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The equations of state of some ideal fluids†

P T Landsberg

Department of Mathematics, University of Southampton, Southampton SO9 5NH, UK

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Abstract. A large class of ideal fluids satisfies the equation $pv = gU$, where U is the internal energy and g is a characteristic constant of the system. The 'ideal quantum gases' are here defined thermodynamically by this equation. These systems then include weakly interacting fermions or bosons either in the non-relativistic or in the extreme relativistic limit. The relationship between different ideal quantum gases can be shown in a diagram with horizontal coordinate g . This ensures that the states of such systems are represented by vertical lines. In order to make such a diagram useful for non-ideal systems one may choose as coordinate $x = B_S/p - 1$, where B_S is the adiabatic bulk modulus of elasticity, which has the value g for an ideal quantum gas. It is desirable to represent the classical ideal gas, which is here defined thermodynamically by $pv = NkT$, 'orthogonally' by a horizontal line and this is achieved by the choice of the coordinate $y = (1 - 1/\gamma)(1 + 1/x)$, where γ is C_p/C_v . The ideal classical gas has then states which lie on $y = 1$.

Such a diagram has the additional remarkable property that important simple systems have states represented by one single point. Systems of this type may be called 'super-ideal' and can be defined by $U = pv/g = ST/j$ where j is a constant and S is the entropy. Examples are: ideal classical gases of given γ , black body radiation, non-relativistic and non-interacting degenerate fermions, a gas of non-interacting non-relativistic bosons below its condensation temperature, and limiting cases of a classical ideal gas of given γ . The coordinates of such systems have the form $[x, y] = [g, j/(j - 1)]$.

The theory of this diagram and the associated equations of state are analysed in detail.

1. Introduction

In a recent paper (Huang 1972) a class of 'super-ideal' gases was defined thermodynamically as comprising fluids which, in a usual notation, satisfy the conditions

$$pv = gU \quad \text{and} \quad TS = jU, \quad (1, 2)$$

where g and j are constants and U is the internal energy. The resulting thermodynamic relations are reasonably simple and apply to systems of weakly interacting particles as given in table 1. For a general range of temperatures in the non-relativistic regime, these systems form a subclass of the class of ideal quantum gases defined earlier by

$$pv = gU,$$

and systems of fermions and bosons are then not super-ideal. It is for this reason that the notion of a super-ideal quantum gas has a more restricted application than the concept of an ideal quantum gas (Landsberg 1961a). Nevertheless, the simplicity of the

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thermodynamics of the super-ideal gas makes it of interest to ask: what is the precise relation between ideal quantum gases and the super-ideal quantum gases?

The answer to this question is readily obtainable from the analysis of the equation $pv = gU$, which is known to imply the existence of a function $f(z)$ such that

$$Uv^g = f(z), \quad z \equiv Tv^g. \quad (3)$$

Also, the entropy of the system is given by a function $h(z)$, where

$$S = h(z), \quad zh' = f', \quad (4)$$

and the prime denotes differentiation with respect to z . To different ideal quantum gases correspond different functions f and h .

The answer to our question can be given in terms of these functions. It is: While f and h are in general complicated functions for ideal quantum gases, they are simple powers in the case of super-ideality. This will now be demonstrated.

2. The special forms of f and h for super-ideal systems

Suppose that $Ae^{\epsilon} d\epsilon$ single-particle energy levels lie in an energy range $d\epsilon$ where A is proportional to volume v , but independent of temperature. The number of particles N in volume v , the internal energy U and the entropy are given most easily in terms of

$$I(a, s, \pm) \equiv \frac{1}{\Gamma(s+1)} \int_0^\infty \frac{x^s dx}{\exp(x-a) \pm 1},$$

$$\theta(a, s) \equiv I(a, s+1, \pm)/I(a, s, \pm),$$

where $\Gamma(s)$ is the gamma function. If μ denotes the chemical potential, one finds for $s > -1$

$$N = A(kT)^{s+1} \Gamma(s+1) I\left(\frac{\mu}{kT}, s, \pm\right) \quad (5)$$

$$U = (s+1)NkT \theta\left(\frac{\mu}{kT}, s\right) \quad (6)$$

$$S = kN \left[(s+2) \theta\left(\frac{\mu}{kT}, s\right) - \frac{\mu}{kT} \right]. \quad (7)$$

A statistical mechanical interpretation of the thermodynamic quantity g is then provided by (Landsberg 1961b, pp 203, 207)

$$g = \frac{1}{s+1}. \quad (8)$$

Now equation (5) shows that, for fixed N , $I(\mu/kT, s, \pm)$ depends on vT^{s+1} , ie μ/kT is a function of $Tv^g \equiv z$, say $v(z)$. Hence $\theta(\mu/kT, s)$ is a function of z , say $\psi(z)$. It follows, by comparing (3) with (6) and (4) with (7), that

$$f(z) = (s+1) Nkz \psi(z) \quad (9)$$

$$h(z) = kN[(s+2)\psi(z) - v(z)]. \quad (10)$$

Equations (9) and (10) show that f and h are in general quite complicated functions of z .

What forms do the functions f and h take in the case when the ideal quantum gas is super-ideal? We now, for the first time, use equation (2) which shows that f and h are simply related for super-ideal systems. Note that the relation

$$dS = \frac{1}{T} dU + \frac{p}{T} dv$$

is by (1) and (2) (if j is finite)

$$dS = \frac{S}{jU} dU + \frac{gS}{jv} dv,$$

whence, with a constant of integration denoted (for later convenience) by $j\lambda^{j-1}$

$$\ln S^j = \ln Uv^g + \ln j\lambda^{j-1}, \quad \text{ie} \quad Uv^g = S^j/j\lambda^{j-1}. \quad (11)$$

This implies by (3) and (4) the following relation between f and h :

$$f(z) = h^j(z)/j\lambda^{j-1}, \quad f'(z) = (h(z)/\lambda)^{j-1}h'(z), \quad (12)$$

where a prime denotes differentiation with respect to $z = Tv^g$. By (4) and (12)

$$h(z) = \lambda z^{1/(j-1)} \quad (j \neq 1). \quad (13)$$

Substituting in (12),

$$f(z) = \frac{\lambda}{j} z^{j/(j-1)} \quad (j \neq 1). \quad (14)$$

Equations (13) and (14) give the form of the functions f and h of the theory of ideal quantum gases for the special case of 'super-ideality'.

The new quantity λ has no simple physical interpretation; it contains a collection of constants for the system under consideration. Expressions for it are given in table 1.

Consider now an ideal *classical* gas, defined here by the thermodynamic relation $pv = NkT$, whose heat capacity ratio $\gamma = C_p/C_v$ is a constant. Such a system is an ideal *quantum* gas, defined here by $pv = gU$, provided

$$f(z) = Nkz/g = C_v z$$

since $g = \gamma - 1$ in this case (see Landsberg 1961b, p 207). This is not in agreement with (14) except, possibly by choosing a limiting case of (14), as will now be shown.

In a super-ideal system let λ and j tend to infinity subject to

$$\lim_{j, \lambda \rightarrow \infty} \left(\frac{\lambda}{j} \right) = C_v.$$

Then the limiting expression of (14) has the required form. Also

$$S = h(z) = \int z^{-1} f'(z) dz = C_v \ln z + S_1 = C_v \ln(Tv^{\gamma-1}) + S_1$$

where S_1 is a constant. Thus, working from the theory of the super-ideal systems, one has to interpret the function $h(z)$ as

$$\int \left(\lim_{j, \lambda \rightarrow \infty} \frac{f'(z)}{z} \right) dz = \int \left(\lim_{j, \lambda \rightarrow \infty} h'(z) \right) dz.$$

As another example of such interpretations, the expression of table 2

$$\frac{\lambda}{j-1} z^{1/(j-1)}$$

has to be interpreted as

$$\lim_{j, \lambda \rightarrow \infty} \left(\frac{\lambda}{j-1} z^{1/(j-1)} \right) = C_v.$$

The limiting case $j, \lambda \rightarrow \infty$ of super-ideal systems thus represents ideal classical gases of constant heat capacity ratio, provided these systems are considered in the limit of infinitely large entropy. Because of equation (13) one can also specify this limit by requiring that

$$\lim_{S, \lambda \rightarrow \infty} \left(\frac{S}{\lambda} \right)^{\lambda/C_v} = \lim_{S, j \rightarrow \infty} \left(\frac{S}{jC_v} \right)^j = Tv^g.$$

Table 1. Special systems.

Label	System	g	j	λ	
A†	Non-relativistic ideal classical gas ($pv = NkT$) with C_p/C_v constant	structureless molecules in one dimension	2	∞	
B†			structureless molecules in two dimensions		1
C†			structureless molecules in three dimensions		$\frac{2}{3}$
D†			diatomic molecules with two rotational degrees of freedom		$\frac{5}{3}$
E†			rigid or triatomic molecules with three rotational degrees of freedom		$\frac{1}{3}$
$\lim_{j, \lambda \rightarrow \infty} \left(\frac{\lambda}{j} \right) = \frac{Nk}{g} = C_v$					
F‡	Non-relativistic gas of fermions	degenerate limit	$\frac{2}{3}$	∞	
C			classical limit		∞
$\left(\frac{4\pi\bar{g}}{3} \right)^{2/3} m \left(\frac{\pi k}{h} \right)^2 N^{1/3}$					
G†	Non-relativistic gas of bosons	below condensation temperature	$\frac{5}{3}$	$\frac{5}{2} \zeta(\frac{5}{2}) \bar{g} k (2\pi mk/h^2)^{3/2}$	
C			classical limit		∞
H§	Black body radiation		$\frac{1}{3}$	$\frac{3}{4} \pi^5 k^4 / h^3 c^4$	
H§	Phonon gas (Debye theory) at low temperature		$\frac{1}{3}$	$\frac{1}{4} \pi^5 (\pi^2 k^4 / h^3) (c_l^{-3} + 2c_t^{-3})$	
I§	Extreme relativistic gas of bosons or fermions		—	$(k^6 / 8h^3 c^3) \pi \bar{g} \chi$	

† From $C_p - C_v = Nk$ it follows that $\gamma - 1 = g = Nk/C_v$, so that $C_v = g^{-1}Nk$. These systems are super-ideal only in the limiting case specified.

‡ N is the number of particles present, \bar{g} is their spin degeneracy ($\bar{g} = 2$ for electrons), k is Boltzmann's constant, $\zeta(\frac{5}{2}) = 1.341$ is a value of the Riemann zeta function.

§ c is the velocity of light in vacuo; c_l and c_t are the velocities of longitudinal and transverse acoustic waves in a solid.

|| The factor χ is, with the notation of § 2,

$$\chi = \frac{[4I(\mu/kT, 3, \pm) - (\mu/kT)I(\mu/kT, 2, \pm)]^4}{[I(\mu/kT, 3, \pm)]^3}.$$

χ has to be a constant for the system to be represented by a point, and this occurs for bosons if $\mu = 0$ when $\chi = 2^8 \zeta(4) = 256 \times 1.823$.

Note that the definitions of an ideal classical gas and of an ideal quantum gas are here in purely thermodynamic terms. The ideal classical gas can also be defined as a system of weakly interacting particles subject to classical statistical mechanics. This would lead to $pv = NkT$ and to certain constant C_v values. By leaving C_v either unspecified or by restricting it to any constant values our thermodynamic definition is more general. Similarly the ideal quantum gas is here specified rather generally. The logical relationships between the various systems are illustrated in figure 1.

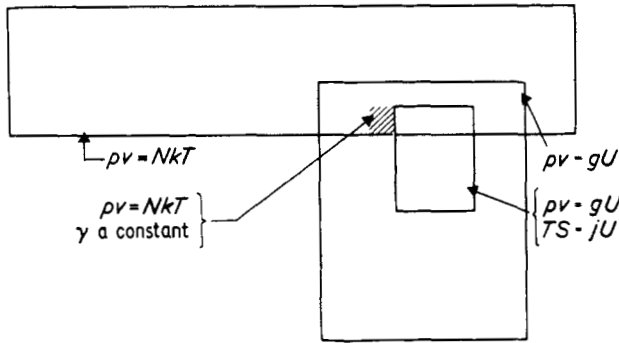


Figure 1. The logical overlaps resulting from the definitions of ideal fluids. For example, it shows that the system ' $pv = NkT, \gamma$ a constant' is not super-ideal, except possibly as a limiting case, but that it is a ' $pv = gU$ ' system, i.e. an ideal quantum gas.

3. Various expressions for the energies in the case of super-ideality

There are six distinct ways of writing U in terms of any two of the four variables v, S, T, p . For example, by equations (3), (12) and (4)

$$U = \frac{f}{v^g} = \frac{h^j}{j\lambda^{j-1}v^g} = \frac{1}{j\lambda^{j-1}}v^{-g}S^j \quad (\equiv C_1v^{-g}S^j). \tag{15}$$

Also by (3) and (14) $Uv^g = f = (\lambda/j)2^{j/(j-1)}$, so that

$$U^{j-1} = \left(\frac{\lambda}{j}\right)^{j-1} v^{-g(j-1)}(Tv^g)^j = \left(\frac{\lambda}{j}\right)^{j-1} v^g T^j. \tag{16}$$

Putting $v = gU/p$ in these two expressions yields

$$U^{1+g} = \frac{1}{jg^g\lambda^{j-1}}p^gS^j \tag{17}$$

$$U^{j-g-1} = \left(\frac{\lambda}{g}\right)^{j-1} g^g T^j p^{-g}. \tag{18}$$

The remaining two ways of writing U are given by equations (1) and (2). Since the Helmholtz free energy, the enthalpy and Gibbs free energy are respectively

$$F, H, G = (1-j, 1+g, 1+g-j)U \tag{19}$$

we also have six alternative ways of expressing each of them, by using equations (1), (2), (15), (16), (17) or (18) in (19). In this way one can find again equations (7) to (10) of

Huang's paper but with his constants C_2, C_3, C_4 now identified in terms of λ :

$$F = \frac{1-j}{j} \lambda (v^g T^j)^{1/(j-1)} \quad (\equiv C_2 v^{g/(j-1)} T^{j/(j-1)})$$

$$H = (1+g) \left(\frac{p^g S^j}{j g^g \lambda^{j-1}} \right)^{1/(g+1)} \quad (\equiv C_3 p^{g(g+1)} S^{j(g+1)})$$

$$G = \frac{1+g-j}{g} (\lambda^{j-1} T^j p^{-g})^{1/(j-g-1)} \quad (\equiv C_4 p^{-g/(j-g-1)} T^{j/(j-g-1)}).$$

His constant C_1 is identified in equation (15) above.

The thermodynamics of the ideal quantum gas frequently involves the combination Tf'/U as seen from table 2 (based on table 27.1 of Landsberg 1961b). In the table α_p is the coefficient of isothermal volume expansion, C_p is the heat capacity at constant pressure and B_T is the isothermal bulk modulus of elasticity. The expressions for the super-ideal gas are obtained from the (known) expressions for the ideal quantum gas by noting by equations (2), (12) and (13) that

$$\frac{Tf'}{U} = \frac{T}{U} \frac{h}{j-1} = \frac{TS}{(j-1)U} = \frac{j}{j-1}. \tag{20}$$

Column 3 of table 2 is in agreement with table 1 of Huang (1972). One may therefore regard column 2 of table 2 as the appropriate generalizations of these relations to the ideal quantum gases. A summary of properties of various systems is given in table 3.

Table 2.

	$pv = gU$ Ideal quantum gas	$pv = gU$ and $TS = jU$. Super-ideal quantum gas
C_v	f'	$\frac{\lambda}{j-1} z^{1/(j-1)}$
$\frac{B_S}{p} = \frac{-v}{p} \left(\frac{\partial p}{\partial v} \right)_S$	$1+g$	$1+g$
$\frac{C_p}{C_v} = \frac{B_S}{B_T}$	$\frac{1+g}{1+S-gTf'/U}$	$\frac{(1+g)(j-1)}{j-g-1}$
B_T/p	$1+g-gTf'/U$	$\frac{j-1-g}{j-1}$
C_p/S	$\frac{1+g}{TS/U} \frac{Tf'/U}{1+g-gTf'/U}$	$\frac{1+g}{j-g-1}$
$T\alpha_p$	$\frac{Tf'/U}{1+g-gTf'/U}$	$\frac{j}{j-g-1}$

4. A diagram in which super-ideal fluids are represented by points and ideal fluids by lines

The ideal quantum gas can be characterized by the constant g of equation (1), and by the variable Tf'/U . In order to make the diagram applicable to other fluids, it is desirable to

Table 3. Summary of four types of systems discussed.

	Ideal quantum gas	Super-ideal gas	Ideal classical gas	Ideal classical gas of constant γ
Definition	$pv = gU$	$pv = gU$ $TS = jU$	$pv = NkT$	$pv = NkT$ γ is a constant
$x = \frac{B_S}{p} - 1$	g	g	$\gamma - 1$	$g = \gamma - 1$
$y = \left(1 - \frac{1}{\gamma}\right)\left(1 + \frac{1}{x}\right)$	$\frac{TC_v}{U}$	$\frac{j}{j-1}$	1	1
Some other consequences	$z = Tv^g$ $Uv^g = f(z)$ $S \doteq h(z)$ $f' = zh'$	$f(z) = \frac{\lambda}{j} z^{j/(j-1)}$ $h(z) = \lambda z^{1/(j-1)}$		$f(z) = C_v z$ $\lambda, j \rightarrow \infty$ $\lim_{\lambda, j \rightarrow \infty} \frac{\lambda}{j} = \frac{Nk}{g} = C_v$

replace these two quantities by generalizations which represent frequently measured parameters. It is clear from Landsberg (1961b, p 203) that for an ideal quantum gas

$$g = \frac{pv}{U} = \boxed{\frac{1}{p}B_S - 1 = \frac{a^2\rho}{p} - 1 \equiv x} \tag{21}$$

where B_S is the adiabatic bulk modulus of elasticity, ρ is the density of the fluid and a is the velocity of sound. We shall take the framed part of (21) as the x coordinate for general fluids.

It is also known from the same reference that for an ideal quantum gas

$$\gamma \equiv \frac{C_p}{C_v} = \frac{(1+g)U}{(1+g)U - gTf'}$$

whence

$$\frac{Tf'}{U} = \left(1 - \frac{1}{\gamma}\right)\left(1 + \frac{1}{g}\right) = \boxed{\left(1 - \frac{1}{\gamma}\right)\left(1 + \frac{1}{x}\right) \equiv y} \tag{22}$$

We shall take the framed part of (22) as the y coordinate for general fluids. For given pressure p and temperature T one then needs experimental estimates of a , ρ and γ to represent the state of the fluid by a point. General fluids will be represented by general curves on this diagram.

Ideal classical gases satisfy $pv = AT$, where A is a constant, so that

$$B_T = p, \quad B_S = \gamma p,$$

and they are represented by the horizontal line $y = 1$, the temperature dependence of the specific heat being still arbitrary. An ideal quantum gas, $pv = gU$, will be represented

by the vertical line $x = g$. If such a fluid is super-ideal it will be represented by the point

$$(x, y) = \left(g, \frac{j}{j-1} \right). \tag{23}$$

The vertical line CG represents the ideal non-relativistic three-dimensional quantum gases of particles having non-zero rest mass. The effect of relativistic particle speeds is to push the system to the left of this line and it ceases to satisfy an equation $pv = gU$ with constant g . Such systems are represented by curves in the region CGHE. In the case of an extreme relativistic gas, however, the system lies on the line EH.

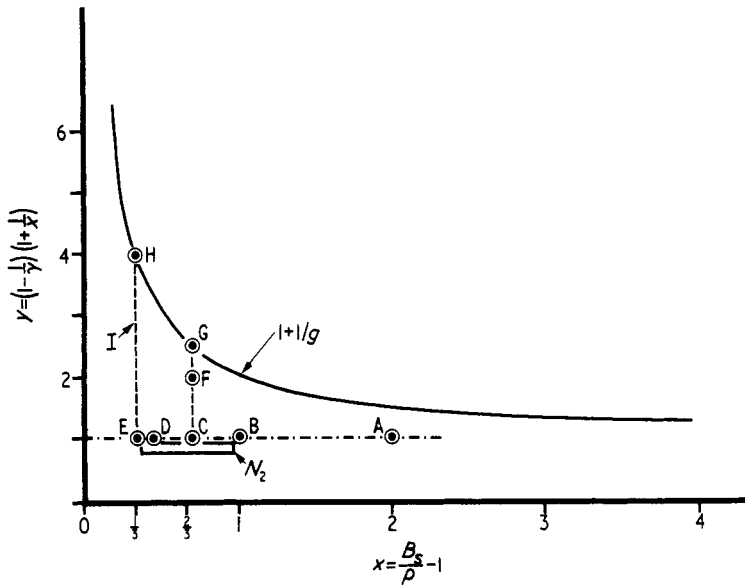


Figure 2. A 'contracted' thermodynamic diagram for fluids. The labelling of the points corresponds to that given in table 1. Super-ideal systems are represented by points, ideal quantum systems by vertical lines and ideal classical systems by the line $y = 1$.

For *ideal quantum systems* the figure has a simple interpretation, as follows. It is clear from equation (8) that as one proceeds to the left of figure 2 the single particle energy level density rises more and more rapidly with the single particle energy E . At $x = 1$ the level density is independent of E ; it behaves as a negative power of E for $x > 1$, and as a position power for $x < 1$. On the other hand, as one proceeds up the vertical axis the heat capacity at constant volume of an ideal quantum gas increases more and more strongly with temperature. This is easily seen if one assumes that $C_v = \kappa T^r$ where κ and r are constants. For then

$$y = \frac{TC_v}{U} = \frac{\kappa T^{r+1}}{\kappa T^{r+1}/(r+1)} = r + 1.$$

5. Conditions for stability

For thermal and mechanical stability one requires

$$C_v > 0, \quad B_S > 0. \quad (24)$$

If the conditions are taken in the form

$$B_S/p > 0, \quad \frac{C_p}{C_v} \geq 0, \quad (25)$$

then they imply for an ideal quantum gas $1 + g > 0$,

$$1 + g - gTf'/U \geq 0.$$

If $g > 0$,

$$Tf'/U \leq 1 + 1/g \quad (26)$$

if $-1 < g < 0$,

$$Tf'/U \geq 1 - 1/|g|. \quad (27)$$

The limit (26) has been shown in figure 2. For ideal quantum systems which lie on this line the equality holds in (26). For such systems (Landsberg 1961b, p 203) $C_p = \infty$ and $y = 1 + 1/g$ is a constant. It follows that such systems are represented by a point and are super-ideal. Therefore they have $y = j/(j-1)$, so that $g = j-1$ in such cases. This applies for example to systems G and H, as may be seen from figure 2 and table 1. Figure 2 thus serves to illustrate the relation between various ideal systems, and it may be hoped that it will also help one to study the relation between ideal and real systems.

6. Real gases

For a real gas one may use the data of Hilsenrath *et al* (1960). Taking nitrogen as an example, we calculate that for the range

$$T = (200, 3000) \text{ K} \quad p = (0.01, 100) \text{ atm.}$$

All states of the gas lie within a rectangle

$$x = (0.38, 1.14), \quad y = (0.78, 0.99).$$

This rectangle lies just below the ideal gas line between $x = \frac{1}{3}$ and $x = \frac{5}{4}$ (see figure 2).

For a liquid like carbon tetrachloride y lies again below unity, but the very much larger bulk modulus pushes the corresponding x values to quite large numbers. For the range (Rowlinson 1969, p 53)

$$T = (250, 343) \text{ K}, \quad p = (0.01, 0.82) \text{ bar}$$

one calculates

$$x = (1.1 \times 10^4, 1.8 \times 10^6), \quad y = (0.69, 0.70).$$

The range of y is again quite narrow.

Acknowledgment

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