The uniqueness of Clausius' integrating factor

Volker C. Weiss[a)]
School of Engineering and Science, International University Bremen, P. O. Box 750561, 28725 Bremen, Germany

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For a closed system that contains an arbitrary pure substance, which can exchange energy as heat and as expansion/compression work, but no particles, with its surroundings, the inexact differential of the reversibly exchanged heat is a differential in two variables. This inexact differential can be turned into an exact one by an integrating factor that, in general, depends on both variables. We identify the general form of the integrating factor as the reciprocal temperature (Clausius' well-known $1/T$), which is guaranteed to be a valid integrating factor by the second law of thermodynamics, multiplied by an arbitrary function of the implicit adiabat equation $\xi(T,V)=\text{constant}$ or $\xi(T,P)=\text{constant}$. In general, we cannot expect that two different equations of state (corresponding to two different substances) predict identical equations for the adiabats. The requirement of having a universal integrating factor thus eliminates the volume-dependent or pressure-dependent integrating factors and leaves only a function of temperature alone: Clausius' integrating factor $1/T$. The existence of other integrating factors is rarely mentioned in textbooks; instead, the integrating factor $1/T$ is usually taken for granted relying on the second law or, occasionally, one finds it "derived" incorrectly from the first law of thermodynamics alone.

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I. INTRODUCTION

A central theme in the history of thermodynamics is the quest for state functions that describe the changes of all measurable equilibrium quantities in terms of a set of thermodynamic state variables, that is, a set of variables that uniquely determine a thermodynamic state. Equilibrium thermodynamics is based on two laws, each of which identifies such a state function. The principle of energy conservation implies that any change of the internal energy U of a closed system is caused by a transfer of heat q into or out of that system or by work w being done on or by the system.[1] In differential form, the first law of thermodynamics thus reads

$$dU=\delta q+\delta w. \tag{1}$$

The differential of the state function U is exact, while the differentials of heat and work are not (see below); the latter fact is indicated by using the symbol δ instead of d for these differentials. Quantities that have exact differentials are state functions, which means that the difference of the values of such a quantity at two different state points depends only on the position of these points, but not on the path that is taken to get from the initial point to the final one. In contrast, for quantities with inexact differentials, the difference depends on the initial and final state points and the choice of the path connecting them.[2]

The introduction of the state function U separates possible processes (those that conserve energy) from impossible processes (those that violate the principle of energy conservation). This separation is not sufficient because not all processes that can happen will happen; some of them are (much) more likely to occur than others. Hence, a second state function is needed to separate the likely (spontaneously occurring) processes from the unlikely ones. If we focus on reversible processes[3] and assume that the system can only exchange heat and expansion/compression work with its surroundings, the infinitesimal amount of work can be expressed as $\delta w_{\text{rev}}=-PdV$, where P denotes the pressure and V the volume of the system. Thus, we obtain

$$dU=\delta q_{\text{rev}}+\delta w_{\text{rev}}=\delta q_{\text{rev}}-PdV. \tag{2}$$

Because δw_{rev} is given by purely mechanical variables, δq_{rev} is the only quantity left to provide us with the sought-for second state function. As state functions have exact differentials, an integrating factor is needed at this point. An integrating factor f is a function that accomplishes the goal of turning an inexact differential, such as δq_{rev}, into an exact one. This new exact differential $f\delta q_{\text{rev}}=dS_{\text{gen}}$, where the subscript "gen" stands for "generalized" in a sense that will become clear later, is now associated with a state function S_{gen}.

The second law of thermodynamics can be divided into two important parts, which are summarized by the following statements:[4]

- (2a) The reciprocal of the absolute temperature $1/T$ is an integrating factor for the differential of the reversibly exchanged heat δq_{rev} for all thermodynamic systems (Carnot's theorem), which implies the existence of a new state function, the entropy S (with the exact differential $dS=T^{-1}\delta q_{\text{rev}}$).
- (2b) In any irreversible adiabatic process, the entropy increases—as implied by Clausius' inequality $dS\geqslant\delta q/T$, where the equality holds only for reversible processes.

In the following, we will illustrate that $1/T$ is an integrating factor for the ideal gas and then ask if, for this fluid, there are other integrating factors for δq_{rev}. It can be shown that, if there is one integrating factor, there are infinitely many more,[5] although most textbooks omit this point. We will identify these alternative integrating factors, but we will not be concerned about whether the state functions S_{gen} (generalized entropies) based on these alternative integrating factors really separate probable from improbable processes, that

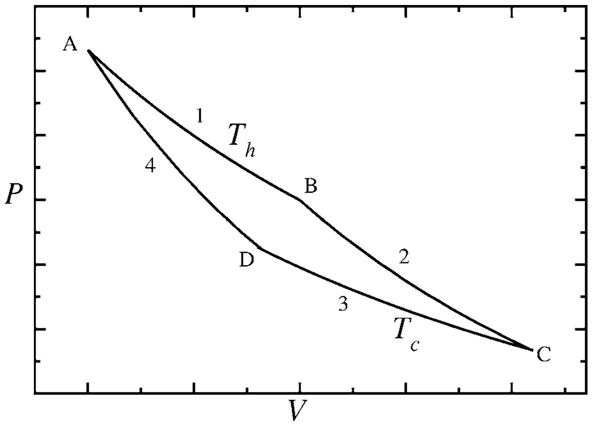

Fig. 1. Representation of the Carnot cycle in the pressure-volume plane. An isothermal expansion (1) at temperature T_h takes the system from state A to state B; the system then expands adiabatically (2) to point C and the temperature drops to T_c. At this temperature, a compression (3) to state point D occurs isothermally. An adiabatic compression (4) completes the cycle and takes the system back to the starting point A at the higher temperature T_h.

is, whether an analogous law of increasing entropy S_{gen} holds for them. Instead, we will concentrate on the question of the uniqueness of the integrating factor that turns δq_{rev} into an exact differential.

Based on Carnot's observation that the efficiency of a reversibly working heat engine depends only on the temperatures of the heat source and the heat sink, Clausius assumed that the integrating factor is a function of temperature T only and gave $1/T$ as the solution to the problem of turning δq_{rev} into an exact differential.[6] Many textbooks[2] use the Carnot cycle to illustrate that $\delta q_{\text{rev}}/T$ is an exact differential for an ideal gas: Starting from point A in Fig. 1, the working substance, a monatomic ideal gas, expands isothermally along path 1 at temperature T_h to state point B. From there, an adiabatic expansion takes it to point C at a lower temperature T_c at which the system is, subsequently, compressed isothermally to point D. An adiabatic compression returns the system to starting point A.

The equations of state for the pressure and the internal energy of a monatomic ideal gas are

$$P = \frac{NkT}{V}, \tag{3}$$

$$U = \frac{3}{2}NkT, \tag{4}$$

where N is the number of particles and k is Boltzmann's constant. During the isothermal expansion 1, the heat transferred to the system is

$$q_1 = NkT_h \ln(V_B/V_A). \tag{5}$$

There is no heat exchange during the adiabatic processes 2 and 4, and we have $q_2 = q_4 = 0$. Upon isothermal compression 3, the heat loss of the system is

$$q_3 = NkT_c \ln(V_D/V_C). \tag{6}$$

From the adiabat equation, which for the monatomic ideal gas is $TV^{2/3}$=constant, we can infer that the four volumes are related by $V_B/V_A = V_C/V_D$. Using this relation, we obtain $q_1/T_h + q_3/T_c = 0$, indicating that the sum (integral) over a closed cycle is zero, as required for a path-independent change.

A more formal way of deriving an integrating factor that does not require using the Carnot cycle considers the first law directly.[7–9] From Eq. (2), the differential of the reversibly exchanged heat is obtained as

$$\delta q_{\text{rev}} = dU + PdV. \tag{7}$$

We regard U as a function of T and V and write its exact differential as

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \tag{8}$$

Substituting Eq. (8) into Eq. (7), we obtain

$$\delta q_{\text{rev}} = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV, \tag{9}$$

where the definition $C_V = (\partial U/\partial T)_V$ has been used. The differential in Eq. (9) is exact if (and only if):

$$\frac{\partial C_V}{\partial V} = \frac{\partial\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]}{\partial T}, \tag{10}$$

which is not the case for the monatomic ideal gas because $Nk/V \neq 0$.

If we now multiply Eq. (9) by a function $f(T)$, such that

$$\frac{\partial[f(T)C_V]}{\partial V} = \frac{\partial\left[f(T)\left(\frac{\partial U}{\partial V}\right)_T + f(T)P\right]}{\partial T} \tag{11}$$

is satisfied, δq_{rev} is turned into an exact differential by the integrating factor $f(T)$. For the monatomic ideal gas, Eq. (11) leads to an ordinary differential equation for $f(T)$:

$$0 = f'(T)P + f(T)\left(\frac{\partial P}{\partial T}\right)_V, \tag{12}$$

where the prime denotes the derivative of f with respect to its argument. Because $(\partial P/\partial T)_V = P/T$ for the ideal gas, the solution of the differential equation (12), which can be written as $0 = Tf'(T) + f(T)$, is

$$f(T) = c_0 T^{-1}, \tag{13}$$

where c_0 is an arbitrary constant. No other function of T alone can turn δq_{rev} into an exact differential; the integrating factor $1/T$ is therefore unique among all $f(T)$. (The value of the constant c_0 is irrelevant as long as $c_0 \neq 0$, so we may choose $c_0 = 1$ for convenience.) The new state function was termed entropy by Clausius, its differential is $dS = \delta q_{\text{rev}}/T$.

The question remains as to whether $f(T) = c_0 T^{-1}$ is the *only* integrating factor for δq_{rev}. Vemulapalli[7] has suggested dividing δq_{rev} by the pressure instead of the temperature to illustrate that there is something special about the integrating factor $1/T$, because multiplication of δq_{rev} by $1/P$ does not yield an exact differential for an ideal gas. Mathematically, however, it can be shown that Pfaff differential forms in two variables, such as the right-hand side of Eq. (9), have infinitely many integrating factors,[5] so that $1/T$ appears to be just one of many. In Sec. II, we will identify these more general integrating factors that, in addition to being functions of the temperature, may also depend on volume or on pressure, respectively. The derivation will show that $P^{-2/5}$, unlike the factor $1/P$ suggested in Ref. 7, is a valid integrating factor for the ideal gas that depends only on the pressure.

Note that we assume $1/T$ to be an integrating factor by virtue of the second law. Although $1/T$ is valid for the ideal gas, its validity cannot be extended to general thermodynamic systems without referring to the second law.[10] Attempts to do so are flawed, but are found, for example, in Refs. 8 and 9.

II. THE GENERALIZED INTEGRATING FACTORS

A. Volume-dependent integrating factors

We first consider an integrating factor of the form $f(T,V)$. The condition for an exact differential after multiplying both sides of Eq. (9) by $f(T,V)$ becomes:

$$\frac{\partial[f(T,V)C_V]}{\partial V}=\frac{\partial}{\partial T}\left[f(T,V)\left(\frac{\partial U}{\partial V}\right)_T+f(T,V)P\right], \tag{14}$$

which, after differentiation, can be rearranged to give the following partial differential equation:

$$C_V\left(\frac{\partial f}{\partial V}\right)_T-\left[P+\left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial f}{\partial T}\right)_V =\left[\left(\frac{\partial P}{\partial T}\right)_V+\left(\frac{\partial(\partial U/\partial V)_T}{\partial T}\right)_V-\left(\frac{\partial C_V}{\partial V}\right)_T\right]f, \tag{15a}$$

$$=\left(\frac{\partial P}{\partial T}\right)_V f, \tag{15b}$$

where Schwarz's theorem $(\partial^2U/\partial V\partial T)=(\partial^2U/\partial T\partial V)$ has been used because U is a state function as we know from the first law of thermodynamics. Equation (15b) is a homogeneous first-order partial differential equation of the general form

$$a(T,V)f_V+b(T,V)f_T=c(T,V)f, \tag{16}$$

where f_x is a shorthand notation for the partial derivative of f with respect to the variable x. One way of solving Eq. (16) is the method of characteristics.[11] The idea of this method is to identify special paths in the (T,V) plane, the characteristics, along which the partial differential equation reduces to an ordinary differential equation, which can then be solved relatively easily. This simplification is achieved by a transformation of variables. We introduce $\xi(T,V)$ and $\eta(T,V)$ and use the chain rule to express Eq. (16) as

$$af_\xi\xi_V+af_\eta\eta_V+bf_\xi\xi_T+bf_\eta\eta_T=cf. \tag{17}$$

With $A=a\xi_V+b\xi_T$ and $B=a\eta_V+b\eta_T$, Eq. (17) becomes

$$Af_\xi+Bf_\eta=cf. \tag{18}$$

The condition for Eq. (18) to reduce to an ordinary differential equation with ξ constant and η as the only variable with respect to which derivatives are taken, is $A=a\xi_V+b\xi_T=0$. On the other hand, if $\xi(T,V)$ is constant, we have $d\xi=\xi_V dV+\xi_T dT=0$, and therefore,

$$\frac{dT}{dV}=\frac{b(T,V)}{a(T,V)}, \tag{19}$$

which represents the defining equation of the desired characteristics in terms of the original variables T and V. For Eq. (15b), the characteristics are given by:

$$\frac{dT}{dV}=-\frac{P+\left(\frac{\partial U}{\partial V}\right)_T}{C_V}. \tag{20}$$

These characteristics are nothing but the adiabats defined by $\delta q_{\text{rev}}=0$; if we use this relation in Eq. (9), we obtain Eq. (20). The reversible adiabats that we are considering here are also referred to as isentropes (lines of constant entropy) because, in a reversible process, there is no change in entropy if no heat is exchanged.

The ordinary differential equation (with respect to η),

$$B(T,V)f_\eta=cf, \tag{21}$$

is simple to solve if we choose η to be a function of just one of the original variables, T or V. Either is possible, but let us choose $\eta=T$ to retain the empirically valid integrating factor $1/T$ in a transparent way. The choice $\eta=V$ would lead to the same result. Furthermore, once we know that $1/T$ is a valid integrating factor, it can be shown that the general integrating factor $f(T,V)$ may be factorized according to $f(T,V)=T^{-1}g(T,V)$,[4,5] where g is a function that we are about to determine. Because Eq. (21) is a first-order partial differential equation, we expect only one arbitrary function to occur in the general solution. Thus, with $\eta_V=0$ and $\eta_T=1$, we arrive at

$$bf_\eta=cf \tag{22}$$

or, for Eq. (15b),

$$-\left[P+\left(\frac{\partial U}{\partial V}\right)_T\right]\frac{\partial f}{\partial T}=\left(\frac{\partial P}{\partial T}\right)_V f. \tag{23}$$

Equation (23) simplifies to a well-known ordinary differential equation if

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial P}{\partial T}\right)_V-P, \tag{24}$$

which is the requirement for $1/T$ to be an integrating factor.[8] If this condition is satisfied, we obtain

$$-T\frac{\partial f}{\partial T}=f, \tag{25}$$

the solution to which we have seen already: $f=c_1T^{-1}$. This result comes as no surprise because we have assumed that Eq. (24) is satisfied, but it goes beyond the result quoted in Eq. (13) because c_1 is actually an arbitrary function of the constant $\xi(T,V)$, and, therefore, a particular combination of the variables T and V as defined by the characteristics, the adiabats, in Eq. (20). The integrating factor can thus be written as $f=T^{-1}g(\xi(T,V))$, where g can be any differentiable function.

For the monatomic ideal gas, the adiabats are defined by the condition $TV^{2/3}=\text{constant}$,[2] and we obtain the generalized integrating factor $f=T^{-1}g(TV^{2/3})$. If we set $\eta=V$ in Eq. (21), we would find $f=V^{2/3}g_1(TV^{2/3})$, an equivalent result because both g and g_1 are arbitrary functions, so we may choose $g_1(x)=g(x)/x$ to obtain identical expressions.

Now that we have identified the general integrating factors for the ideal gas, we need to determine if they hold for other systems as well. For convenience, we consider the simplest system that shows deviations from ideal gas behavior: The hard sphere fluid. The interaction between two particles of this system is infinite if the two spheres overlap, that is, if the separation of their centers, r, is less than the diameter σ of the spheres; the interaction is equal to zero if $r>\sigma$. Due to the lack of a natural temperature scale for this system (neither zero nor infinity is suitable for defining a temperature scale), the virial coefficients B_n are determined only by σ. For example, the second virial coefficient is given by $B_2=2\pi\sigma^3/3$.

The pressure of the hard sphere fluid will be higher than that of an ideal gas at the same number density $\rho=N/V$ at any given temperature due to the excluded volume.[12] The internal energy is the same as for the ideal gas because the spheres cannot overlap and there is no interaction if they do not overlap. For low densities, the pressure can be represented by a virial series:[13]

$$P = kT\rho + kT\sum_{n=2}^{\infty} B_n(T)\rho^n. \tag{26}$$

For the hard sphere fluid, the virial coefficients B_n do not depend on temperature, and we have

$$P = kT\rho + kT\sum_{n=2}^{\infty} B_n\rho^n, \tag{27}$$

$$U = \frac{3}{2}NkT. \tag{28}$$

In this case, the adiabats can be calculated explicitly from Eq. (20):

$$TV^{2/3}\exp\left(-\frac{2}{3}\sum_{n=2}^{\infty}\frac{1}{n-1}\frac{N^{n-1}}{V^{n-1}}B_n\right) = \text{constant}. \tag{29}$$

Because Eq. (24) is satisfied for the hard sphere fluid (just as for the ideal gas, implying the validity of $1/T$ as an integrating factor for both of them), the generalized integrating factor for the hard sphere fluid can be written as:

$$f = T^{-1}h\left[TV^{2/3}\exp\left(-\frac{2}{3}\sum_{n=2}^{\infty}\frac{1}{n-1}\frac{N^{n-1}}{V^{n-1}}B_n\right)\right], \tag{30}$$

where h is an arbitrary differentiable function. The only way that the function f can be the same as for the ideal gas, $f=T^{-1}g(TV^{2/3})$, is if $h=g=$constant due to the different ways in which g and h depend on T and V. The requirement of having a universally applicable integrating factor leaves only T^{-1}.

To illustrate the consequences of this requirement explicitly, we define a generalized entropy based on the integrating factor of the monatomic ideal gas, $f=T^{-1}g(TV^{2/3})$. At this point, the requirement that the entropy based on any integrating factor should be an extensive quantity (a homogeneous function of the first degree) rules out all nonintensive integrating factors, that is, all but the one obtained from $g=1$ (or, at least, $g=$constant). (This argument, however, will not apply to the pressure-dependent integrating factors of Sec. II B.) For volume-dependent integrating factors, it is, nevertheless, instructive to ignore this additional requirement for the time being and to continue by defining:

$$dS_{\text{gen}} = T^{-1}g(TV^{2/3})\,\delta q_{\text{rev}}. \tag{31}$$

The application of the Legendre transformation to replace S_{gen} by the variable T results in the following generalized Helmholtz free energy:

$$A_{\text{gen}} = U - \frac{T}{g(TV^{2/3})}S_{\text{gen}}. \tag{32}$$

The condition that both the internal energy U and the generalized Helmholtz free energy A_{gen} have to be state functions and thus have exact differentials yields two Maxwell relations. Introducing the notation $x=TV^{2/3}g'/g$, where the prime indicates differentiation with respect to the argument, we write

$$\left(\frac{\partial(T/g)}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \tag{33}$$

$$-\left(\frac{\partial[S(1-x)/g]}{\partial V}\right)_T = \left(\frac{\partial[2xTS/(3Vg)-P]}{\partial T}\right)_V, \tag{34}$$

which for $g=1$, implying $x=0$, reduce to the well-known Maxwell relations in standard thermodynamics.

For the differential of the generalized entropy, which is obtained by inserting Eq. (9) into Eq. (31),

$$dS_{\text{gen}} = \frac{g}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{g}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV, \tag{35}$$

to be exact, we obtain the condition

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + \frac{T}{1-x}\left(\frac{\partial P}{\partial T}\right)_V - \frac{2}{3}\frac{x}{1-x}\frac{T}{V}\left(\frac{\partial U}{\partial T}\right)_V, \tag{36}$$

which, by construction, is satisfied by the monatomic ideal gas, but not necessarily by other fluids. For $x=0$ ($g=$constant), Eq. (36) reduces to Eq. (24). To check the validity of Eq. (36) for substances other than the monatomic ideal gas, we need the equations of state, $P(T,V)$ and $U(T,V)$, of those fluids. The number of particles N is assumed to remain constant. If we substitute Eqs. (27) and (28) for the hard sphere fluid and match each power of the density, keeping in mind that $dB_n/dT=0$, we obtain:

$$B_n = \frac{1}{1-x}B_n, \tag{37}$$

which can be satisfied only if $x=0$, which implies that $g=$constant. We conclude that, of all the mathematically possible integrating factors, only Clausius' choice of $1/T$ works successfully for both the ideal gas and the hard sphere fluid.

B. Pressure-dependent integrating factors

In the quest for pressure-dependent integrating factors, it is more appropriate to start from the exact differential of the enthalpy rather than the internal energy. Using the definition of the enthalpy, $H=U+PV$, an infinitesimal amount of reversibly exchanged heat can be expressed as

$$\begin{aligned}\delta q_{\mathrm{rev}} &= dH - VdP,\\ &= C_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP,\end{aligned} \tag{38}$$

where the exact differential of $H(T,P)$ and $C_P=(\partial H/\partial T)_P$ have been used. Adiabats ($\delta q_{\mathrm{rev}}=0$) are defined by

$$\frac{dT}{dP} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T - V}{C_P}. \tag{39}$$

We multiply both sides of Eq. (38) by a function $f(T,P)$ and require the product $(f\delta q_{\mathrm{rev}})$ to be an exact differential; the condition for $f(T,P)$ is

$$\frac{\partial (fC_P)}{\partial P} = \frac{\partial}{\partial T}\left\{ f\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\right\}. \tag{40}$$

If we rearrange the terms and use

$$\frac{\partial^2 H}{\partial P \partial T} = \frac{\partial^2 H}{\partial T \partial P}, \tag{41}$$

we obtain a partial differential equation for $f(T,P)$:

$$C_P\left(\frac{\partial f}{\partial P}\right)_T - \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left(\frac{\partial f}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial T}\right)_P f. \tag{42}$$

The characteristics of Eq. (42) are the adiabats given by Eq. (39). Each characteristic defines a path in the (T,P) plane, which is represented implicitly by $\xi(T,P)=\text{constant}$. We exploit the constancy of $\xi(T,P)$ and, for convenience and to ensure the validity of statement (2a) of the second law, that is, $1/T$ is one of the integrating factors, we set $\eta=T$ as the new variable. Equation (42) then simplifies to

$$-\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left(\frac{\partial f}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial T}\right)_P f. \tag{43}$$

All thermodynamically acceptable equations of state satisfy

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P, \tag{44}$$

which is ensured by statement (2a) of the second law of thermodynamics. Hence, we arrive, once more, at

$$-T\frac{\partial f}{\partial T} = f, \tag{45}$$

with the solution $f=c_2T^{-1}$, where c_2 is now a function of T and P as dictated by the adiabat equation $\xi(T,P)=\text{constant}$. The complete solution thus reads $f=T^{-1}g(\xi(T,P))$, where g is an arbitrary differentiable function.

For the monatomic ideal gas, we obtain $f=T^{-1}g(TP^{-2/5})$. Choosing $\eta=P$ in the process of solving the partial differential equation (42) using the method of characteristics yields $f=P^{-2/5}g_1(TP^{-2/5})$, an equivalent result. If Vemulapalli[7] had suggested division by $P^{2/5}$ instead of just P, he would have found that $P^{-2/5}$ (obtained by setting $g(y)=y$ or $g_1=1$) is a valid integrating factor for the monatomic ideal gas and that in the context of finding valid integrating factors without referring to the second law of thermodynamics, there is nothing special about the integrating factor $1/T$.

The analogous integrating factor $f(T,P)$ for the hard sphere fluid is much more difficult to obtain in explicit form. It would involve an arbitrary function h of T and P in a combination that is determined by the adiabats so as to satisfy Eq. (39), that is, $h(\xi(T,P))$, where $\xi=\text{constant}$ is an implicit representation of the adiabats. This particular combination will be different from the ideal gas combination $TP^{-2/5}$. A universally applicable integrating factor is obtained only if we require $g=h=\text{constant}$, thus eliminating the pressure-dependent integrating factors and leaving only $1/T$.

Thermodynamically, the properties of a pure substance are entirely determined by just two state variables if we keep the number of particles constant. In addition to T and V or T and P, a complete description of the system is also possible in terms of P and V. If we set up a partial differential equation to determine the integrating factor $f(V,P)$ in a way that is analogous to the treatments of $f(T,V)$ and $f(T,P)$, we find $f=V^{2/3}g(V^{2/3}P^{2/5})$ or, equivalently, $f=P^{-2/5}g_1(V^{2/3}P^{2/5})$, where g and g_1 are arbitrary differentiable functions for the ideal gas. Both forms involve the adiabat equation for the monatomic ideal gas, so we cannot expect these integrating factors to be valid for other systems. Imposing statement (2a) of the second law on the partial differential equation for the integrating factors in terms of P and V, which amounts to insisting on $1/T$ being a valid solution, leads to the requirement that

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha^2 TV}{\kappa_T}, \tag{46}$$

which is a well-known result derived in a rather unconventional way. Here α is the thermal-expansion coefficient and κ_T denotes the isothermal compressibility.

III. CONCLUSIONS

Based on the method of characteristics for solving partial differential equations, we have identified integrating factors that turn the inexact differential of the reversibly exchanged heat into an exact one. If the integrating factor is restricted to be a function of temperature alone, Clausius' integrating factor $f=cT^{-1}$, with c being a nonzero constant, is obtained, as implied by the second law of thermodynamics. If we allow f to depend on two variables, temperature and volume or temperature and pressure, then there are infinitely many more integrating factors, a fact that is known from the properties of a differential in two variables. If we assume the validity of the second law, thereby ensuring that $1/T$ is an integrating factor, these more general integrating factors are formed by multiplying T^{-1} by an arbitrary differentiable function of the respective implicit adiabat equation $\xi(T,V)=\text{constant}$ or $\xi(T,P)=\text{constant}$ to give $f=T^{-1}g(\xi)$. Since the functional relationships implied by the adiabat equations will, in general, be different for different substances, the only way of having a universally applicable integrating factor that is valid for all substances is to require g to be a constant. Thus, Clausius' result $f=1/T$ is recovered (choosing $g=1$ is a convention). It is remarkable that there is no need to refer to statement (2b) of the second law of thermodynamics to eliminate all the alternative integrating factors. (In general, it is necessary to refer to statement (2a) to ensure the existence of an integrating factor.) Clausius probably never considered more general integrating factors because he knew about Carnot's result that the efficiency of a heat engine depends only on the temperatures between which the engine operates.

From the equations of state alone, Clausius' integrating factor $1/T$ can be shown to work for all imperfect gases that have a regular virial expansion ("regular" means that only integer powers of the density occur in the expansion and that the virial coefficients exist). The question remains whether it is a valid integrating factor for all substances because the equations of state needed to evaluate Eqs. (24), (44), and (46) for an arbitrary substance are not available, in general. What ensures the general validity of $1/T$ as an integrating factor is the second law of thermodynamics in one of its standard versions according to Kelvin, Clausius, or Carathéodory.[4,5,14,15]

Although mathematics alone ensures the existence of integrating factors for differentials in two variables, there is no guarantee of the integrability of differentials in three (or more) variables. The second law ensures that $1/T$ is valid even in these cases by eliminating all potential equations of state that violate the second law by failing to have $1/T$ as an integrating factor for the differential of the reversibly exchanged heat. In particular, Carathéodory's work focused on identifying the minimal extra-mathematical assumptions that would imply the second law of thermodynamics and, thereby, ensure the existence of an integrating factor for all thermodynamic systems.[4,5,16–22] Carathéodory's principle, in combination with the theorem that bears his name, states that, "to ensure the existence of an integrating factor for a differential in more than two variables, there have to be states in the immediate vicinity of any given equilibrium state that cannot be reached from this state by adiabatic processes." One can then show that the integrating factor may be chosen to be a function of temperature alone, and refer to the ideal gas to identify it as $1/T$. Without Carathéodory's or an equivalent formulation of the second law, the existence of an integrating factor for an arbitrary system cannot be taken for granted.[10,15] An exception is the special case of having a differential in just two variables, which is the case studied in this paper, because mathematics alone guarantees the existence of integrating factors.

There have been attempts to demonstrate that the entropy concept follows from the first law and the process of turning the inexact differential of the reversibly exchanged heat into an exact one[23] (cf. the comment in Ref. 10). An equivalent procedure is to infer the validity of $1/T$ as an integrating factor for all substances from its validity for the ideal gas.[8,9] Djurdjević and Gutman[8] presented what they claimed to be proof that $1/T$ is an integrating factor for all substances by constructing a cyclic process in which the nonideal substance is in contact with an ideal gas, but the proof seems to anticipate the result by assuming that there is an integrating factor for the arbitrary substance without referring explicitly to the second law, which would then guarantee that $1/T$ is one such integrating factor. Following their line of reasoning, it would be possible to show that each integrating factor for the ideal gas works for any arbitrary substance as well. This conclusion is clearly incorrect, as we showed for the hard sphere fluid.

A different way of phrasing that $1/T$ is an integrating factor for an arbitrary substance rests on the version of the second law of thermodynamics that states that all reversibly working Carnot engines, regardless of their working fluid, must have the same efficiency, which depends only on the temperatures between which the Carnot engine operates.[2] If any two reversibly working engines had different efficiencies, we could convert heat completely into work by coupling two engines, using the more efficient one as a heat engine and the less efficient one as a refrigerator such that there is no net discharge of heat to the reservoir at the lower temperature, thereby violating Kelvin's version of the second law. The validity of the second law thus guarantees the existence of the integrating factor $1/T$; it is therefore, as Widom phrased it, a "law of nature, not of mathematics."[24]

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[a] Present address: Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Petersenstrasse 20, 64287 Darmstadt, Germany; electronic address: v.weiss@theo.chemie.tu-darmstadt.de

[1] The transfers of heat and of work are two ways in which the system can exchange energy with its surroundings. "Heat" denotes the transfer of energy due to a (possibly infinitesimally small) temperature difference, while "work" is energy exchanged due to a (possibly infinitesimally small) pressure difference between the system and its surroundings. The system itself possesses neither heat nor work, just energy.

[2] See, for example, Peter Atkins and Julio de Paula, *Atkins' Physical Chemistry*, 7th Ed. (Oxford University Press, Oxford, 2002), pp. 73–120.

[3] The term "reversible" denotes a special way of conducting the transfer of heat or work in a given process. It ensures that, at all times, the differences in temperature and pressure between the system and its surroundings are only infinitesimal; that is, the temperature and pressure are matched in such a way that heat and/or work are just transferred in the desired direction (to or from the system), but the values of the temperature and pressure are equal for the system and for its surroundings for all practical purposes. The total entropy of the supersystem consisting of the system and its surroundings remains constant in a reversible process, implying that the change in entropy of the system is exactly equal, but opposite in sign, to the change in entropy of the surroundings.

[4] S. M. Blinder, "Carathéodory's formulation of the second law," in *Physical Chemistry: An Advanced Treatise*, edited by H. Eyring, B. Henderson, and W. Jost (Academic, New York, 1971), Vol. 1, Chap. 10.

[5] Arnold Münster, *Chemische Thermodynamik* (VCH, Weinheim, 1969), pp. 27–38; English translation, *Classical Thermodynamics* (Wiley-Interscience, New York, NY, 1970).

[6] Stephen G. Brush, *The Kind of Motion We Call Heat: A History of the Kinetic Theory of Gases in the 19th Century* (North-Holland, Amsterdam, 1986), Book 2, pp. 566–583.

[7] G. Krishna Vemulapalli, "A simple method for showing entropy is a function of state," J. Chem. Educ. **63**, 846–846 (1986).

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[9] Donald A. McQuarrie and John D. Simon, *Physical Chemistry: A Molecular Approach* (University Science Books, Sausalito, CA, 1997), pp. 820 and 844–845, Problem 20–5.

[10] John C. Wheeler, "Entropy does not follow from the first law: Critique of 'Entropy and the first law of thermodynamics'," Chem. Educ. **8**, 171–176 (2003).

[11] See, for example, E. C. Zachmanoglou and Dale W. Thoe, *Introduction to Partial Differential Equations with Applications* (Dover, Mineola, NY, 1986), pp. 133–137.

[12] This statement will be true at low and moderate densities as the first nine virial coefficients are positive; it is unknown if B_n becomes negative for any higher value of n. See Stanislav Labík, Jiří Kolafa, and Anatol Malijevský, "Virial coefficients of hard spheres and hard disks up to the ninth," Phys. Rev. E **71**, 021105–1–8 (2005).

[13] See for example, Terrell L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, Mineola, NY, 1986), pp. 261–285.

[14] A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge University Press, London, 1957), pp. 29–42.

[15] Francis W. Sears and Gerhard L. Salinger, *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics*, 3rd Ed. (Addison-Wesley, Reading, MA, 1975), pp. 138–141 and 168–172.

[16] H. A. Buchdahl, "On the principle of Carathéodory," Am. J. Phys. **17**, 41–43 (1949).

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[23] Panos Nikitas, "Entropy and the first law of thermodynamics," Chem. Educ. **7**, 61–65 (2002).

[24] Ben Widom, "Thermodynamics, equilibrium," in *Encyclopedia of Applied Physics*, edited by George L. Trigg and Edmund H. Immergut (Wiley-VCH, Weinheim, 1997), Vol. 21, pp. 281–310.