

GENERAL DEFINITION OF THE PERFECT GAS CONCEPT

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ABSTRACT

A differential equation of state is presented for a monatomic gas without virial interactions between its particles. Together with suitable boundary conditions this defines a macroscopic concept of the 'perfect' gas.

INTRODUCTION

Since the time of Boyle, Mariotte and Gay-Lussac many people have considered how an 'ideal' (or 'perfect') gas should be defined. Rather early, the relation

$$p = \nu kT \quad (1)$$

was accepted, p being the pressure, ν the number density (v^{-1}) and T the absolute temperature of the gas. As is well known, this thermal equation of state does not completely determine the thermodynamic properties of the substance. If one also wishes the caloric equation of state, one must know an additional function of one variable, e.g. the molecular heat distribution $c_v(T)$ whence the molecular energy

$$u(T) = \int c_v(T) dT \quad (2)$$

may be obtained. From both equations of state one derives the molecular entropy

$$s(T, \nu) = \int c_v(T) T^{-1} dT - \log p \quad (3)$$

and from these the chemical potential

$$\mu(T, p) = kT + u(T) - Ts(T, p/kT) \quad (4)$$

which contains the whole thermodynamic information about the substance, because it is a thermodynamic potential. An important quantity measuring the 'power of diffusion' is the fugacity $\varphi = e^{-\mu/kT}$. We call a fluid that obeys equation 1 an *ideal gas*, distinguishing this notion from that of a 'perfect gas', which we are going to describe.

A simple microscopic model that yields equation 1 by classical statistical mechanics (both Galilei or Lorentz invariant), assumes the gas to consist of particles that have no virial interactions which means zero range repulsions, the potential energy of which vanishes in the mean, nevertheless leading to thermal equilibrium. The isochoric heat c_v is determined by the intrinsic dynamics of the particles (molecules). In the simplest case of elementary particles (atoms) one obtains

$$c_v(0) = \frac{3}{2}k, \quad c_v(\infty) = 3k \quad (5)$$

for the 'non-relativistic' or *low velocity* limit N and the 'extreme-relativistic' or *high velocity* limit E.

The same microdynamic picture yet with quantum instead of classical kinematics no longer reproduces equation 1, although one is still inclined to consider such a gas to be ('ideal' or) 'perfect'. Only in the 'quasiclassical' limit C of *large quantum numbers* is the equation 1 regained asymptotically, whereas in the limit D of *long de Broglie waves* the gas behaviour 'degenerates' completely. These remarks lead to the *microscopic* version¹ of our concept: A *perfect gas* should consist of elementary particles without virial interactions. As temperature and fugacity are unrestricted, all limiting cases (N, E, C, D, and their combinations NC, EC, ND, ED) are contained as limiting cases of the normal situation, which of course is treated by Lorentz invariant quantum statistics. In this respect the perfect gas concept is thermally much broader than that of an ideal gas. On the other hand, it is much narrower with regard to the caloric properties of the gas.

What is the macroscopic equivalent of this fundamental microscopic abstraction? H. Einbinder introduced² and P. T. Landsberg proposed³ the relation

$$p = g\varepsilon \text{ with } \begin{cases} g = \frac{2}{3} \text{ for N} \\ g = \frac{1}{3} \text{ for E} \end{cases} \quad (6)$$

between pressure and the energy density $\varepsilon \equiv v:u$ as a macroscopic characterization of what we call a perfect gas. We shall discuss this definition 6 only in the two indicated limiting cases 6_N or 6_E . So we are left with the problem of interpolating between these two asymptotes.

I. DIFFERENTIAL EQUATION OF STATE

According to our microscopic definition of the perfect gas, we have to consider the well known phase space integrals:

$$v = B \int_0^\infty dw \frac{[w(w + 2mc^2)]^{\frac{1}{2}}}{e^{\alpha + \beta w} - 1} (w + mc^2) \quad (7)$$

$$\varepsilon = B \int_0^\infty dw \frac{[w(w + 2mc^2)]^{\frac{1}{2}}}{e^{\alpha + \beta w} - 1} (w + mc^2) w \quad (8)$$

$$p = \frac{1}{3}B \int_0^\infty dw \frac{[w(w + 2mc^2)]^{\frac{1}{2}}}{e^{\alpha + \beta w} - 1} (w + 2mc^2) w \quad (9)$$

with

$$B \equiv 4\pi c^{-3} h^{-3} (2s + 1) \quad (10)$$

In these equations m , s , w denote the (rest) mass, the spin, and the kinetic energy of the identical particles, respectively (c being the velocity of light *in vacuo* and h Planck's quantum of action). The statistical parameter ι takes the values 0, +1, -1 for Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics, respectively. As usual,

$$\alpha \equiv -\frac{\mu}{kT}, \quad \beta \equiv \frac{1}{kT}, \quad \gamma \equiv \frac{p}{kT} \quad (11)$$

are the equilibrium variables for particle, energy and volume exchange, respectively.

The partial derivatives of the phase space integrals combine to the following differential relations:

$$\partial_\beta v = \partial_\alpha \varepsilon \quad (12)$$

$$\beta \partial_\alpha p + v = 0, \quad \beta \partial_\beta p + \varepsilon + p = 0 \quad (13)$$

and

$$\partial_\beta (3p - \varepsilon) = mc^2 \partial_\alpha (2\varepsilon - 2p) \quad (14)$$

Of these, equations 12 and 13 are general thermodynamic identities, true for any homogeneous substance. This can be seen from the total differential

$$d\gamma = -v d\alpha - \varepsilon d\beta \quad (15)$$

of the thermodynamic potential $\gamma(\alpha, \beta)$. Its Maxwell relation 12 is therefore a simple consequence of 13.

On the other hand, the relation 14 is specific for the gas, as indicated by the occurrence of the mass parameter m . We propose to use equation 14 as the defining relation of the *macroscopic* concept of a *generalized perfect gas*. From this derivation it is clear that the microscopic formulation must be contained in the macroscopic one. Furthermore, Landsberg's definition, though it might be more general than the microscopic one, is asymptotically regained from ours, since in the limits of infinite or zero masses, 6_N or 6_E are particular solutions of 14. To what extent our macroscopic definition is more general than the microscopic one, is a question that remains to be examined.

II. GENERAL SOLUTION OF DIFFERENTIAL EQUATION

Our problem now is to find the general solution of equation 14 for the two functions $p(\alpha, \beta)$ and $\varepsilon(\alpha, \beta)$ which are interconnected by the second equation of 13. Because of 15 we may switch to the one potential $\gamma(\alpha, \beta)$ arriving at the second order partial differential equation

$$[(\partial_\beta^2 + 3\beta^{-1} \partial_\beta - 3\beta^{-2}) + mc^2(2\partial_\beta + 3\beta^{-1}) \partial_\alpha] \gamma = 0 \quad (16)$$

It is homogeneously linear and of hyperbolic type with non-constant coefficients.

Replacing α, β, γ by the dimensionless variables

$$x \equiv \alpha - mc^2\beta, \quad y \equiv mc^2\beta, \quad z \equiv B_0^{-1}\beta^3\gamma \quad (17)$$

we achieve a considerable simplification that transforms 16 into

$$(\partial_x^2 - \partial_y^2 - 3y^{-1}\partial_y)z = 0 \quad (18)$$

This version immediately exhibits the characteristic curves $x + y = \alpha$ and $x - y = \omega$, where each of the parametrizing constants α and ω may assume any real value.

The next step is to construct a convenient form of the general solution that yields the unknown $z(x, y)$ in terms of arbitrary initial distributions $z(x, \bar{y})$ and $\partial_y z(x, \bar{y})$ at any isotherm $y = \bar{y}$. Using the Green-Riemann method of integration of hyperbolic equations⁴, this solution reads

$$z(x, y) = \frac{1}{2}(y/\bar{y})^{\frac{3}{2}} [z(x - y + \bar{y}, \bar{y}) + z(x + y - \bar{y}, \bar{y})] + \frac{1}{2} \int_{x-y+\bar{y}}^{x+y-\bar{y}} d\bar{x} [\partial_y z(\bar{x}, \bar{y}) - z(\bar{x}, \bar{y})(3\bar{y}^{-1} + \partial_y)] R(x - \bar{x}, y, \bar{y}) \quad (19)$$

where $R(x - \bar{x}, y, \bar{y})$ denotes Riemann's propagator. Its defining properties

$$(\partial_x^2 - \partial_y^2 + 3y^{-1}\partial_y)R(x - \bar{x}, y, \bar{y}) = 0$$

and

$$R(y - \bar{y}, y, \bar{y}) = (y/\bar{y})^{\frac{3}{2}} = R(\bar{y} - y, y, \bar{y})$$

are fulfilled by the function

$$R(x - \bar{x}, y, \bar{y}) \simeq (y/\bar{y})^{\frac{3}{2}} P_{\frac{3}{2}}(2q + 1), \quad q = \frac{(y - \bar{y})^2 - (x - \bar{x})^2}{4\bar{y}y} \quad (20)$$

as is shown in the Appendix. Legendre's function $P_{\frac{3}{2}}(1 + 2q) \equiv F(-\frac{3}{2}, \frac{5}{2}; 1; -q)$, primarily defined for $-1 < q \leq 1$ by the hypergeometric series, may be continued analytically to all positive values of q .

For infinite values of q one finds⁵ the asymptotic expressions

$$P_{\frac{3}{2}}(2q + 1) \approx (8/\pi)q^{\frac{3}{2}}, \quad P'_{\frac{3}{2}}(2q + 1) \approx (12/\pi)q^{\frac{1}{2}} \quad \text{for } q \rightarrow \infty \quad (21)$$

Using this result, we deduce the initial-value representation

$$z(x, y) = \frac{1}{2} \lim_{\bar{y} \rightarrow 0} (y/\bar{y})^{\frac{3}{2}} [z(x - y + \bar{y}, \bar{y}) + z(x + y - \bar{y}, \bar{y})] - \frac{4^{-\frac{1}{2}}}{\pi} \int_{x-y}^{x+y} d\bar{x} \lim_{y \rightarrow 0} \bar{y}^{-3} [y^2 - (x - \bar{x})^2]^{\frac{1}{2}} \{6yz(\bar{x}, 0) - [y^2 - (x - \bar{x})^2] \partial_y z(\bar{x}, 0)\} \quad (22)$$

the boundary strip of which has been shifted to the limit of infinite temperature.

III. PHYSICAL SOLUTIONS

This form of the general solution of equation 18 can be converted into the more convenient form

$$z(x, y) = \frac{1}{3} \left\{ \int_{-\infty}^{x-y} g_-(\bar{x}) + \int_{x+y}^{\infty} g_+(\bar{x}) \right\} [(x - \bar{x})^2 - y^2]^{\frac{3}{2}} d\bar{x} \quad (23)$$

provided the indefinite integrals converge at infinity. Apart from this *zeroth boundary condition*, which is rather weak, the border distributions $g_-(x)$ and $g_+(x)$ may be expressed by a linear function in terms of the initial distributions $z(x, 0)$ and $\partial_y z(x, 0)$.

We are now in a position to formulate our *first boundary condition*

$$g_-(x) = 0 \quad (24)$$

for which no simple physical interpretation is known.

On the other hand, our *second boundary condition* postulates simply that for extreme dilution a generalized perfect gas should behave as an ideal one. Because of 15, 12 and 11 the equation 1, now to read asymptotically only, can be reduced to $\gamma \approx v$ or

$$\partial_x \gamma \approx -\gamma \quad \text{for } \alpha \rightarrow \infty \quad \text{with } \beta \text{ fixed} \quad (25)$$

By 17, this can be transformed to $\partial_x z \approx -z$ for $x \rightarrow \infty$ with y fixed. Because of the identity $\partial_x^4 z(x, 0) = 2g_+(x)$ we arrive at

$$g_+(x) \approx B e^{-x} \quad (26)$$

with an integration constant $B > 0$, the value of which remains undetermined in this context.

We see now that the zeroth boundary condition is already contained in the first and second ones. Inserting 24 and 26 into 23 yields with 17 Jüttner's classical result⁶

$$\gamma(\alpha, \beta) \approx \frac{1}{3} B \beta \int_0^{\infty} dw e^{-\alpha w} \sqrt{[w(w + 2mc^2)]^3} \quad \text{for } \alpha \rightarrow \infty \quad (27)$$

is retained. This amounts to the ideal asymptote

$$\gamma(\alpha, \beta) = B e^{-\alpha} \beta^{-1} e^{\beta} K_2(\beta) \quad \text{for } C \quad (28)$$

where K_2 denotes the modified Bessel function. The undetermined integration constant B may be absorbed into the fugacity $e^{-\alpha}$. Simple consequences of 28 are the 'ideal' gas law 1 and the monotonic property $c'_v(T) > 0$ with the limits 5.

Thus our macroscopic definition of a generalized perfect gas has been fully developed. It is determined by the differential equation of state 18 together with the two implicitly formulated boundary conditions 24 and 26. From 18, 23 and 24 it follows that one function of one variable is arbitrary up to the asymptotic behaviour 26. This situation is similar to that of an ideal gas where one function, $c_v(T)$, remains underdetermined.

The microscopic concept of a perfect gas proves to be the choice

$$g_+(x) = B(e^x - \iota)^{-1} \quad (29)$$

with the value of B given by 10.

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APPENDIX

The interpretation of $(\partial_{\bar{x}}^2 - \partial_y^2 + 2\lambda y^{-1}\partial_y)z = 0$ is sketched.

Riemann's initial-value representation of the general solution reads

$$z(x, y) = \frac{1}{2}(y/\bar{y})^\lambda [z(x - y + \bar{y}, \bar{y}) + z(x + y - \bar{y}, \bar{y})] \\ + \frac{1}{2} \int_{x-y+\bar{y}}^{x+y-\bar{y}} d\bar{x} [\partial_y z(\bar{x}, \bar{y}) - z(\bar{x}, \bar{y})(2\lambda \bar{y}^{-1} + \partial_{\bar{y}})] R_\lambda(x - \bar{x}, y, \bar{y})$$

if

$$(\partial_x^2 - \partial_y^2 + 2\lambda y^{-1}\partial_y)R(x - \bar{x}, y, \bar{y}) = 0$$

and

$$R_\lambda(y - \bar{y}, y, \bar{y}) = (y/\bar{y})^\lambda = R_\lambda(\bar{y} - y, y, \bar{y})$$

By these conditions the propagator $R_\lambda(x - \bar{x}, y, \bar{y})$ is uniquely determined. It may be calculated from the double power series

$$R_\lambda(x - \bar{x}, y, \bar{y})$$

$$= \sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty} \frac{(\mu + \nu)!}{\mu! \nu!} \left(\frac{\lambda}{\mu}\right) \left(\frac{\lambda}{\nu}\right) \frac{(x - \bar{x} - y + \bar{y})^\mu (x - \bar{x} + y - \bar{y})^\nu}{(2\bar{y})^{\mu+\nu}}$$

if $(x - \bar{x})^2 + (y - \bar{y})^2 < \bar{y}^2$ or even $|(x - \bar{x}) - (y - \bar{y})| < 2\bar{y}$ and $|(x - \bar{x}) + (y - \bar{y})| < 2\bar{y}$. As is easily verified, $R_\lambda(x - \bar{x}, y, \bar{y}) = (y/\bar{y})^\lambda G_\lambda(q)$ with $q \equiv \frac{1}{4}(y\bar{y})^{-1} [(y - \bar{y})^2 - (x - \bar{x})^2]$, if

$$[q(1 + q)\partial_q^2 + (1 + 2q)\partial_q - \lambda(\lambda + 1)]G_\lambda(q) = 0,$$

This is Legendre's differential equation, if $2q + 1 = \frac{1}{2}(y\bar{y})^{-1} [y^2 + \bar{y}^2 - (x - \bar{x})^2]$ is taken as argument instead of q . The solution $G_\lambda(q) = P_\lambda(2q + 1)$ is uniquely determined by its value 1 at $2q + 1 = 1$, this being a singular point of the ordinary differential equation.

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