)_p = 0$.

$$0 = (d P)_p = \partial_V P (d V)_p + \partial_T P (d T)_p$$

$$(d V)_p = -(\partial_T P / \partial_V P) (d T)_p$$

$$C_p = -(\partial_V U + P) (\partial_T V)_p + \partial_T U$$

We compute $C_V = (d Q / d T)_V$ similarly

$$(d Q)_V = ((\partial_V U + P) (\partial_V V) + (\partial_T U)) (d T)_V = (\partial_T U) (d T)_V$$

$$C_V = \partial_T U$$

We have

$$\frac{C_p}{C_V} = 1 - \frac{(\partial_V U + P) (\partial_T V)_p \partial_T P}{\partial_T U \partial_V P}.$$

We now compute $\left(\frac{d P}{d V} \right)_s$ where we consider $S = \text{constant}$ another submanifold of \mathbb{R}^2 on which V again depends on T .

$$(d P)_S = (\partial_T P) (d T)_S + (\partial_V P) (d V)_S$$

$$0 = T (d S)_S = (d U)_S + P (d V)_S = \partial_T U (d T)_S + (\partial_V U + P) (d V)_S$$

$$(dT)_S = -\frac{\partial_V U + \partial_V P}{\partial_T U} (dV)_S$$

Now we compute

$$(dP)_S = \left((\partial_V P) - (\partial_T P) \frac{\partial_V U + P}{\partial_T U} \right) (dV)_S$$

$$\left(\frac{dP}{dV} \right)_S = \partial_V P - (\partial_T P) \frac{\partial_V U + P}{\partial_T U}$$

Since T is one of our independent variables, it is easy to compute

$$\left(\frac{dP}{dV} \right)_T = \partial_V P$$

To prove the result, we will compute the ratio $\frac{\Gamma_1}{\chi}$

$$\frac{\Gamma_1}{\chi} = \left(\frac{dP}{dV} \right)_S \bigg/ \left(\frac{dP}{dV} \right)_T = \left(\partial_V P - (\partial_T P) \frac{\partial_V U + P}{\partial_T U} \right) \bigg/ \partial_V P = 1 - \frac{(\partial_V U + P) (\partial_T V)_p \partial_T P}{\partial_T U \partial_V P} = \frac{C_p}{C_V}$$

We note that the result does not depend on this particular gas model except that for dependence of U and P on T and V - and that $\partial_T U, \partial_V P$ are non-zero.

Thermal Energy Equation

With an appropriate relationship between P and T , we want to write P as a function of ρ and s . At this stage we are assuming, absent of any other physical relation, that P, ρ are independent (of each other). We expect that P and ρ (dynamic variables) already do depend on T, s (thermal variables); but, in an adiabatic situation, it will be convenient to express $P = P(\rho, s)$ whereby $s = \text{constant}$ (adiabatic and reversible thermodynamic processes). To be sure that we may change our system from independent variables P, ρ to one of independent variables T, ρ , we consider the system

$$\begin{pmatrix} \rho \\ P \end{pmatrix} = \begin{pmatrix} \rho \\ P(T, \rho) \end{pmatrix}$$

We then apply the Inverse Function Theorem (or the Implicit Function Theorem). We need that the following does not vanish:

$$\text{Det} \begin{pmatrix} \frac{\partial \rho}{\partial T} & \frac{\partial \rho}{\partial P} \\ \frac{\partial P}{\partial T} & \frac{\partial P}{\partial \rho} \end{pmatrix} = \begin{vmatrix} \frac{\partial \rho}{\partial T} & \frac{\partial \rho}{\partial P} \\ \frac{\partial P}{\partial T} & \frac{\partial P}{\partial \rho} \end{vmatrix} = \begin{vmatrix} \frac{\partial \rho}{\partial T} & 1 \\ \frac{\partial P}{\partial T} & 0 \end{vmatrix} = -\frac{\partial P}{\partial T}$$

So we are able to set $T = T(P, \rho)$, and $P = P(\rho)$ (as a differentiable functions, provided

$$\frac{\partial P(T, s)}{\partial T} \neq 0 \tag{8}$$

(We abuse notation here: The function p may differ when express terms of different variables.) A typical expression for P is one of the form (see eqn. 9)

$$P = C_1 T \rho + C_2 T^4.$$

This would arise from an equation of state for an ideal gas along with black-body radiation (cf. Section 1.17 of *Astrophysical Fluid Dynamics*, Gordan Ogilvie). Since C_1, C_2, ρ are supposed to be non-negative and one C_1, C_2 positive, we find that (9) indeed holds.

Now, to derive the thermal energy equation we apply the Chain Rule and then use $\frac{Ds}{Dt} = 0$ to obtain

$$\frac{DP(\rho)}{Dt} = \frac{Ds}{Dt} \frac{\partial P}{\partial s} + \frac{D\rho}{Dt} \frac{\partial P}{\partial \rho} = \frac{D\rho}{Dt} \frac{\partial P}{\partial \rho} \tag{9}$$

We have, by the way, an alternate way to compute Γ_1 . Setting $u = \ln p(\rho)$, $v = \ln \rho$,

$$\Gamma_1 = \left(\frac{\partial \ln P}{\partial \ln \rho} \right)_s = \frac{\partial u}{\partial v} = \frac{\partial_\rho u}{\partial_\rho v} = \frac{\partial_\rho P / P}{1/\rho} = \frac{\rho}{P} \frac{\partial P}{\partial \rho} \quad (10)$$

And, finally, we derive (1) [see also (3) of the “A Baby Hydrodynamics Model”] by (9) and (10) and by substitution:

$$\frac{\partial P(\rho)}{\partial \rho} = \Gamma_1 \frac{P}{\rho}$$

$$\frac{DP}{Dt} = \Gamma_1 \frac{P}{\rho} \cdot \frac{D\rho}{Dt}$$

References

1. Landau and Lifshitz, “Course of Theoretical Physics vol. 3: Quantum Mechanics, Non-relativistic Theory,” 3rd ed, Pergammon Press, 1976.
2. Landau and Lifshitz, “Course of Theoretical Physics vol. 5: Statistical Physics 1,” 3rd ed, Pergammon Press, 1980.
3. Reed and Roy, “Statistical Physics for Students of Science and Engineering”, Dover , 1995.
4. Kittel, Kroemer, “Thermal Physics”, Freedman and Co., 1980.
5. G. Olgilvie, Mathematical Tripos, Part III: Astrophysical Fluid Dynamics, 2008 http://www.damtp.cam.ac.uk/user/gio10/afd_notes.pdf
6. Hrabrovsky, Winfield, Firmess, “A Baby Hydrodynamics Model” <http://www.madscitech.org/csg/BabyModel.nb>