

The principal equations of state for classical particles, photons, and neutrinos

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Abstract

Functions, not dynamical equations, are the definitive mathematical objects in equilibrium thermodynamics. However, more than one function is often described as “the” equation of state for any one physical system. Usually these so named equations only capture incomplete physical content in the relationships between thermodynamic variables, while other equations, no less worthy of the name equation of state, go inconsistently by other names. While this approach to terminology can be bewildering to newcomers, it also obscures crucial properties of thermodynamic systems generally. We introduce specific principal equations of state and their complements for ideal gases, photons, and neutrinos that have the complete thermodynamic content from which all other forms can be easily deduced. In addition to effortlessly clarifying many smaller classical issues, they also make properties like the second law of thermodynamics and local thermodynamic equilibrium completely visual.

1 Introduction

Aside from physical notions such as heat and work, thermodynamics appears centered around differentials because of expressions such as

$$dU = TdS - PdV + \sum_i \mu_i dN_i, \quad (1)$$

where the variables have their usual meaning of internal energy, temperature, entropy, pressure, volume, chemical potential, and particle number, respectively. This equation of differentials, known as the Gibbs equation [7], is typically described as fundamental. However, the assumption of thermodynamic equilibrium implies that a differentiable function $U = f(S, V, N_1, N_2, \dots)$ exists such that

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \sum_i \frac{\partial U}{\partial N_i} dN_i, \quad (2)$$

where $T, P, \{\mu_i\}$ are suitably identified as the first derivatives, $\partial U/\partial S$, $-\partial U/\partial V$, and $\{\partial U/\partial N_i\}$. Why neither this function

$$U = f(S, V, N_1, N_2, \dots) \quad (3)$$

nor the alternative entropy representation, which represents an inverse in U ,

$$S = q(U, V, N_1, N_2, \dots) \quad (4)$$

are emphasized instead of differentials is a matter of style, history, and tradition.

The differential of a differentiable function is simply an alternative expression of the function itself, up to a constant, in its independent variables. It is easy to confuse the abstract mathematical change in the sense of a differential with actual physical dynamics, so care must be taken not to confuse that differential with physical dynamics in itself. In fact, strictly speaking the equation of state makes no reference to time. It is timeless. Of course that does not mean that time has no role in thermodynamics by any means. But in dynamical systems language, thermodynamic equilibrium would be realized at best as a fixed point or a singular point in a vector flow field. Few fields represent simple functions in this way, but many encounter functions expressed as differentials for the first and only time through the unique customs of thermodynamics.

This picture is further obscured by the traditional offering of equations involving partial derivatives (intensities) as “the” equations of state. The equations

$$PV = kNT \quad (5)$$

and

$$U = \frac{3}{2}kNT \quad (6)$$

are often referred to as equations of state, but in terms of the above designations they rather represent a system of partial differential equations when written out in full,

$$kN \frac{\partial U}{\partial S} + V \frac{\partial U}{\partial V} = 0, \quad (7)$$

$$3kN \frac{\partial U}{\partial S} - 2U = 0. \quad (8)$$

Solutions of these equations do not in themselves tell us about, for example, μ . To have an explicit relation with those variables fully accessible requires that these partial differential equations be integrated followed by input of new information from theory or experiment to set the resulting integration constants. Partial differential equations in other partial derivatives are sometimes given names other than “equation of state,” however, though they are no less worthy of the name. They all stem from a common *principal equation of state*, Eq. (3), containing all information about the system. These alternative partial differential equations are even depicted at times as being entirely foreign to thermodynamics. For example, the relation for radiation $PV = U/3$, or

$$3 \frac{\partial U}{\partial V} V + U = 0, \quad (9)$$

is often described as an external result of electromagnetic theory [4] instead of originating as it does from the same principal equation of state as does the Stefan–Boltzmann law $U = aT^4V$, or

$$aV \left(\frac{\partial U}{\partial S} \right)^4 - U = 0. \quad (10)$$

The principal equation of state implicitly defines, through its various partial derivatives, a family of equations whose members will be referred to here as *secondary equations of state*. Thus, for example, the ideal gas law or the Stefan–Boltzmann law are secondary equations of state, despite their relative historical prominence. While the existence of the form of Eq. (3) is often presumed, it is rarely explicitly presented historically. Indeed it is given such scant attention, that it is not even clear whether the straightforward cases have all been published or even computed. But there is valid insight to be gained from looking at these functions directly, which imply limitations for all equations of state.

Accordingly this paper shows:

1. The principal equation of state in the case of several physical systems (i.e., ideal gases, Van der Waals gases, photons, neutrinos) not only produces all the better known secondary equations of state, but it also shows other well-known relationships to be secondary equations of state, too.
2. The principal equation of state's convexity makes the second law of thermodynamics inherent to the equation of state, making it visually apparent, and putting a general constraint on physically consistent empirical equations of state.
3. The principal equation of state implies a complementary principal equation expressed in intensive variables only, which makes the distinction between local thermodynamic equilibrium and full equilibrium visually apparent.
4. The complementary principal equation clarifies why no one intensity can represent a system in local thermodynamic equilibrium.

2 The principal equation of state and its complement

In this paper we consider systems with a common equilibrium manifold exclusively. We do not treat physical mixtures or frozen states. In principle all values of $(U, S, V, N_1, N_2, \dots)$ exist mathematically, but only those which satisfy Eq. (3) are equilibrium states. Furthermore off of the manifold, though mathematically well defined, points do not necessarily represent physical thermodynamic states or even represent them uniquely. They may also represent transients or a projection from a higher dimensional space with variables not visible in this space. However well-defined mathematical points of the space $(U, S, V, N_1, N_2, \dots)$ are, they do not imply a unique physical state except on the equilibrium manifold. Some people extend the set of extensive variables with internal variables to fully specify non-equilibrium states. We refrain from this since we are not interested in the non-equilibrium states per se but only in the equilibrium manifold. We use the well-defined mathematical structure of the full $(U, S, V, N_1, N_2, \dots)$ space, without the need to ascribe any particular physical meaning to points off of the equilibrium manifold, other than of course how they frame the mathematical structure of the equilibrium manifold itself.

The essential property of extensive thermodynamic variables is additivity, which implies that the principal equation of state function must be first degree homogeneous:

$$\lambda U = \lambda f(S, V, N_1, N_2, \dots) = f(\lambda S, \lambda V, \lambda N_1, \lambda N_2, \dots), \quad (11)$$

from which we observe by differentiation with respect to λ then setting $\lambda = 1$,

$$U = \frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \sum_i \frac{\partial U}{\partial N_i} N_i. \quad (12)$$

On substitution of $T, P, \{\mu_i\}$,

$$U = TS - PV + \sum_i \mu_i N_i. \quad (13)$$

It is customary to use the Legendre transformation $G = U - TS + PV$ to arrive at the Gibbs free energy $G = \sum_i \mu_i N_i$. Yet we have used little more than the Euler property of homogeneous functions [1]. But Eq. (13) untransformed is at least as physically compelling. It leads to a complementary pair of differentials, the Gibbs equation (1) and the Gibbs–Duhem equation [5]:

$$dU = TdS - PdV + \sum_i \mu_i dN_i, \quad (14)$$

$$0 = SdT - VdP + \sum_i N_i d\mu_i, \quad (15)$$

which in turn imply Eq. (3), of course, and a second complementary equation:

$$0 = g(T, P, \mu_1, \mu_2, \dots). \quad (16)$$

Note that Eq. (16) has a dimension one less than Eq. (3): The property of system scale is missing because all variables are intensive.

The principal equation of state (3) with additivity formally implies the existence of a manifold in the space formed from extensities only. That manifold is a (perhaps piecewise) smooth subset of that space defined by the function. The term “manifold” provides a single convenient word to describe curves, surfaces, and their extensions into higher dimensions. The two equations (3) and (16) form a complementary pair. They will be referred to respectively as the *principal equation of state* and the *complementary principal equation of state*. One equation represents a manifold in extensity space, while its complement is a manifold in intensity space. The two equations are equivalent and contain the same information except for a lack of scale in Eq. (16). This feature is used in a subsequent section to frame understanding of local thermodynamic equilibrium for a non-equilibrium system.

3 Convexity and the second law

Any thermodynamic state on the equilibrium manifold can be defined by a position vector, $\mathbf{r} = (U, S, V, N_1, N_2, \dots)$ in extensity space, where $\mathbf{r} \in \mathbb{R}^{n+1}$. Here n is the number of independent variables of the extensity space, i.e., the number of arguments for f . Of course points off of the manifold can be similarly located, but only position vectors that fall on the manifold defined by Eq. (3) constitute unconstrained equilibrium states. Locations off that surface can be reached mathematically by using the additivity of mutually independent equilibrium systems, although those points do not generally correspond to physically realizable states. Thus an equilibrium state of a homogeneous system is fully represented by a position vector \mathbf{r} rooted in the origin and ending on the surface. By virtue of the scaling property Eq. (11), $\lambda\mathbf{r}$ is just a scaled version of the same thermodynamic state. Thus changes of state along radial lines from the origin are degenerate in that no internal thermodynamic process is required to move between them. They only correspond to different amounts of the same equilibrium system. This is a global requirement on all thermodynamic systems. This scaling is illustrated in Figure 1, where the shaded bandshell-like surface is the equilibrium surface within the 3-dimensional space of $\{S, U, V\}$. The green rays emanating from the origin represent equivalent equilibrium states, differing only in magnitude, e.g., states \mathbf{r}_1 and $2\mathbf{r}_1$.

On the other hand, joining two independent systems denoted by their state vectors \mathbf{r}_1 and \mathbf{r}_2 that do not follow on the same radial line is a different matter. Pure additivity would yield a state $\mathbf{r}_1 + \mathbf{r}_2$. That is, the resulting entropy would be given (incorrectly) by

$$S(\mathbf{r}_1) + S(\mathbf{r}_2) = S(\mathbf{r}_1 + \mathbf{r}_2) \quad (17)$$

based on pure extensivity, if state functions did not have to reflect the second law. But the second law of thermodynamics requires that not all extensivities can be additive after an irreversible interaction between systems defined by \mathbf{r}_1 and \mathbf{r}_2 . In particular, if U, V, N_1, N_2, \dots remain additive (i.e., their total amounts remain fixed before and after the systems are joined), then the total entropy must increase,

$$S(\mathbf{r}_1) + S(\mathbf{r}_2) \leq S(\mathbf{r}_1 + \mathbf{r}_2). \quad (18)$$

At this point it is important to remember that the space depicted in Figure 1 represents possible extensivities of a system, equilibrium as well as

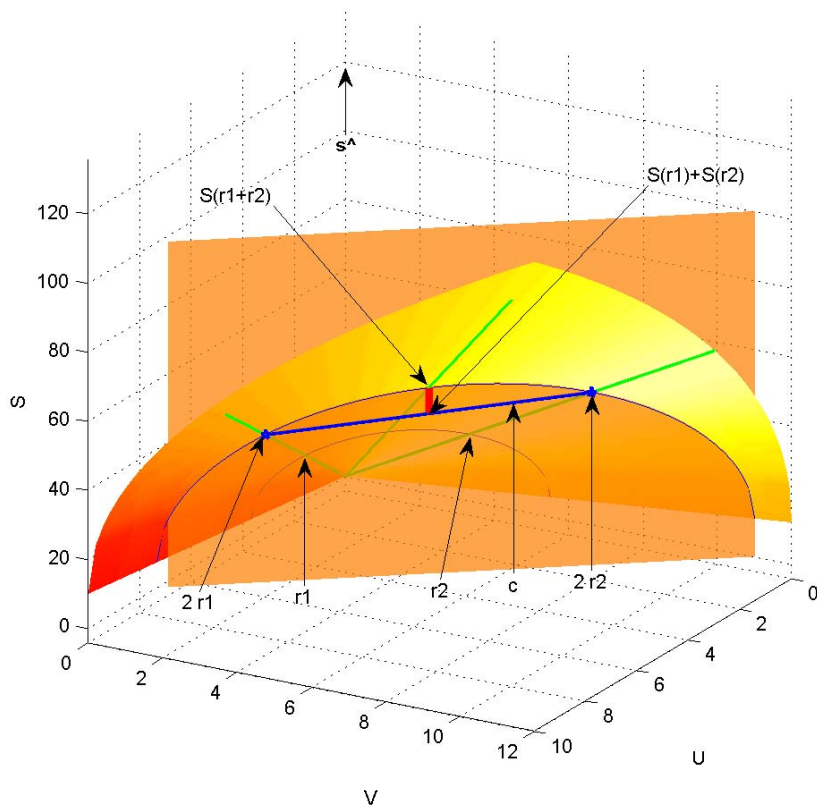


Figure 1. Equilibrium surface $S(U, V)$ (shaded bandshell-like surface) in the space of extensive variables $\{S, U, V\}$. The green rays emanating from the origin represent equivalent equilibrium states, differing only in magnitude, e.g., states \mathbf{r}_1 and $2\mathbf{r}_1$. The vector \mathbf{c} (thick blue line) is a chord connecting the two equilibrium points $2\mathbf{r}_1$ and $2\mathbf{r}_2$ on the equilibrium surface but otherwise being under the surface and thus passing through non-equilibrium states. The equilibrated mixture of \mathbf{r}_1 and \mathbf{r}_2 is indicated as $S(\mathbf{r}_1 + \mathbf{r}_2)$ and the entropy produced in the equilibration is shown as the short thick red line.

non-equilibrium. This is a challenging idea unless it is appreciated that all extensities, unlike intensities, have a well-defined existence out of equilibrium. Energy, number, volume, and even entropy, unlike intensities, do not derive their existence from thermodynamic equilibrium. We may imagine a system with any combination of these. As mentioned above, these values may be transient, only realized at some instant, or they may be constrained over all time. A point in extensity space provides no means to distinguish between such systems and does not represent a specific thermodynamic

state even if it is a well-defined point. Only those points that are on the manifold will be in a unique thermodynamic equilibrium, fully defined by the variables of the space, requiring no constraints or alternative presumptions to remain where they are in the state space indefinitely.

In contrast, intensities have no meaning for points off the manifold because intensities are slopes on a particular manifold in extensity space. Only points on that manifold represent *equilibrium states*. Any other points represent *out of equilibrium* conditions which do not capture particular dynamical properties. But external considerations generally imply an unspecified relaxation to some point on the equilibrium surface through some unspecified particular non-equilibrium processes when unconstrained.

While most of the present paper is cast in the energy picture, $U = f(S, V, N_1, N_2, \dots)$, this irreversibility effect is most conveniently illustrated in the entropy picture, $S = q(U, V, N_1, N_2, \dots)$, as in Figure 1. However, they are equivalent.

The vectors $2\mathbf{r}_1$ and $2\mathbf{r}_2$ are position vectors on the equilibrium surface because of scaling. Then the vector $\mathbf{c} = 2\mathbf{r}_2 - 2\mathbf{r}_1$ joining $2\mathbf{r}_1$ to $2\mathbf{r}_2$ (marked in blue in Figure 1) must also touch the surface at $2\mathbf{r}_1$ and $2\mathbf{r}_2$, and $S(2\mathbf{r}_1)$ and $S(2\mathbf{r}_2)$ must also be equilibrium entropies. Further, the state $\mathbf{r}_1 + \mathbf{r}_2$ bisects \mathbf{c} .

Using scaling, inequality (18) can be expressed in terms of the average of these equilibrium entropies:

$$S(\mathbf{r}_1) + S(\mathbf{r}_2) = \frac{S(2\mathbf{r}_1) + S(2\mathbf{r}_2)}{2} \leq S(\mathbf{r}_1 + \mathbf{r}_2). \quad (19)$$

The vector \mathbf{c} and the unit vector along the S -axis $\hat{\mathbf{s}}$ together define a plane. This is the vertical plane in Figure 1 which is drawn semitransparent in order to allow view of the origin, the original equilibrium states \mathbf{r}_1 and \mathbf{r}_2 , and the full green scaling rays. In that plane \mathbf{c} defines a chord to the curve created by the intersection of the plane with the equilibrium surface. In that plane we may assign a parameter t to denote the position \mathbf{r} along the vector linearly, such that $\mathbf{r}(t_1) = 2\mathbf{r}_1$ and $\mathbf{r}(t_2) = 2\mathbf{r}_2$. We may then re-express Eq. (19) in terms of the position parameter t ,

$$\frac{S(t_1) + S(t_2)}{2} \leq S\left(\frac{t_1 + t_2}{2}\right), \quad (20)$$

where we recall that $\mathbf{r}_1 + \mathbf{r}_2$ produces a point that bisects the chord in the plane induced by \mathbf{c} and $\hat{\mathbf{s}}$. Thus that point on the chord occurs at a value of t that is the average of the end values. The irreversibility indicated by this

inequality, i.e. the difference between the equilibrated entropy $S(\mathbf{r}_1 + \mathbf{r}_2)$ and the unequilibrated, merely scaled entropy $S(\mathbf{r}_1) + S(\mathbf{r}_2)$, is shown by the thick red line in Figure 1.

As the states represented by t_1 and t_2 are arbitrary, Eq. (20) reduces to the standard definition of a convex function, $S(t)$ in the plane defined by \mathbf{c} and $\hat{\mathbf{s}}$. Note that while the practical distinction between concavity and convexity is important in fields such as optics, mathematically speaking convexity implies concavity viewed from the opposite direction. Thus both properties are conventionally characterized under the general heading of “convexity,” which is the convention used here. Furthermore, as long as \mathbf{r}_1 and \mathbf{r}_2 are not parallel, this reasoning is true for any such plane, thus requiring the surface itself be convex.

The second law of thermodynamics consequently necessitates the convexity of the principal equation of state function in the entropy picture, Eq. (4) and equivalently the convexity of the principal equation of state function in the energy picture, Eq. (3). Thus the second law of thermodynamics shows up in the convexity of the equilibrium surface. Not only is this conceptually important, the principal equation of state guarantees agreement with the second law for all processes.

A corollary of the second law arising from convexity is that pure additivity of constrained equilibria cannot take one “above” the entropy equilibrium surface. Pure additivity leads to a position on a chord joining the end points $2\mathbf{r}_1$ and $2\mathbf{r}_2$ which always lies “below” the equilibrium surface because of convexity. Thus values of S greater than the value on the surface, for given values of U, V, N_1, N_2, \dots , are not achievable in this way. Extensity space is divided into two physically different parts, the “upper” part of which can only be reached through irreversible processes. In the energy picture, $U = f(S, V, N_1, N_2, \dots)$, which is convex, “above” should be replaced by “below,” etc.

We now return to the energy picture and observe that the eigenvalues of the Hessian are the practical indicator for convexity. At some \mathbf{r} we may define a parameter t along a direction represented by the vector $\mathbf{h} = \langle h_1, h_2, \dots, h_n \rangle$. Then

$$U(t) = U(0) + \left. \frac{dU}{dt} \right|_{t=0} t + \frac{1}{2} \left. \frac{d^2U}{dt^2} \right|_{t=0} t^2 + O(t^3). \quad (21)$$

The second term is the derivative along \mathbf{h} with respect to t , while the third is the second directional derivative. Along \mathbf{h} we have the following equation.

$$U(\mathbf{r} + t\mathbf{h}) = U(\mathbf{r}) + \sum_{i=1}^n U_{h_i}(\mathbf{r})h_it + \frac{1}{2} \sum_{j=1}^n \sum_{i=1}^n U_{h_i h_j}(\mathbf{r})h_i h_j t^2 + O(t^3). \quad (22)$$

Here we have used the notation $U_x = \partial U / \partial x$. The double sum is the second directional derivative which can be rewritten as

$$\sum_{j=1}^n \sum_{i=1}^n U_{h_i h_j}(\mathbf{r})h_i h_j = \mathbf{h}^T \mathcal{H}(\mathbf{r}) \mathbf{h}, \quad (23)$$

where \mathcal{H} is the matrix of second derivatives, U_{ij} , known as the Hessian. As the right side is a quadratic form in \mathbf{h} , the sign of the second derivative or curvature for any direction \mathbf{h} is determined by the eigenvalues of \mathcal{H} . In particular, convexity guarantees for the case of the energy representation, Eq. (3), that the eigenvalues will all be positive except when \mathbf{h} is a direction that implies a position vector \mathbf{r} on the equilibrium surface. In that case the eigenvalue must be 0 because scaling requires that the surface be flat in that direction. Therefore all Hessians of principal equations of state will certainly have one zero eigenvalue, and it follows that their determinants will always vanish. Moreover because they are symmetric, all eigenvectors other than \mathbf{r} will be orthogonal to the position vector \mathbf{r} .

We conclude this section by observing that the second law manifests itself visually in graphs of the principal equation of state by the curvature of the surface. Furthermore, empirically developed equations of state, which are common in some areas of chemistry and engineering, must conform to this property.

4 Local equilibrium and the complementary function

The complementary function $g(T, P, \mu_1, \mu_2, \dots)$ arising from Eq. (16) has a different character which illustrates the notion and extent of local equilibrium. While the extensity space containing $U = f(S, V, N_1, N_2, \dots)$ has physical meaning for energies “above” the equilibrium manifold because such points are physically accessible in principle by the additivity of independent subsystems in terms of additive extensities, this is not so off the manifold in intensity space. Unlike the analogous case of extensity space, no strict definition exists for intensities off the equilibrium manifold. Thus relaxation of the definitions of intensities would be required to discuss points off the manifold there. However, one can imagine approximate temperatures and chemical potentials that need not satisfy

$0 = g(T, P, \mu_1, \mu_2, \dots)$ exactly but approximately. This permits realistic discussion of approximate equilibrium scenarios that may only hold locally in configuration space (i.e., local equilibrium), which are of great importance because real world measurements normally take place in local equilibrium environments.

In this scenario there is no scale to the equilibrium, so that the scale property has no importance, given that the system has no formal “extent.” But unlike extensity space, physical systems are just represented by single points in intensity space, irrespective of what their scale in configuration space may be. Thus an equilibrium-like point in configuration space makes as much sense in intensity space as an extended system does. But classical local equilibrium is more than just a limiting case of equilibrium at any point in configuration space, which holds uniformly, of course, at all points within an extended equilibrium system. Local equilibrium, unlike proper equilibrium, permits the equilibria of points in configuration space to vary continuously. Thus a local equilibrium system is not strictly speaking in proper thermodynamic equilibrium, but the extent that its points in configuration can be represented by (approximate) local intensities that satisfy $0 = g(T, P, \mu_1, \mu_2, \dots)$ gives meaning to the concept.

Essentially we imagine splitting the full system into a number of smaller systems, each one in equilibrium but out of equilibrium with its neighbors. We then imagine taking a limit to zero volume for the small systems. Air temperature for example not only makes empirical sense, but one argues theoretically that the probability density function of molecules in the air is nearly locally mixed, and Gaussian or Maxwellian. This is a reasonable approximation as long as distances ℓ in configuration space are small compared to the gradients in local thermodynamic intensities, \mathcal{I}_i , divided into the local measured intensity:

$$\ell \ll \frac{\mathcal{I}_i}{d\mathcal{I}_i/dx}. \quad (24)$$

Since intensity space ignores scale, every point in this space corresponds to a ray in extensity space, on the equilibrium manifold to the extent that local equilibrium actually has meaning. Only in global equilibrium will all of these local thermodynamic states agree and have the same intensities. That is, in global equilibrium there will be unique values for $T, P, \mu_1, \mu_2, \dots$, corresponding to a single point on the intensity manifold, for all points on a scaling ray in extensity space.

But local equilibrium, satisfying $0 = g(T, P, \mu_1, \mu_2, \dots)$, will be representable in intensity space, too. Unlike *global equilibrium*, it will not

appear as a point, but as a finite domain on the equilibrium manifold, with a nonzero and definable set diameter. The extent to which the local equilibrium achieves global equilibrium is the degree to which this domain approximates a single point on the manifold. Thus, if the domain is small by some suitable measure compared to other differences in question, it may be regarded as in global equilibrium for practical purposes. But if questions posed concern changes within the domain, then a global equilibrium approximation makes no sense.

5 Principal equations of state and thermodynamic geometry

Manifold convexity makes a reliable structure on which to characterize distance. In 1975 Weinhold suggested using the Hessian of Eq. (22) as a metric in an abstract thermodynamic space [10]. Subsequently, thermodynamic lengths were calculated using this and the closely related entropy metric and it was found [9] that these lengths can bound the dissipation in a process generally. Specifically,

$$\Delta A \geq \frac{L^2 \theta}{\tau}, \quad (25)$$

where ΔA is the availability (exergy) lost in the process, L is the thermodynamic length of the process path,

$$L = \int_{\text{process path}} \sqrt{d\mathbf{X} \frac{d^2 U}{d\mathbf{X} d\mathbf{X}} d\mathbf{X}}, \quad (26)$$

θ is the relaxation time of the system, and τ is the duration of the process. Here \mathbf{X} is the vector of all the independent extensive variables, $\{S, V, N_1, N_2, \dots\}$ in this case. This is clearly a tighter bound than the traditional statement $\Delta A \geq 0$ since the right-hand side of Eq. (25) is strictly positive for any non-equilibrium process.

Since Eq. (26) uses the Hessian of the energy (or alternatively the entropy) function, we need the complete principal equation of state for the system in order to proceed. Thus a large part of the considerations presented in this paper were necessitated by these dissipation calculations and optimizations of paths, not least the principal equation for the ideal gas presented in the next section. A recent review of such thermodynamic geometric optimizations may be found in Ref. [2].

6 Examples of principal equations of state

6.1 Photons and neutrinos

We will begin the examples with the case of photons and neutrinos. Although the principal equation for these does not seem to have been presented or studied previously, and they are perhaps the least familiar particles for thermodynamic study, they are certainly the simplest structurally. We will subsequently deal with cases of increasing structural complexity.

Following Ref. [6], the energy of unpolarized particles in the phase space volume $d^3 p d^3 r$ is

$$dU = 2n\epsilon \frac{d^3 p d^3 r}{h^3}, \quad (27)$$

where n is the mean occupation number for either photons or neutrinos, ϵ is the energy per particle, and h is Planck's constant. The entropy of that same volume is

$$dS = 2k[\mp(1 \mp n) \ln(1 \mp n) - n \ln n] \frac{d^3 p d^3 r}{h^3}, \quad (28)$$

where k is Boltzmann's constant. The upper signs correspond to neutrinos (bosons) and the lower to photons (fermions). The energy density U/V , from direct integration [6], is **Error: bosons and fermions interchanged**

$$\frac{U}{V} = \frac{15 \mp 1}{4} \left(\frac{\sigma}{c}\right) T^4, \quad (29)$$

where σ is the Stefan–Boltzmann constant and c is the speed of light. Similarly for the entropy density S/V ,

$$\frac{S}{V} = \frac{4}{3} \frac{15 \mp 1}{4} \left(\frac{\sigma}{c}\right) T^3. \quad (30)$$

By eliminating T and solving for U we find the explicit principal equation of state,

$$U = \left(\frac{81}{1024}\right)^{\frac{1}{3}} \left(\frac{c}{\sigma V}\right)^{\frac{1}{3}} S^{\frac{4}{3}} \quad (31)$$

for photons while for neutrinos we find

$$U = \left(\frac{81}{896}\right)^{\frac{1}{3}} \left(\frac{c}{\sigma V}\right)^{\frac{1}{3}} S^{\frac{4}{3}}. \quad (32)$$

Some notable partial derivatives are worth noting. For example,

$$\frac{\partial U}{\partial N} = \mu = 0 \quad (33)$$

for both photons and neutrinos, easily demonstrating a fact often merely asserted to students. This lack of N -dependence of U is a direct consequence of Eqs. (27) and (28). More fundamentally it arises from the fact that the photon number is not conserved. Note that no number of any kind appears in the final principal equation of state. When considering this, care must be taken not to confuse an ensemble mean occupation number, n , for which there is no conserved quantum number, with a specific conserved number, N , which typically is associated with some fundamental conserved number like charge, or baryon number, etc. Thus the number of variables shrinks to 2, S and V , and the state space of Figure 1 becomes 2-dimensional. Moreover, the Hessian becomes 2×2 and there are thus only 2 eigenvalues, one of which is 0.

$$-\frac{\partial U}{\partial V} = P = \frac{1}{3} \frac{U}{V} \quad (34)$$

is a relationship typically deduced in texts on electromagnetic theory (e.g. Ref. [4]), but it arises here directly from the principal equation of state. It represents simply another secondary equation of state. Equation (34) leads to the complementary principal equations of state by substituting for U ,

$$0 = (15 \mp 1) \left(\frac{\sigma}{c} \right) T^4 - 12P. \quad (35)$$

The Hessian for *photons* is

$$\begin{aligned} \mathcal{H}_p &= \left(\frac{c}{144\sigma} \right)^{\frac{1}{3}} \begin{bmatrix} V^{-\frac{1}{3}} S^{-\frac{2}{3}} & -V^{-\frac{4}{3}} S^{\frac{1}{3}} \\ -V^{-\frac{4}{3}} S^{\frac{1}{3}} & V^{-\frac{7}{3}} S^{\frac{4}{3}} \end{bmatrix} \\ &= \left(\frac{c}{144\sigma S^2 V^7} \right)^{\frac{1}{3}} \begin{bmatrix} V^2 & -VS \\ -VS & S^2 \end{bmatrix}. \end{aligned} \quad (36)$$

It has eigenvalues 0 as do all systems (see discussion following Eq. (23)) and

$$\left(\frac{c}{144\sigma S^2 V^7} \right)^{\frac{1}{3}} (S^2 + V^2), \quad (37)$$

which is strictly positive. The zero eigenvalue corresponds to the eigenvector

$$\begin{bmatrix} S \\ V \end{bmatrix}, \quad (38)$$

as expected. In that direction there is no curvature in the manifold because it is the direction in which the extensivities scale. All other directions will

have positive directional derivatives. Since eigenvectors of symmetric matrices are orthogonal, the second eigenvector must be

$$\begin{bmatrix} -V \\ S \end{bmatrix}. \quad (39)$$

Note that in Eq. (37) mixed unit objects emerge. This is a consequence of the path in extensity space, which is a mixture of changes in coordinates of unlike units. Either an explicit or an implicit relationship between S and V adopted will set its direction. This tells us that the actual magnitude of Eq. (37) will be unit dependent and not physically important on its own. However, most importantly, the sign is not dependent on these things.

The Hessian for *neutrinos* is very similar,

$$\begin{aligned} \mathcal{H}_n &= \left(\frac{c}{126\sigma} \right)^{\frac{1}{3}} \begin{bmatrix} V^{-\frac{1}{3}} S^{-\frac{2}{3}} & -V^{-\frac{4}{3}} S^{\frac{1}{3}} \\ -V^{-\frac{4}{3}} S^{\frac{1}{3}} & V^{-\frac{7}{3}} S^{\frac{4}{3}} \end{bmatrix} \\ &= \left(\frac{c}{126\sigma S^2 V^7} \right)^{\frac{1}{3}} \begin{bmatrix} V^2 & -VS \\ -VS & S^2 \end{bmatrix}, \end{aligned} \quad (40)$$

and its eigenvalues are again 0 and the positive quantity

$$\left(\frac{c}{126\sigma S^2 V^7} \right)^{\frac{1}{3}} (S^2 + V^2). \quad (41)$$

These neutrinos have the same eigenvectors Eqs. (38) and (39) since the eigenvalues only differ by a numerical constant.

The principal equation of state shows by inspection that both neutrino and photon radiation functions of state agree with the second law, but also that both have zero chemical potential.

6.2 Ideal and nearly ideal gases

For a single component ideal gas, the usual equations for U , P , and μ (cf. Eqs. (5) and (6)) lead to the following system of partial differential equations:

$$kN \frac{\partial U}{\partial S} + V \frac{\partial U}{\partial V} = 0, \quad (42)$$

$$3kN \frac{\partial U}{\partial S} - 2U = 0, \quad (43)$$

$$\frac{\partial U}{\partial N} + k \frac{\partial U}{\partial S} \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3h^2 N} \right)^{\frac{3}{2}} \right] = 0, \quad (44)$$

where m is the mass per particle. The solution is

$$U = \frac{3h^2 e^{-\frac{5}{3}}}{4\pi} \frac{N}{m} \left(\frac{N}{V}\right)^{\frac{2}{3}} \exp\left(\frac{2}{3} \frac{S + K}{kN}\right), \quad (45)$$

where K is an arbitrary integration constant independent of S , V , and N . The scaling property tells us that K must either be a new scalable variable in addition to S , V , and N , which it cannot be since there are no further independent variables, or it must be zero. The principal equation of state for an ideal gas then becomes

$$U = \frac{3h^2 e^{-\frac{5}{3}}}{4\pi} \frac{N}{m} \left(\frac{N}{V}\right)^{\frac{2}{3}} \exp\left(\frac{2}{3} \frac{S}{kN}\right). \quad (46)$$

If we solve this equation for S , to find the equivalent entropy representation, the result is known as the Sakur–Tetrode equation for the entropy of an ideal gas,

$$S = kN \left[\frac{3}{2} \ln\left(\frac{mU}{N}\right) + \ln\left(\frac{V}{N}\right) + \frac{5}{2} + \frac{3}{2} \ln\left(\frac{4\pi}{3h^2}\right) \right]. \quad (47)$$

Thus the entropy principal equation of state is already known but not with the designation as an equation of state. The energy expression (46) can be found only rarely [8].

Convexity is suggested by the exponential dependence on S . The Hessian \mathcal{H}_g is straightforward to compute as

$$\begin{aligned} & \begin{bmatrix} 2V^2N^2 & -2kN^3V & 2V^2N(kN - S) \\ -2kN^3V & 5k^2N^4 & -kVN^2(5kN - 2S) \\ 2V^2N(kN - S) & -kVN^2(5kN - 2S) & V^2(5k^2N^2 - 4kSN + 2S^2) \end{bmatrix} \\ & \times \frac{h^2}{6\pi mk^2} \frac{1}{N^2V^3} \left(\frac{V}{N}\right)^{\frac{1}{3}} \exp\left(\frac{2S}{3kN} - \frac{5}{3}\right). \end{aligned} \quad (48)$$

As expected, inspection shows that the vector

$$\begin{bmatrix} S \\ V \\ N \end{bmatrix} \quad (49)$$

in the direction of simple scaling of the system is an eigenvector with eigenvalue $\lambda_0 = 0$, ensuring the determinant of the Hessian must be 0. This eigenvalue corresponds to motion on the equilibrium surface [3].

Dropping the positive scalar multiplying the matrix in Eq. (48) for simplicity, the remaining two eigenvalues, λ_+ and λ_- , are

$$\lambda_{\pm} = \alpha \pm \beta, \quad (50)$$

where

$$\alpha = \left[\frac{5}{2} N^2 \left(k - \frac{2}{5} \frac{S}{N} \right)^2 + N^2 + \frac{3}{5} S^2 \right] V^2 + \frac{5}{2} N^4 k^2, \quad (51)$$

and

$$\begin{aligned} \beta = \frac{1}{2} \{ & -16 V^4 N^3 S k - 4 k^2 V^2 N^4 S^2 - 40 k^3 V^2 N^5 S - 40 V^4 N^3 k^3 S \\ & + 36 V^4 N^2 k^2 S^2 - 4 k^2 N^6 V^2 - 4 V^4 N^4 k^2 + 8 V^4 N^2 S^2 \\ & + 50 k^4 V^2 N^6 - 16 V^4 S^3 k N + 25 N^8 k^4 + 4 V^4 S^4 \\ & + 25 V^4 N^4 k^4 + 4 V^4 N^4 \}^{\frac{1}{2}}. \end{aligned} \quad (52)$$

The eigenvalues of symmetric matrices are real, so the argument of the root in Eq. (52) must be positive or zero. These two eigenvalues correspond to two, usually different, relaxation times [3]. It is not surprising that an ideal gas would have such two different relaxation times since it is well known that, e.g., pressure and temperature disturbances relax at different speeds, pressure relaxation usually being much quicker than temperature relaxation. As noted above for photons and neutrinos, these eigenvalues are of mixed units indicating that the corresponding eigen-directions are not purely pressure and temperature relaxation but some mixtures.

To confirm that these complicated expressions for eigenvalues are actually positive, consider the characteristic polynomial for the matrix in Eq. (48). Since we are given one eigenvalue (i.e., zero), we can focus on the remaining two factors of the cubic polynomial, reducing the problem to a quadratic:

$$\lambda (\lambda - \lambda_+) (\lambda - \lambda_-) = 0 \Rightarrow (\lambda - \lambda_+) (\lambda - \lambda_-) = 0. \quad (53)$$

For nonzero physical variables this implies,

$$\begin{aligned} \lambda_+ + \lambda_- &= 2\alpha \\ &= 2 \left[\frac{5}{2} N^2 \left(k - \frac{2}{5} \frac{S}{N} \right)^2 + N^2 + \frac{3}{5} S^2 \right] V^2 + 5 N^4 k^2 \\ &> 0. \end{aligned} \quad (54)$$

From Eq. (50)

$$\lambda_+ \lambda_- = \alpha^2 - \beta^2 = 6 V^2 k^2 N^4 (V^2 + N^2 + S^2) > 0. \quad (55)$$

The only way for the sum and product of real λ_+ and λ_- to be both positive, is for both λ_+ and λ_- to be positive or zero.

Extending the results above to a multicomponent ideal gas differing by particle numbers N_i and masses m_i is not technically challenging, since each type of gas appears as an independent statistical weight in the entropy. Thus, the principal equation of state becomes

$$U = \frac{3h^2 e^{-\frac{5}{3}}}{4\pi} N \prod_{i=1}^n \left[\left(\frac{N_i}{V} \right)^{\frac{2}{3}} \frac{1}{m_i} \right]^{\frac{N_i}{N}} \exp\left(\frac{2}{3} \frac{S}{kN}\right). \quad (56)$$

A slight modification for a multicomponent ideal gas differing by number N_i and m_i and individual heat capacity per number C_i follows from the entropy perspective. The constants ζ_i take internal structure into account. C_V is the overall heat capacity per particle such that $U = C_V N T$:

$$U = \frac{C_V h^2 e^{-1 - \frac{k}{C_V}}}{2k\pi} N \prod_{i=1}^n \left[\left(\frac{N_i}{V} \right)^{\frac{k}{C_i}} \frac{1}{\zeta_i m_i} \right]^{\frac{C_i N_i}{C_V N}} \exp\left(\frac{S}{C_V N}\right). \quad (57)$$

Again from the entropy perspective, a Van der Waals gas partition function leads to

$$U = \frac{3h^2 e^{-\frac{5}{3}}}{4\pi m} N \left(\frac{N}{V - Nb} \right)^{\frac{2}{3}} \exp\left(\frac{2}{3} \frac{S}{kN}\right) - \frac{aN^2}{V}, \quad (58)$$

where suitable empirical constants a and b were introduced.

7 Conclusions

The case of the ideal gas shows that the principal equation of state puts thermodynamic constraints on what is possible in terms of equations of states. Correctly derived, its curvature ensures fulfillment of the second law. It is emphasized that many of the so called equations of state such as “the ideal gas law” only provide part of the picture, usually under the tacit assumption of keeping one thing or another fixed during the process. For optimizations via thermodynamic geometry the full equation of state, including all degrees of freedom, is essential. The principal equation of state also clearly demonstrates many key principles of thermodynamics with minimal effort

and maximum clarity. Moreover, it suggests that the better model for studying this subject from a structural point of view is through radiation rather than the ideal gas which is mathematically more challenging.

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