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

Christopher Essex[1] and Bjarne Andresen[2]

[1]Department of Applied Mathematics, The University of Western Ontario
London, Ontario N6A 5B7, Canada

[2]Niels Bohr Institute, University of Copenhagen
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

essex@uwo.ca, andresen@fys.ku.dk

Functions, not differential equations, are the definitive mathematical objects of equilibrium thermodynamics. They are described as "the equation of state" suggesting only one exists, but such equations take many forms for any particular physical system. Often the relationships between the forms are obscure, unexplored, or even wrongly depicted as external to thermodynamics.

Here we explore classical equations of state for ideal particles, photons, and neutrinos. The usual equations of state are interpreted here as partial differential equations, which lead to a unique, fully extensive equation of state. These forms are rarely, if ever, expressed explicitly. They are designated as the *principal equation of state*. The principal equation of state is a unique form that acts as a generator for all other forms of the equation of state. Moreover, certain obscure properties, such as zero chemical potential for photons, become plain to see. Despite their diverse physical contexts they have certain distinctive properties in common, some of which are not fully understood.

The traditional equations of state for an ideal gas of different species are

$$U = NC_V T$$

$$PV = NkT$$

$$\mu_i = kT\left[\ln\left(\frac{N_i}{V}\right) - \frac{C_V}{k}\ln(m_i kT) + g\right]$$

with the number N_i of species i, summing to a total of N particles. The mass of a particle of species i is m_i, and g is a constant collecting a number of basic constants of nature. These equations, involving intensive as well as extensive variables, are just different projections of the principal equation of state $U(S, V, \{N_i\})$, where the intensive variables come in as coefficients in the total differential

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$

The full principal equation of state for the multi-component ideal gas reads

$$U=\frac{h^2 C_V}{2\pi k}\exp\left(-1-\frac{k}{C_V}\right)N\prod_i\left[\left(\frac{N_i}{V}\right)^{\frac{k}{C_V}}\left(\frac{1}{\varsigma_i m_i}\right)^{\frac{C_i}{C_V}}\right]^{\frac{N_i}{N}}\exp\left(\frac{S}{NC_V}\right)$$

where ζ_i accounts for internal degrees of freedom of species *i* while C_i is the heat capacity per particle for the species. This equation acts as a generator for all the usual equations through differentiation and possibly keeping one of the variables constant. It is also the starting point for calculating the Hessian or metric in thermodynamic geometry,

$$\mathbf{M}=D^2U=\left\{\frac{\partial^2 U}{\partial X_i \partial X_j}\right\}$$

where ***X*** is the full set of extensive arguments for *U*: *S*, *V*, $\{N_i\}$.

For a single-component monatomic ideal gas this principal equation of state reduces to

$$U=\frac{3}{4}\frac{h^2}{\pi}\exp\left(-\frac{5}{3}\right)\frac{N}{m}\left(\frac{N}{V}\right)^{2/3}\exp\left(\frac{2}{3}\frac{S}{Nk}\right)$$

which has a striking resemblance to the expression for a van der Waals gas,

$$U=\frac{3}{4}\frac{h^2}{\pi}\exp\left(-\frac{5}{3}\right)\frac{N}{m}\left(\frac{N}{V-bN}\right)^{2/3}\exp\left(\frac{2}{3}\frac{S}{Nk}\right)-\frac{aN^2}{V}$$

in which *a* and *b* are the van der Waals coefficients.

The principal equation of state for photons is

$$U=\frac{3}{16}\left(\frac{12c}{\sigma V}\right)^{1/3}S^{4/3}$$

and for neutrinos

$$U=\frac{3}{56}\left(\frac{588c}{\sigma V}\right)^{1/3}S^{4/3}$$

In both cases *c* is the speed of light and σ the radiation constant. The small numerical difference arises because photons are bosons and neutrinos are fermions. Note that these latter two equations do not depend on the particle number *N*, and consequently their chemical potential $\mu=\partial U/\partial N=0$. Furthermore, we note that the classical equation of state *P*=(*U/V*)/3, often depicted as external to thermodynamics, also occurs for neutrinos, and it arises directly from these equations. They also yield something less well-known but entirely analogous for entropy: *P/T*=(*S/V*)/4.

The Hessians indicate that all principal equations of state considered here are convex functions, but they also are all singular. Why? Is this a necessary property for all thermodynamic systems?