ORIGINAL ARTICLE

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Thermodynamics of an ideal generalized gas:
I. Thermodynamic laws

Abstract The equations of state for an ideal relativistic, or generalized, gas, like an ideal quantum gas, are expressed in terms of power laws of the temperature. In contrast to an ideal classical gas, the internal energy is a function of volume at constant temperature, implying that the ideal generalized gas will show either attractive or repulsive interactions. This is a necessary condition in order that the third law be obeyed and for matter to have an electromagnetic origin. The transition from an ideal generalized to a classical gas occurs when the two independent solutions of the subsidiary equation to Lagrange's equation coalesce. The equation of state relating the pressure to the internal energy encompasses the full range of cosmological scenarios, from the radiation to the matter dominated universes and finally to the vacuum energy, enabling the coefficient of proportionality, analogous to the Grüeisen ratio, to be interpreted in terms of the degrees of freedom related to the temperature exponents of the internal energy and the absolute temperature expressed in terms of a power of the empirical temperature. The limit where these exponents merge is shown to be the ideal classical gas limit. A corollary to Carnot's theorem is proved, asserting that the ratio of the work done over a cycle to the heat absorbed to increase the temperature at constant volume is the same for all bodies at the same volume. As power means, the energy and entropy are incomparable, and a new adiabatic potential is introduced by showing that the volume raised to a characteristic exponent is also the integrating factor for the quantity of heat so that the second law can be based on the property that power means are monotonically increasing functions of their order. The vanishing of the chemical potential in extensive systems implies that energy cannot be transported without matter and is equivalent to the condition that Clapeyron's equation be satisfied.

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Incomparable thermodynamic laws

Thermodynamics distinguishes itself on being able to take into account processes involving heat transfer. According to Thomson [11], heat is the 'uncontrollable' form of work, and temperature is its measure. James Prescott Joule appreciated that heat and work were interconvertible, depending only on a constant for the units chosen to measure heat and mechanical work.

The first law was formulated as an expression for the conservation of internal energy even in the presence of heat transfer. The second law placed limitations on the amount of heat that could be converted into mechanical work. According to William Thomson (Lord Kelvin) [12]

> "it is impossible to construct an engine which when operated in a cycle will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work."

The second law also succinctly sums up observations of nature like "heat always passes from hotter to colder, and never in the reverse direction" [3], at constant volume. It also asserts that "heat will be absorbed as a gas expands to keep its temperature constant."

Carnot [4] not only discovered that there is an upper bound to the efficiency of engines operating in a closed cycle but also called attention to a truly mathematical invariant quantity that inspired Kelvin's later researches into the discovery of that entity. This invariant would be the same for all substances at the same temperature, and Kelvin equated it with the temperature measured on the ideal gas absolute scale. This factor proved to be an integrating denominator for the quantity of heat and became a matter of contention between Rudolf Clausius and Kelvin for its true authorship [10]. Thus, the entropy, like the internal energy, and in contrast to the quantity of heat, was identified as a point function which had the advantage of depending only on the instantaneous state of the body and not on the process by which the body arrived in that state.

To the best of our knowledge, there has never been any question of the compatibility of the first and second laws of thermodynamics. Certainly, the two laws are compatible for a classical ideal gas (ICG) because of the separability of the temperature and volume afforded by the logarithmic function. However, this is not true, in general, for an ideal generalized gas (IGG), or a 'quantum' gas (IQG) [7], which is the low-temperature extension of an ICG. Here, we make the distinction between an IGG and an ICG in that the former can be valid at all temperatures and not only in the high-temperature limit. This means that the transition between an IGG and an ICG occurs in a manner different than taking the high-temperature limit, and one in which we shall explore in the last section of this paper.

For an IGG, as well as an IQG, power laws are involved that contain products of different powers of the temperature and volume. And, in fact, one finds that for all processes other than those involving pure heat conduction, the power means derived from the first and second laws are incomparable.

In order to rectify this incompatibility, we will prove a corollary to Carnot's theorem, asserting that the ratio of the work done in a complete cycle to the heat absorbed on expansion at constant temperature is "the same for all substances at the same temperature." The corollary states that the ratio of the work done in a complete cycle to the heat absorbed on volume expansion at constant temperature is "the same for all substances at the same volume." This, in effect, replaces the isotherms of the Carnot cycle by isochores without affecting the efficiency of the cycle.

In addition to the inverse temperature, another integrating factor for the quantity of heat will be shown to exist [6] and leads to a new adiabatic potential, which will be comparable to the entropy, and differ from it by a power of the adiabatic variable. The difference between this new potential and the entropy is that it is not a first-order homogeneous function of the volume. This will enable a comparison of means involving processes which require work where, otherwise, the first and second laws would be mute since both the internal energy and the entropy are first-order homogeneous functions of the volume for an IGG.

The existence of a new adiabatic potential raises the question as to the actual content and predictive power of the second law. The irresistible increase in the entropy during an irreversible process will now be confronted with the same inevitable decrease in the new adiabatic potential. Irreversibility will have to be detached from quasi-static processes, which occur as a passage through a sequence of equilibrium states [1]. Irreversibility will apply to those processes where the initial and final states differ with respect to either their temperatures, or their volumes, or both. An equilibration resulting in the conservation of one of the two adiabatic potentials will depend on whether the temperature ratio of the two states or their inverse volume ratios, raised to a characteristic power, is equal to the ratio of quantities of heat absorbed or rejected at these temperatures or volumes. One conserving equilibration will be necessary in order to secure a final uniform state with a common mean value. General statements can be made about such conserving equilibrations: An entropy conserving equilibration has the lowest common final mean temperature or volume, implying that the maximum amount of work has been performed. In addition, thermal efficiency can never be inferior to mechanical efficiency.

In a companion paper [8], these statements will be translated into comparable power means and the lack of absoluteness of these potentials as a class of equivalent means. The metrizability of such a space of equivalent means will also be studied; the notion of a metric is entirely foreign to classical thermodynamics. Probability distributions and probabilistic notions will enter naturally whenever processes inside the system occur in an uncontrollable manner, like heat transfer and deformations. Evolution criteria will be shown to emanate from the fundamental property that power means are monotonically increasing functions of their order. Numerous mathematical inequalities will then be shown, like the Tchebychef and Jensen inequalities, which all predict an increase in entropy on the average or a decrease on the average of the complementary adiabatic potential. These mathematical inequalities will eliminate the need to have recourse to experiment, albeit one single experiment, to determine the sign of the entropy change or to that of the complementary adiabatic potential.

Power laws

If the absolute temperature, T, and volume, V, are chosen as the independent variables, the integrability condition for the entropy is

$$T\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial E}{\partial V}\right)_T + p, \tag{1}$$

where p is the pressure, and E is the internal energy. If the product pV measures the absolute temperature scale, then

$$\left(\frac{\partial E}{\partial V}\right)_T = 0. \tag{2}$$

In other words, in order for Boyle's law to be identical with the absolute temperature, it is necessary and sufficient that the internal energy be a *linear* function of the temperature alone [2].

If the pressure were to vary as some power of the temperature, say T^α, then from Eq. (1), we would have

$$\left(\frac{\partial E}{\partial V}\right)_T = \left[\left(\frac{\partial \ln p}{\partial \ln T}\right)_V - 1\right]p = (\alpha - 1)p. \tag{3}$$

Thus, the ICG condition (Eq. (2)) that pV measures the absolute temperature separates two domains: one in which Eq. (3) is positive, $\alpha > 1$, and the attractive nature of the gas implies that it will condense, and another region in which Eq. (3) is negative, $\alpha < 1$, and repulsion prevails, implying that the system has a zero-point energy [6].

Every gas comprised of mechanically noninteracting particles obeys an equation of state of the form [6]

$$pV = sE(V, T), \tag{4}$$

where $s>0$ is proportional to the adiabatic exponent. Introducing Eq. (4) into Eq. (1) converts it into the differential equation

$$E = T\left(\frac{\partial E}{\partial T}\right)_V - \frac{V}{s}\left(\frac{\partial E}{\partial V}\right)_T. \tag{5}$$

Treating Eq. (5) as a Lagrange equation, the auxiliary equations are

$$\frac{\mathrm{d}T}{T} = -\frac{s\mathrm{d}V}{V} = \frac{\mathrm{d}E}{E}.$$

There are two independent solutions, $TV^s=c$ and either $E/T=a$ or $EV^s=b$, where a, b, and c are arbitrary constants. The general solution is $\Psi_1(a, c)=\Psi_1(E/T, TV^s)=0$, i.e.,

$$E = T\psi_1(TV^s), \tag{6}$$

or $\Psi_2(b, c)=\Psi_2(EV^s, TV^s)=0$, i.e.,

$$E = V^{-s}\psi_2(TV^s), \tag{7}$$

where Ψ_i and ψ_i are arbitrary functions. The coefficients of E, namely, $1/T$ and V^s, will later be appreciated as integrating factors for the quantity of heat.

The functions ψ_i are solutions to the adiabatic equation

$$T\left(\frac{\partial \psi_i}{\partial T}\right)_V - \frac{V}{S}\left(\frac{\partial \psi_i}{\partial V}\right)_T = 0. \tag{8}$$

The auxiliary equations to Eq. (8) are

$$\frac{\mathrm{d}T}{T} = -\frac{s\mathrm{d}V}{V} = \frac{\mathrm{d}\psi_i}{0}.$$

There are again two independent solutions, $\psi_i=a$ and $TV^s=b$, so that the general solution to Eq. (8) is $\psi_i=\psi_i(z)$, in which T and V^s appear only through the combination $z=TV^s$.

For $\psi_1=$const., Eq. (6) is the thermal equation of state for an ICG, while for $\psi_2=$const., Eq. (7) is the zero-point energy. Whereas $E=aT$ is an approximate relation, valid in the high-temperature limit, so too $E=bV^{-s}$ can be considered an approximate relation, this time valid in the low-temperature limit [6]. These are the extreme cases where the internal energy is a function of either the absolute temperature, in the high-temperature limit, or the volume, in the low-temperature limit. The zero-point expresses the fact that particle interactions are repulsive, $(\partial E/\partial V)_T<0$, and such a system would be entirely mechanical since $\mathrm{d}Q=\mathrm{d}E+$

$p\mathrm{d}V=0$. However, there is another possibility in which the internal energy, as well as the entropy, tends to zero monotonically with the temperature.

The thermal equation of state (6) can be considered as an IGG, i.e., one for which the particle number, $N=\psi_1(V, T)$, is variable, being a function of the temperature. This will provide a very profound analogy between a two-phase classical system, like a Carnot engine, that was analyzed by Clapeyron by an equation bearing his name, and an IGG which does not conserve the number of particles.

In the case that E tends to zero monotonically with T, $\psi_2(z)$ may be approximated by $L(z) = cT^\alpha V^{s\alpha}$ at low temperatures, where all we demand for the present is that $\alpha>0$. According to Eq. (4), the internal energy, $E = cT^\alpha V^{(\alpha-1)_s}$, gives a pressure $p = scT^\alpha V^{(\alpha-1)s-1}$. For dynamic stability, we require

$$\left(\frac{\partial p}{\partial V}\right)_T = [(\alpha - 1)s - 1]\frac{p}{V} < 0.$$

However, if the internal energy is to retain its property of being a first-order homogeneous function, we must have $(\alpha-1)s=1$, implying

$$\left(\frac{\partial p}{\partial V}\right)_T = 0, \tag{9}$$

or a phase equilibrium [6]. Varying the volume at constant temperature leaves the vapor pressure constant by having the liquid either evaporate or condense. This is precisely the condition under which the Clapeyron equation is valid. For an IGG, the volume of the second phase is nil since there is no longer particle conservation, $N=\psi_1(V, T)$ $\neq$const. This fine balance keeps the pressure independent of the volume and the internal energy a first-order homogeneous function

$$p = scT^{q/r} \quad E = cT^{q/r}V. \tag{10}$$

In the low-temperature limit, $\psi_2(z)$ can be replaced by

$$L(z) = a + cz^{q/r}, \tag{11}$$

where $a>0$. Then, since $EV^s=L(z)$

$$E = V^{-s}\left(a + cz^{q/r}\right),$$

and $(\partial E/\partial V)_T<0$ if a is finite, or $(\partial E/\partial V)_T>0$ if a vanishes, and $q>r$. In the latter case, the pressure must satisfy Eq. (9), so that $s=r/(q-r)$. Furthermore, $E/T=\psi_1(z)=L(z)/z$, and $\mathrm{d}(EV^s)/z=\mathrm{d}L(z)/z=:\mathrm{d}S$, where

$$S(z) = \frac{q}{q - r}cz^{1/s} = \frac{q}{q - r}\psi_1(z) \tag{12}$$

is the entropy.

Hence, no decision can be made between the Planck ($S=0$ at $T=0$) and the Nernst (S=const. at $T=0$) formulations of the third law because the concept of absolute entropy is meaningless. Moreover, we will see in the following paper that an absolute $L(z)$ is also meaningless since only its difference is measurable.

The difference between the enthalpy,

$$H = U + pV = (1+s)cT^{q/r}V,$$

and T times the entropy, Eq. (12), is

$$G = \left(1 + s - \frac{q}{q-r}\right)cT^{q/r}V. \tag{13}$$

The Gibbs free energy (Eq. (13)) presents itself as a measure of non-extensivity and vanishes when $s=r/(q-r)$ [6].

The second laws

The quantity of heat, dQ, which must be absorbed by a body to make its temperature rise to $T+dT$ and its volume expand to $V+dV$ is

$$dQ = MdV + NdT. \tag{14}$$

This caloric equation, familiar to nearly all the thermodynamicists, undoubtedly fell out of favor due to the fact [5]

"that Q cannot be a function of V and T, if these variables are independent of each other. For if it were, then by the well-known law of the differential calculus, that if a function of two variables is differentiated with respect to both of them, the order of differentiation is indifferent"

and this was definitely not so with Eq. (14). In fact, the exactness condition of the internal energy,

$$dU = dQ - pdV = (M-p)dV + NdT,$$

shows that their difference gave [12]

$$\frac{dp}{dT} = \frac{\partial M}{\partial T} - \frac{\partial N}{\partial V}. \tag{15}$$

This led Planck [9] to remark that the notation dQ

has frequently given rise to misunderstanding, for dQ has been repeatedly regarded as the differential of a known finite quantity Q. This faulty reasoning may be illustrated by the following example.

And the example Planck gave resulted in Eq. (15), which Thomson took merely as a statement of the first law.

The statement that he took as the second law was Clapeyron's equation

$$\frac{dp}{dT} = \frac{M}{C(T)} \tag{16}$$

where $C(T)$ is the reciprocal of the Carnot function, which Thomson showed was equal to the absolute temperature, T. That is, the ratio of the total work done in an infinitesimal cycle, $\frac{dp}{dT}dTdV$, to the ratio of the heat absorbed in the first branch of the Carnot cycle, MdV,

$$\frac{\frac{dP}{dT}dT}{M} = \frac{dT}{C(T)} \tag{17}$$

must be the product of dT and a function of T only. The "very remarkable theorem that $dp/dT/M$ must be the same for all substances at the same temperature was first given (although not in precisely the same terms) by Carnot" [12].

For an ICG, $M=p$, because the internal energy is a function of the absolute temperature alone, and N, as Clausius realized, "can be a function of T only. It is even probable that this magnitude [N], which represents the specific heat of the gas at constant volume, is a constant."

In contrast, for an IGG,

$$M = \left(1 + \frac{1}{s}\right)p = \frac{q}{r}p, \tag{18}$$

and

$$N = \frac{q}{r}\frac{E}{T}, \tag{19}$$

or, equivalently,

$$\frac{M}{N} = \frac{sT}{V}.$$

Expression (18) invalidates Clausius' conclusion that "a permanent gas, when expanded at constant temperature, takes up only so much heat as is consumed doing external work during the expansion." Clausius' conclusion is based on the fact that the working substance was an ICG, obeying $pV=T$, while Eq. (18) shows that an IGG absorbs more since $q>r$, or that the internal energy is a function of volume at constant temperature.

To convert dQ into the total differential of a certain function, we introduce the integrating factor λ and require

$$\frac{\partial \lambda M}{\partial T} = \frac{\partial \lambda N}{\partial V}. \tag{20}$$

The exactness condition (Eq. (20)) can be rearranged to read

$$\left(\frac{\partial M}{\partial T} - \frac{\partial N}{\partial V}\right) = N\frac{\partial \ln \lambda}{\partial V} - M\frac{\partial \ln \lambda}{\partial T}. \tag{21}$$

By a composite system argument, λ can only be a function of T or V. Consider two simple fluids in thermal contact; such a system will have three independent variables T, V_1 and V_2. The integrating factor can only be a function of the common variable T [3]. Hence,

$$\frac{\left(\frac{\partial M}{\partial T} - \frac{\partial N}{\partial V}\right)}{M} = \frac{d \ln \lambda}{dT}.$$

On the strength of the exactness condition for the internal energy (Eq. (15)), this is equivalent to the Clapeyron's equation (Eq. (17)), and on the strength of Carnot's theorem, $C(T)=T$ is the integrating denominator for the increment in the heat, dQ, giving the entropy, (Eq. (12)), which depends on V and T only through the combination $z=TV^s$.

Now consider two simple fluids in mechanical contact, for which the independent variables are V, T_1, and T_2. Again, the integrating factor λ can only be a function of the variable in common to both subsystems so that the exactness condition (Eq. (21)) now reduces to

$$\frac{\frac{dp}{dT} dT dV}{N dT} = d \ln \lambda(V). \tag{22}$$

By interchanging isochores for isotherms, NdT is the quantity of heat absorbed in the first segment of an equivalent Carnot cycle, as we shall discuss in the next section. The very remarkable fact, equivalent to Carnot's theorem, is that the right-hand side is the product of dV and a function only of the volume. Thus, $dp/dT/N$ is the same for all substances at the same volume. For an IGG, $\lambda(V)=V^s$ [6], which reduces to $\lambda(V) = V^{R/C_v}$ for an ICG, where C_v is the heat capacity at constant volume, and R is the gas constant, which will only be introduced in conjunction with C_v.

The integrating factor $\lambda(V)$ for the increment in the heat, dQ, now gives the point function (Eq. (11)), which, again, depends on V and T only through the combination, z. However, whereas the entropy (Eq. (12)) is extensive, the potential (Eq. (11)) is not.

Consider any two states 1 and 2, with $T_1>T_2$ for concreteness. Any process connecting the two states will be said to be irreversible if

$$z_1 > z_2. \tag{23}$$

Rearranging Eq. (23), we get $V_1^s/V_2^s > T_2/T_1$ so that the thermal efficiency,

$$\eta_t = 1 - \frac{T_2}{T_1} \geq 1 - \frac{V_1^s}{V_2^s} = \eta_v,$$

can never be inferior to the mechanical efficiency, η_v.

If Q_1 and Q_2 are quantities of heat absorbed and rejected at T_1 and T_2, respectively, then we say that there is *thermal equilibration* if

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1} \geq \frac{V_1^s}{V_2^s},$$

whereas there is *mechanical equilibration* if

$$\frac{V_1^s}{V_2^s} = \frac{Q_2}{Q_1} \leq \frac{T_2}{T_1}.$$

More work can be accomplished during a thermal equilibration than a mechanical one since the system achieves a lower final temperature, T_2.

For any infinitesimal narrow Carnot cycle, the ratio Q_2/Q_1 may be replaced by its differential, dQ_2/dQ_1. Thermal equilibration results when

$$\oint \frac{dQ}{T} = 0, \tag{24}$$

and

$$\oint V^s dQ \geq 0, \tag{25}$$

while mechanical equilibration requires

$$\oint V^s dQ = 0, \tag{26}$$

and

$$\oint \frac{dQ}{T} \leq 0, \tag{27}$$

since any irreversible cycle is necessarily less efficient than a Carnot cycle, $dQ_2/dQ_1 < T_2/T_1$.

For processes of pure thermal conduction, we would identify Eq. (26) with the first law, and the conservation of energy over the entire cycle, and Eq. (27) as the statement of the second law. However, for purely mechanical interactions, neither Eq. (27) nor the first law would give an evolutionary criterion since the internal energy and entropy are first-order homogeneous functions of the volume. The criteria of mechanical equilibration would fix the final volume as the weighted arithmetic mean of the partial volumes according to Eq. (25), while Eq. (24) shows that L would tend to decrease since the arithmetic mean is inferior to the power mean of order $q/(q-r)$.

If we split the cycle up into two segments, $A \rightarrow B$, and $B \rightarrow A$, where the former contains all the irreversibility, then Eq. (25) gives

$$\int_A^B V^s dQ > L_B - L_A,$$

while Eq. (27) becomes

$$S_B - S_A > \int_A^B dQ/T.$$

If the infinitesimal increment in the heat is the sum of the infinitesimal heat dQ_e introduced into the system or extracted from it, and the sum of irreversible heat transfers within the system,

$$dQ = dQ_e + \sum_{i=1}^n dQ_i,$$

then for an isolated system $dQ_e = 0$,

$$L_B - L_A < \sum_{i=1}^n \int_A^B V^s dQ_i, \tag{28}$$

under the condition that $\sum_{i=1}^n \oint dQ_i/T = 0$, or

$$S_B - S_A > \sum_{i=1}^n \int_A^B \frac{dQ_i}{T}, \tag{29}$$

under the condition that $\sum_{i=1}^n \oint V^s dQ_i = 0$. Inequality (29) is referred to as Clausius' inequality, while inequality (28) appears to be novel.

For each individual process of heat transfer, dQ_i will appear twice: once as a positive quantity and once as a negative quantity. The second law (Eq. (29)) asserts that the integrating denominator in the former is smaller than in the latter, since 'heat flows spontaneously from a hotter to a colder body at constant volume.' Alternatively, according to Eq. (28), 'as heat is absorbed the gas expands at constant temperature,' so that the integrating factor of the former will be smaller than the latter.

Either Eq. (28) or Eq. (29) can be taken as statements of the second law, depending on the constraints imposed. It is quite remarkable that both criteria can be formulated in terms of *comparable* means, and their fundamental property that the power mean is a monotonic increasing function of its order will be investigated thoroughly in the following paper.

An equivalent Carnot cycle

An equivalent cycle to that of Carnot can be obtained by replacing isothermals by isochores. This will prove a very remarkable theorem that $dp/dT/N$ must be the same for all substances at the same volume, which is precisely analogous to Carnot's theorem that $dp/dT/M$ must be the same for all substances at the same temperature.

The cycle consists of:

1. Absorption of a quantity of heat Q_1, at a constant volume V_1, by compression which raises the absolute temperature from T_1 to T_2 and consequently increases the pressure
2. An adiabatic expansion to a state of larger volume V_2 and lower temperature T_3

3. The rejection of a quantity of heat Q_2 by expansion which lowers the temperature to T_4 at constant volume V_2
4. An adiabatic compression which restores the system to volume V_1 and temperature T_1

The adiabatic branches provide the following ratios:

$$\frac{V_1^s}{V_2^s} = \frac{T_3}{T_2} = \frac{T_4}{T_1}.$$

The ratio of the heat rejected, $|Q_{3\to4}|$, to the heat absorbed, $Q_{1\to2}$ is

$$\frac{|Q_{3\to4}|}{Q_{1\to2}} = \frac{V_1^s}{V_2^s},$$

and the efficiency of the engine

$$\eta_v = 1 - \frac{V_1^s}{V_2^s},$$

is the same as the Carnot thermal efficiency, η_t.

Now, for an infinitesimal cycle, the ratio of the total work performed to the heat absorbed at constant volume is Eq. (22), which is the same for all substances at the same volume. This, as we have shown in the last section, is equivalent to Carnot's theorem (Eq. (17)).

Both Eqs. (17) and (22) give the same Clapeyron equation, which, when integrated, give the pressure in Eq. (10), independent of volume for a homogeneous system. While it was realized that dp/dT was a function of the temperature alone [5], it was not appreciated that the mechanical ICG equation of state, $pV=T$, could not be used to evaluate the work.

The transition IGG→ICG

The absolute temperature, T, and the empirical temperature, t, will coincide only for an ICG. For an ICG, pV reads the temperature, and E is a function of the temperature alone, independent of the volume. In contrast for an IGG, p will be independent of the volume, and E will be a function of it. In addition, E will no longer be a linear function of the temperature.

The only demand made by the zeroth law is that when two identical systems are placed in thermal contact, their empirical temperatures be the same when a state of mutual thermal equilibrium has been reached. Once the empirical scale has been chosen, the absolute temperature must be a monotonically increasing function of it, viz.,

$$T(t) = t^r,$$

with $r \geq 1$.

On the empirical temperature scale, E will vary as t^q, where $q \geq r$ with the equality sign pertaining to the ICG limit. Whereas the exponent r is related to the average

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kinetic energy of the particles, the exponent q is related to additional forms of energy, like the energy required to create or annihilate particles, since for an IGG, the particle number is not conserved. As a matter of fact, the vanishing of the difference of the two exponents will signal the transition from an IGG to an ICG, as we shall now show. This is in distinction to the transition between an IQG and an ICG, which occurs only in the high-temperature limit.

It is notable that in the limit as $q \rightarrow r$, the entropy (Eq. (12)) is of the indeterminate form 0/0. Applying L'Hôpital's rule, we get

$$\lim_{q \rightarrow r} S(z) = c \ln z,$$

where $z = TV^{R/C_v}$. Identifying c as C_v gives

$$\lim_{q \rightarrow r} S(z) = C_v \ln T + R \ln V.$$

In the same limit,

$$\lim_{q \rightarrow r} L(z) = C_v T^{R/C_v},$$

and consequently, either

$$dE = T dS(z) - p dV = C_v dT$$

or

$$dE = \frac{1}{V^{R/C_v}} dL(z) - p dV = C_v dT,$$

which is the thermal equation of state of an ICG.

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