CONDITIONS FOR IDEAL-GAS BEHAVIOR

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By using the tools of quantum physics, we find conditions for ideal-gas behavior for any system consisting of either one structureless particle, or many atoms or molecules.

For one structureless particle of mass m, confined in a volume V at temperature T and pressure p, ideal-gas behavior is obtained only if

$$kT \gg h^2/8mV^{2/3}$$

where k and h are the Boltzmann and Planck constants, respectively. This condition is valid at relatively high temperatures but independent of pressure. The equation of state is $pV = kT$.

For n atoms or molecules, each of mass m, confined in V at T and p, ideal-gas behavior is obtained only if

$$ph^3/(2\pi m)^{3/2}(kT)^{5/2} \ll q_s \exp(\varepsilon_0/kT)$$

where q_s is the partition function — sum over states — of the internal structure of the atom or molecule, and ε_0 the lowest energy eigenvalue of the internal structure of the atom or molecule. Here the condition is valid at relatively high temperatures and relatively low pressures. The equation of state is $pV = nkT$.

NOMENCLATURE

A	Helmholtz free energy
$b_1, b_2, \ldots$	admissible values for any of the occupation numbers v_{ij}
c_p	specific heat per molecule at constant pressure
c_v	specific heat per molecule at constant volume
D_j	$= \exp\left(\dfrac{\mu - \varepsilon_j}{kT}\right)$
E_i	i-th energy eigenvalue of a simple system
g	number of degenerate energy eigenstates of a point (structureless) particle
G_i	i-th energy eigenstate of a simple system
h	Planck's constant
$\hbar$	$= h/2\pi$
$\hat{H}_{internal}$	Hamiltonian operator for the internal structure of a molecule

$\hat{H}_{mol}$	Hamiltonian operator of one molecule in a potential that depends only on the coordinates of that molecule
$\hat{H}_1$	Hamiltonian operator of a point particle in a force-free box
k	Boltzmann's constant
m	mass of either a point particle or a molecule
n	(expectation) value of the number of molecules of a simple system
n_i	i-th number of molecules eigenvalue of a simple system
n_{max}	maximum eigenvalue of the number of molecules
p	pressure
q_s	partition function of internal structure of a molecule
Q	partition function of a point particle in a box
Q_g	grand partition function of a simple system
r_x, r_y, r_z	positive integers
R	gas constant
s	specific entropy per molecule
S	entropy
T	temperature
u	specific internal energy per molecule
U	internal energy
v	specific volume per molecule
V	volume
x_i^0	quantum-mechanical (not statistical) probability that upon an energy measurement the result is E_i, and upon a number of molecules measurement the result is n_i
$\epsilon_j, \epsilon_j(r,s), \epsilon_r$	one-particle energy eigenvalues
ϵ_0	lowest energy eigenvalue of the internal structure of a molecule
ϵ_s	energy eigenvalue of the internal structure of a molecule for $s = 0,1,2,...$
μ	chemical potential
ν_{ij}	ij-th occupation number, that is, number of molecules of i-th energy eigenstate of a simple system having one-particle energy ϵ_j
ν_j	(expectation) value of ν_{ij} or one-particle distribution function

1. INTRODUCTION

At relatively high temperatures T and sufficiently low pressures p, every substance behaves as a single-phase fluid in which each molecule is so weakly coupled to the other molecules that it hardly experiences their presence. Under such conditions and to a very high degree of accuracy, it is found experimentally that the equation of state is given by the relation

$$pV = nRT \qquad (1)$$

where V and n are the volume and the amount of the substance, and R is the gas constant. If the amount is expressed in number of molecules, $R = k$ = Boltzmann's constant = 1.38066 J/(K molecule), and if it is expressed in moles, R = 8.3145 J/(K mol).

If equation (1) is valid, we say that the substance behaves as an *ideal gas* or is an *ideal gas*. It is noteworthy that the term "ideal" refers strictly to the mathematical simplicity of the equation of state, and not to any thermodynamic optimality, such as reduction of the detrimental effects of irreversibility.

In the literature, it is agreed that equation (1) is valid for nonzero temperatures [1] such that

$$kT > h^2/8mV^{2/3} \qquad (2)$$

and moderate pressures, where h is Planck's constant, and m the mass of each molecule. Condition (2) is necessary in order for the partition function or sum over states to be replaced by an integral or, equivalently, for the spectrum of discrete energy eigenvalues of the system to be approximated by a continuum. However, no explicit condition is provided for the pressure.

The purpose of this paper is to review the quantum-thermodynamic justification of and the sufficient conditions for the validity of equation (1) both for a system consisting of one structureless particle (point mass) in a box, and for a simple system [2] consisting of n molecules, each having translational, rotational, vibrational, and electronic degrees of freedom. The derivations were first presented in Reference [3].

2. TEMPERATURES AND PRESSURES FOR IDEAL GAS BEHAVIOR

2.1 One Structureless Particle in a Box

As a first example of conditions for ideal gas behavior, we consider a system consisting of one structureless (point) particle of mass m, confined in a field-free volume V. Without loss of generality, we assume that the volume is cubical. Thus, the Hamiltonian operator $\hat{H}_1$ and its energy eigenvalues are

$$\hat{H}_1 = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] \qquad (3)$$

$$\epsilon_r = \frac{h^2}{8mV^{2/3}}\left[r_x^2 + r_y^2 + r_z^2\right] \tag{4}$$

where r_x, r_y, and r_z are positive integers, and $\hbar = h/2\pi$.

If each energy eigenstate is g-fold degenerate because of spin considerations, the partition function or sum over states is

$$Q = g\sum_{r_x=1}^{\infty} \sum_{r_y=1}^{\infty} \sum_{r_z=1}^{\infty} \exp\left[-\frac{h^2}{8mV^{2/3}kT}\left(r_x^2 + r_y^2 + r_z^2\right)\right] = g\left[\sum_{r=1}^{\infty} \exp\left(-\frac{h^2r^2}{8mV^{2/3}kT}\right)\right]^3 \tag{5}$$

Moreover, if the temperature satisfies condition (2), the summation over the positive integers r can be closely approximated by an integral so that

$$Q = g\left[\int_0^{\infty} \exp\left(-\frac{h^2r^2}{8mV^{2/3}kT}\right)dr\right]^3 = g\left(\frac{2\pi mkT}{h^2}\right)^{3/2}V \tag{6}$$

The partition function can be used to find the Helmholtz free energy A, the pressure p, the internal energy U, and the entropy S by means of the relations

$$A = -kT\ln Q = -kT\ln V - \frac{3}{2}kT\ln T - kT\ln\frac{g(2\pi mk)^{3/2}}{h^3} \tag{7}$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{kT}{V} \quad \text{or} \quad pV = kT \tag{8}$$

$$U = -T\left(\frac{\partial(A/T)}{\partial\ln T}\right)_V = \frac{3}{2}kT \tag{9}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = k\ln\frac{g(2\pi m)^{3/2}(kT)^{5/2}V}{h^3} + \frac{3}{2}k \tag{10}$$

So, if condition (2) is satisfied, we see (equation (8)) that a particle in a box behaves as an ideal gas.

For very small temperatures, $0 < kT \ll h^2/8mV^{2/3}$, only a few terms predominate in the partition function. Retaining only the largest four terms, we find that the partition function is given by the relation

$$Q \sim g\left[\exp\left(-\frac{3h^2}{8mV^{2/3}kT}\right) + 3\,\exp\left(-\frac{6h^2}{8mV^{2/3}kT}\right)\right] \tag{11}$$

and that $pV \neq kT$, that is, the point particle in the box does not behave as an ideal gas although no forces are exerted on it by any other particle!

2.2 Simple Systems

As a second example of conditions for ideal gas behavior, we consider a simple system [2] consisting of identical molecules of mass m that interact only with short-range forces, and on which a measurement of energy yields an energy eigenvalue of one of many Hamiltonian operators associated with the system. Each Hamiltonian operator corresponds to an integer number of molecules, and this number ranges from 1 to a maximum value $n_{max} < \infty$. Each molecule has three translational degrees of freedom, plus other degrees of freedom associated with its internal structure. The latter degrees of freedom are rotational, vibrational, and electronic.

Such a description of the system is novel to quantum thermodynamics. It yields the grand canonical distribution for stable equilibrium states in terms of quantum probabilities rather than statistical probabilities.

The system admits many energy eigenstates, each characterized by an energy eigenvalue and an integer number of molecules. For convenience, we number all the energy eigenstates sequentially as $G_1, G_2, ..., G_p ...$, and denote the energy eigenvalues as $E_1, E_2, ..., E_p ...$, the integer number of molecules eigenvalues as $n_1, n_2, ..., n_p ...$, and the quantum-mechanical probabilities associated with a stable equilibrium state as $x_1^0, x_2^0, ..., x_i^0, ...$ In this notation, a different symbol is used for each energy eigenstate characteristic even though two or more of these symbols may represent the same value. For example, different symbols E_k and E_ℓ are used for two of the energies of a 2-fold degenerate energy eigenstate even though these two energies are numerically equal. Again, different symbols n_k and n_ℓ are used for the numbers of molecules eigenvalues of two energy eigenstates of the same Hamiltonian operator even though these two numbers of molecules are equal.

For a stable equilibrium state at temperature T and chemical potential μ, and (expectation) values U of the internal energy, and n of the number of molecules, we have the following relations

$$x_i^0 = \frac{\exp[(\mu n_i - E_i)/kT]}{Q_g} \tag{12}$$

$$Q_g = \sum_i \exp\left(\frac{\mu n_i - E_i}{kT}\right) \tag{13}$$

$$U = \sum_i x_i^0 E_i \tag{14}$$

$$n = \sum_i x_i^0 n_i \tag{15}$$

where Q_g is the grand partition function, and U and n vary continuously even though E_i and n_i for all i vary discretely. In addition, the entropy S of this state is given by the relation

$$S = -k\sum_i x_i^0 \ln x_i^0 \tag{16}$$

Though identical in appearance, here the entropy S is a property of the system and not a measure of ignorance because the probabilities x_i^0 are quantum-mechanical (inherent to the nature of physical systems) and not probabilities resulting from ignorance. In addition, and most importantly, they are a denumerable set because they are associated with the energy eigenstates only and not with every possible wave-function state of the system.

Upon substituting equation (12) in equation (16), using equations (13) to (15) and the Euler relation [4]

$$U = TS - pV + \mu n \tag{17}$$

we find

$$pV/kT = \ln Q_g \tag{18}$$

We see from equations (1) and (18) that the simple system behaves as an ideal gas only if $\ln Q_g$ (equation (13)) is equal to the number of molecules n. So the question arises "under what conditions on temperature and pressure is this equality achieved?"

To answer this question, we should at least evaluate the energy eigenvalues E_i. However, not only the evaluation of the energy eigenvalues but also the manipulation of the transcendental

relations of stable equilibrium states are very difficult if not practically impossible mathematical tasks. Explicit results can be found only under certain limiting conditions. We introduce some of these limiting conditions under the headings of dilute gases, one-particle approximation, and constant-potential approximation in the next three subsections.

Dilute gases. We assume that the eigenvalues of the number of molecules range between 1 and $n_{max} < \infty$, and that the (expectation) value of the number of molecules $n \ll n_{max}$. Clearly, the larger the temperature and the smaller the pressure for a given volume, the smaller the value of n, and the more likely that the system behaves as a dilute gas. A numerical justification of the condition $n \ll n_{max}$ is provided later.

One-particle approximation. For a given eigenvalue n_i of the number of molecules, we assume that the intermolecular force on a molecule is given approximately by a function of the coordinates of the particular molecule and not of the relative distance of that molecule and others. It is evident that the approximation is better the smaller the value of n_i. Nevertheless, it is used for all values of n_i of a dilute gas.

As a result of this approximation, the Hamiltonian operator corresponding to n_i can be expressed as a sum of Hamiltonian operators each associated with one molecule, that is, the Hamiltonian operator can be separated into additive parts, each of which depends on the coordinates of one molecule only. Each of the separated Hamiltonian operators defines a *one-particle energy eigenvalue problem*. The one-particle energy eigenstates can be combined to approximate the energy eigenstates of the dilute gas and then to compute equations of stable equilibrium states. When this is done the analysis is said to be approached by means of the method of the *one-particle approximation*.

The one-particle approximation is appropriate for dilute gases because the properties of such gases depend primarily on the energy eigenstates corresponding to small values n_i. For example, because in equation (15) n is much smaller than n_{max} and all x_i^{θ} are positive, the dependence of n on $n_i > n$ is weak, and errors introduced by the one-particle approximation are negligible.

Denoting the one molecule Hamiltonian operator by $\hat{H}_{mol}$ and its energy eigenvalues by e_j, we can express the energy eigenvalues of the dilute gas as follows. In the energy eigenstate G_i of energy E_i and number of molecules n_i, the gas can be thought of as made up of v_{ji} molecules

with one-particle energy e_1, ν_{i2} molecules with one-particle energy e_2,..., ν_{ij} molecules with one particle energy e_j,... so that E_i is given by the relation

$$E_i = \nu_{i1}e_1 + \nu_{i2}e_2 + \cdots + \nu_{ij}e_j + \cdots = \sum_j \nu_{ij}e_j \quad \text{for all } i \tag{19}$$

where

$$\sum_j \nu_{ij} = n_i \quad \text{for all } i \tag{20}$$

Each of the integers ν_{ij} is called an *occupation number*. Using equations (19) and (20) in equations (12), (13), and (15), we find

$$x_i^0 = \frac{\exp\left(\sum_j \nu_{ij}[(\mu - e_j)/kT]\right)}{Q_g} \tag{21}$$

$$Q_g = \sum_i \exp\left[\sum_j \nu_{ij}\frac{\mu - e_j}{kT}\right] \tag{22}$$

$$n = \sum_i x_i^0 n_i = \sum_i x_i^0 \sum_i \nu_{ij} = \sum_j \sum_i x_i^0 \nu_{ij} = \sum_j \nu_j \tag{23}$$

where ν_j is the (expectation) value of the number of molecules having one-particle energy e_j. This value is called the *one-particle distribution function*, and satisfies the relation

$$\nu_j = \sum_i x_i^0 \nu_{ij} \tag{24}$$

As shown in the Appendix, depending on whether the molecules are fermions or bosons, equations (22) to (24) become

$$\ln Q_g = \sum_j \ln\left[1 \pm \exp\left(\frac{\mu - e_j}{kT}\right)\right]^{\pm 1} \tag{25}$$

$$n = \sum_j \left[\exp\left(\frac{e_j - \mu}{kT}\right) \pm 1\right]^{-1} \tag{26}$$

$$v_j = \frac{1}{\exp[(e_j - \mu)/kT] \pm 1} \qquad \text{for all } j \tag{27}$$

where the plus sign in $\pm$ holds for fermions and the minus sign for bosons.

We can easily show that $\ln Q_g$ is almost equal to n if the chemical potential μ is very much smaller than zero because then $\exp[(\mu - e_j)/kT]$ (equation (25)) is much smaller than unity, and $\exp[(e_j - \mu)/kT]$ (equation (26)) much larger than unity for all j. To translate this conclusion into explicit restrictions on temperature and pressure, however, we need to introduce another approximation.

Constant-potential approximation. In the constant-potential approximation, the one-molecule Hamiltonian operator $\hat{H}_{mol}$ is written as a sum of two operators, that is,

$$\hat{H}_{mol} = \hat{H}_t + \hat{H}_{internal} \tag{28}$$

where we assume that the translational potential energy is zero and, therefore, $\hat{H}_t$ is given by equation (3) and depends only on the translational degrees of freedom x, y, z of the center of mass of a molecule, and $\hat{H}_{internal}$ is the Hamiltonian operator that describes the internal structure of the molecule and depends on its rotational, vibrational, and electronic degrees of freedom.[1]

Because here $\hat{H}_{mol}$ is separable into two Hamiltonian operators, its j-th energy eigenvalue satisfies the relation

$$e_j(r,s) = e_r + \varepsilon_s \tag{29}$$

where e_r is any one of the eigenvalues of $\hat{H}_t$ (equation (4)), and ε_s any one of the energy eigenvalues of $\hat{H}_{internal}$. For the sake of clarity, we emphasize that if there are M energy eigenvalues e_r of $\hat{H}_t$, and N energy eigenvalues ε_s of $\hat{H}_{internal}$, the molecule has $M \times N$ energy eigenvalues $e_j(r,s)$.

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[1] If the translational potential energy differs from zero, we approximate it by a constant (potential energy independent of x, y, z), and accordingly modify the results.

If relation (2) is valid, and the chemical potential μ is so negative that

$$\frac{\mu - \varepsilon_0}{kT} < 0 \tag{30}$$

then each exponential in equation (25) is much smaller than unity, and each exponential in equation (26) is much larger than unity, and these two equations and equation (18) yield

$$\frac{pV}{kT} = \ln Q_s = \sum_j \exp\left(\frac{\mu - e_j}{kT}\right) = n \tag{31}$$

$$= \exp\left(\frac{\mu}{kT}\right) \sum_{s=0} \exp\left(-\frac{\varepsilon_s}{kT}\right)\left[\int_0^\infty \exp\left(-\frac{h^2 r^2}{8mV^{2/3}kT}\right)dr\right]^3 = \exp\left(\frac{\mu}{kT}\right) q_s \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

where

$$q_s = \sum_{s=0} \exp\left(-\frac{\varepsilon_s}{kT}\right) \tag{32}$$

We see that conditions (2) and (30) are sufficient for the molecules to behave as an ideal gas, that is, for pV to equal nkT (first line of equation (31)). Moreover, we note that q_s (equation (32)) is the partition function of the internal structure of the molecule.

Now, upon combining the first and last terms in equation (31), solving for μ, and substituting the result in relation (30), we find

$$\mu = kT\ln\frac{ph^3}{q_s(2\pi m)^{3/2}(kT)^{5/2}} \tag{33}$$

$$\frac{ph^3}{(2\pi m)^{3/2}(kT)^{5/2}} < q_s\exp\left(\frac{\varepsilon_0}{kT}\right) \tag{34}$$

Thus we conclude that relatively high temperatures and relatively low pressures that satisfy relation (34) correspond to ideal gas behavior of the molecules.

Of course, the chemical potential (equation (33)) may be used to obtain practical expressions for the specific energy, the specific entropy, and the specific heats of the ideal gas, all expressed per molecule. Indeed,

$$u = U/n = -T^2\left[\frac{\partial(\mu/T)}{\partial T}\right]_p - pv = \frac{3}{2}kT + kT\frac{\partial \ln q_s}{\partial \ln T} \tag{35}$$

$$s = S/n = -\left(\frac{\partial \mu}{\partial T}\right)_p = k\ln\frac{q_s(2\pi m)^{3/2}(kT)^{5/2}}{ph^3} + \frac{5}{2}k + kT\frac{\partial\ln q_s}{\partial T} \qquad (36)$$

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p = \frac{5}{2}k + 2kT\frac{\partial\ln q_s}{\partial T} + kT^2\frac{\partial^2\ln q_s}{\partial T^2} \qquad (37)$$

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v = \frac{3}{2}k + 2kT\frac{\partial\ln q_s}{\partial T} + kT^2\frac{\partial^2\ln q_s}{\partial T^2} \qquad (38)$$

3. CONCLUSIONS

We introduce the novel idea that, in general, an energy measurement result on a simple system yields both an energy eigenvalue and a number of molecules eigenvalue. These eigenvalues are necessary to the evaluation of the grand partition function as well as (expectation) values of other stable equilibrium state properties of the system.

By a series of judiciously chosen approximations, we find explicit conditions on the temperatures and pressures for which any substance behaves as an ideal gas.

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APPENDIX: Fermions and Bosons

Depending on the nature of the identical molecules of a system, the admissible energy eigenfunctions can be either antisymmetric or symmetric. Antisymmetric energy eigenfunctions are admissible for a collection of molecules called fermions, and symmetric energy eigenfunctions are

admissible for a collection of molecules called bosons. For example, electrons are fermions, and photons are bosons. The distinction between fermions and bosons can also be stated in terms of the admissible values of the occupation numbers v_{ij}.

Fermions. Each one-particle energy eigenstate can be occupied by at most one fermion, that is, the admissible values of v_{ij} are

$$v_{ij} = 0 \text{ or } 1 \quad \text{for all } i \text{ and } j \tag{A-1}$$

For example, a spin-orbital of an atom can be either empty or occupied by only one electron.

Bosons. Each one-particle energy eigenstate can be occupied by any number of bosons, that is, the admissible values of v_{ij} are

$$v_{ij} = 0,1,2,... \quad \text{for all } i \text{ and } j \tag{A-2}$$

For example, any number of photons may occupy the same one-particle energy eigenstate.

Explicit use of the admissible values of v_{ij} in equations (22), (23), and (24) results in simplified forms for Q_g, n, and v_j. Indeed, if we introduce the short-hand notation

$$D_j = \exp\left(\frac{\mu - e_j}{kT}\right) \quad \text{for all } j \tag{A-3}$$

and $b_1,b_2,...$ are the admissible values for any of the numbers v_{ij}, then we can easily verify that equation (22) can be written in the forms

$$Q_g = \sum_i D_1^{v_{i1}} D_2^{v_{i2}}...D_j^{v_{ij}}... = \left(D_1^{b_1} + D_1^{b_2} + ...\right)\left(D_2^{b_1} + D_2^{b_2} + ...\right)...\left(D_j^{b_1} + D_j^{b_2} + ...\right)... \tag{A-4}$$

If the dilute gas consists of fermions, the admissible values of v_{ij} are $b_1 = 0$, $b_2 = 1$, and $b_i = 0$ for $i \geq 3$. Accordingly, equation (A-4) becomes

$$Q_g = (1 + D_1)(1 + D_2)...(1 + D_j)... = \prod_j\left[1 + \exp\left(\frac{\mu - e_j}{kT}\right)\right] \tag{A-5}$$

$$\ln Q_g = \sum_j \ln\left[1 + \exp\left(\frac{\mu - e_j}{kT}\right)\right] \tag{A-6}$$