

Multivalued specific heat

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Multivalued specific heat

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Specific heat is usually analyzed only for common thermodynamic processes, leaving us with the impression that it can always be expressed as a single-valued function of temperature. In this paper, we show that specific heat functions may be multivalued even for processes that are mathematically simple, such as an ideal gas following a linear path with a negative slope in the pressure–volume diagram. Although this example has been studied previously, we show that the multivalued approach provides additional physical insights, and we establish the conditions that any path must satisfy in order to have a single-valued specific heat. As a final application of our approach, we demonstrate a geometric theorem. © 2022 Published under an exclusive license by American Association of Physics Teachers.

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I. INTRODUCTION

Heat capacity was introduced by Joseph Black around 1760 when modern thermodynamics was being developed.¹ In modern notation, we define the heat capacity C as

$$C(T) = \lim_{\Delta T \rightarrow 0} Q/\Delta T, \quad (1)$$

where Q is the heat associated with a temperature change from T to $T + \Delta T$. The heat capacity is frequently a function of temperature.

Black defined this concept empirically. However, many important advances emerged when physicists searched for microscopic models of matter capable of predicting the heat capacity. A landmark development was Dulong and Petit’s empirical recognition that the heat capacity per mole—the molar specific heat c —is the same for all solids and equal to approximately $3R \approx 25 \text{ J}/(\text{mol K})$, where R is the ideal gas constant.^{2–4} This universality put physicists on the path to the discovery of the equipartition theorem and the kinetic theory of gases and led Boltzmann to propose a model of a solid as a set of independently oscillating atoms.^{1,5} However, Dulong and Petit’s law must be modified at low temperatures where thermal energies are smaller than the quantum energy level separation, and Einstein adapted Boltzmann’s model by treating the harmonic motion of the atoms quantum mechanically to explain the behavior of the specific heat of solids at low temperatures.⁶ This was arguably the departure point of modern solid state physics. While it is not the purpose of this paper to present a detailed historical account, we emphasize that the route to a proper understanding of specific heat led to some unexpected and important developments, as evidenced by the cited references.

It is well known that specific heat is path dependent, but students usually only express it for ideal gases undergoing isobaric or isochoric processes. In these cases, the molar specific heat c can be used to evaluate the heat exchanged through the expression

$$Q = \int_{T_1}^{T_2} n c dT, \quad (2)$$

where n is the number of moles present. However, one must be cautious when applying Eq. (2) for an arbitrary case, since a multivalued specific heat function might be required. For example, we will show that if an ideal gas follows a path in a pressure–volume diagram that is a straight line with negative slope; then, the specific heat is multivalued as a function of temperature. This problem has been studied in the literature and contains many interesting features, such as a segment where heat enters in the system and another where it leaves.⁷ Furthermore, in this process, we have a portion where the specific heat is negative, and also a point where it changes abruptly from $-\infty$ to $+\infty$.^{8,9} An interesting geometrical method has been devised to find the point where the specific heat is zero in this process.¹⁰ These authors circumvented the need to employ a multivalued function by expressing the specific heat as a function of volume instead of temperature. However, in order to evaluate the integral in Eq. (2), we need to express the specific heat as a function of temperature, which is not possible using a single-valued function. Similar problems appear for more general processes, such as elliptical cycles and parabolic paths.^{11,12}

The purpose of this paper is twofold. First, we explore the conditions that a path must satisfy in order to have a single-valued specific heat. The intuitive answer is that the path on the P – V diagram must not be tangent to an isotherm because the temperature changes non-monotonically when moving through the tangency point, frequently resulting in points on opposite sides of the tangent point that have the same temperature but unequal specific heats. However, a careful demonstration of this result is subtle, and in Sec. II, we provide one by introducing general thermodynamic variables and employing the implicit function theorem of basic calculus. While in analytical mechanics, it can be useful to define a variable devoid of a physical meaning (for example, the canonical transformations), in thermodynamics, we meet this procedure much less frequently; our general variables provide an example of this. Although present in most calculus courses, the implicit function theorem, which underlies the operation of implicit differentiation, is rarely applied to physical problems, and we believe that the application presented here may help students to build intuition regarding it.

Our second purpose is to re-examine the straight-line example. In Sec. III, we show that once we express the specific heat as a function of temperature, new features can be appreciated. Our results also enable us to enunciate and demonstrate a geometric theorem. Section IV offers some concluding remarks.

II. WHEN IS IT POSSIBLE TO DEFINE A SPECIFIC HEAT?

In undergraduate courses, we emphasize that the specific heat depends upon the path, henceforth denoted by Π . This is a consequence of the fact that heat is not a state variable. In a more formal way than Eq. (2), we define the molar specific heat as the function $c(T; \Pi)$ such that

$$Q_{i \rightarrow f; \Pi} = \int_{T_i}^{T_f} n c(T; \Pi) dT. \quad (3)$$

A good way to start a discussion with students is to ask them to evaluate the integral in the case that $T_i = T_f$. They are likely to tell you that it is zero. Then, ask them to consider an ideal gas in the linear process depicted in Fig. 1(a), where we choose the initial and final states to lie on an isotherm so that they have the same temperature. In this case, there is no variation in the internal energy of the gas (because $T_i = T_f$), and therefore, the heat lost by the gas must be equal to the work performed on the gas in the process. The work is given by the area below the line in Fig. 1, which is not zero, giving a contradiction with the first law of thermodynamics. This contradiction is resolved by realizing that it is not possible to assign a single-valued specific heat to this process. This can be readily understood once we turn our attention to the differential form of Eq. (3),

$$c(T; \Pi) = \frac{1}{n} \cdot \frac{dQ_{i \rightarrow f; \Pi}}{dT}, \quad (4)$$

where dQ is the heat exchanged in an infinitesimal portion of the process and dT is the temperature variation over it. For an infinitesimal process, the specific heat is well defined as long as $dT \neq 0$. If we represent the process in a P - V diagram, then a point around which we have $dT=0$ is a point where the path is tangent to an isotherm. For the example depicted in Fig. 1(a), we have a tangency only at point O . If we consider two different points in the path with the same temperature, they will not have the same $c(T; \Pi)$ and, hence,

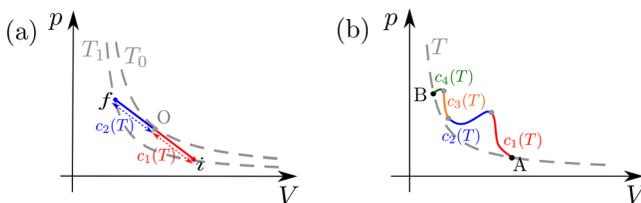


Fig. 1. (a) A straight (red and blue solid) line with negative slope is tangent to an isotherm (dashed gray curve) at $T = T_0$. Isotherms with $T < T_0$, such as the one shown for T_1 , intercept the line in two points. The specific heat of the process represented by the full line must be split in two different functions $c_1(T)$ and $c_2(T)$. (b) A more generic process connecting two points (A and B) on the same isotherm. The gray dots on the path represent the points of tangency to isotherms (not indicated). Each point separates one branch in the specific heat from another. In this particular example, we have four branches.

we cannot assign a single-valued function $c(T; \Pi)$ to the entire straight line. To see this, consider two different points with the same temperature (for example, the points i and f in Fig. 1(a)) and consider an infinitesimal temperature dT along the process. The variation of internal energy is the same in both cases, but the work performed by the gas is not, thus yielding a different heat exchange in each case and, therefore, a different specific heat. In fact, if the specific heat were equal for a pair of points having the same temperature around the temperature maximum, their contribution to the heat exchange would cancel, a contradiction as pointed out above.

This argument can be generalized for an arbitrary process connecting two points on the same isotherm, as illustrated in Fig. 1(b). In a few words, given any process Π , we must first identify all the points where it is tangent to some isotherm and then consider different specific heats, which span between the tangency points. In the particular example depicted in Fig. 1(b) we need four functions, while in Fig. 1(a) we need only two.

Although it is clear that this separation is a necessary condition in order to define the specific heat, is it always sufficient? In order to provide a rigorous demonstration, we need some extra tools. Henceforth, we drop the ideal gas hypothesis and turn our attention to a general thermodynamic system whose state can be uniquely defined once the temperature T and the volume V are given; a real gas with a fixed number of particles is an example. Systems requiring more variables can be treated by a straightforward generalization of our procedure. With this assumption, the heat exchanged in any reversible process can be cast as

$$dQ = f(T, V) dT + g(T, V) dV, \quad (5)$$

where f and g are state functions. To understand their physical meaning, note that when the volume is kept constant, this formula reduces to Eq. (3) (with Π being an isochoric process), and therefore, $f(T, V)$ is just the heat capacity at constant volume. Analogously, g is related to a latent heat capacity.¹⁴ In order to gain more physical insight, consider Eq. (5) for an ideal gas, where the change in internal energy can always be written as $dU = nc_v dT$.¹⁵ From the first law of thermodynamics, we can write $dQ = nc_v dT + PdV = nc_v dT + \frac{nRT}{V} dV$, where in the last step, we employed the ideal gas equation of state. Therefore, to evaluate the heat exchange in any processes, the specific heat at constant volume can be employed, regardless of whether or not the volume is held fixed. However, this will account for only one parcel of the heat. The same is true for systems more general than an ideal gas, albeit with a different function $g(T, V)$. From now on we consider again the general case, but the reader may always apply our results to an ideal gas to gain intuition.

Now compare Eqs. (5) and (3). In the latter, we are trying to write the heat exchanged in terms of just one function. The price to be paid is that now the required function is no longer a state function but instead depends upon the path. Is such exchange always possible? In order to answer this question, we consider an arbitrary path defined implicitly by the equation $h(P, V) = M$, where M is a constant.

Instead of using the pair (T, V) as the independent variables describing the gas, we assume that it is possible to employ alternatively the pair (T, M) as independent variables, which uniquely define the state of the gas. In general,

M has no physical meaning, and therefore, we call it a generalized thermodynamic variable, a nomenclature adopted from analytical mechanics. In this case, we may re-write Eq. (5) in the form

$$\vec{d}Q = f_M(T, M) dT + g_M(T, M) dM, \quad (6)$$

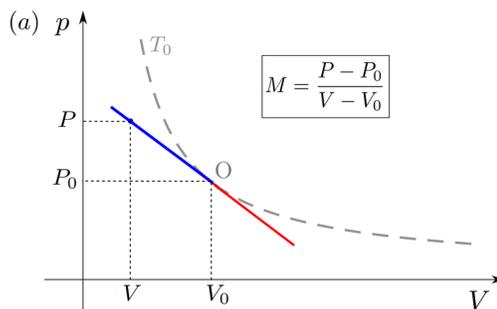
where f_M and g_M are state functions and the index M is added as a reminder that they are different functions from those appearing in Eq. (5). In a process, where M is constant, we obtain

$$\vec{d}Q = f_M(T, M) dT. \quad (7)$$

On comparing this expression with Eq. (4), we see that f_M is nothing more than the heat capacity with M constant, or, in other words, the heat capacity associated with a process $h(P, V) = \text{constant}$. We now provide some examples. First, for an isobaric process, $M = P$. Since the pair (T, P) uniquely defines the system state (together with the number of moles, assumed fixed), we may recognize in Eq. (7) the heat exchange for an isobaric process in which case f_M is just the familiar specific heat at constant pressure, c_P . As a second example, consider an ideal gas undergoing an isothermal process. In this case, we may choose $M = PV$. Since M is proportional to temperature, the pair (M, T) does not uniquely specify a state and, therefore, we cannot write Eq. (7) for this process. This is natural, since the specific heat is not defined on an isotherm. This is valid regardless of the hypothesis of an ideal gas, and in the general case, we will just have a different expression for M as a function of pressure and volume. The results obtained here are valid for any thermodynamical system whose state is defined by two state variables; to generalize our results for systems presenting more independent variables, we would have to add more terms to Eq. (6).

Therefore, it is possible to define the specific heat if, and only if, the pair (T, M) defines uniquely the state of the system. Expressing the pressure as a function of T and V , the path can be recast in the form $h(T, V) = M$. The pair (T, M) is sufficient to furnish the state of the gas if, and only if, we can write V as a function of T and M . The conditions for this to be possible are established by the implicit function theorem of undergraduate calculus.¹³ For reasonable physical processes, this theorem requires that (there are some subtleties; see the Appendix)

$$\left(\frac{\partial T}{\partial V}\right)_h \neq 0, \quad (8)$$



that is, the temperature must vary monotonically as we perform the process, which is exactly the result anticipated in the discussion following Fig. 1. In Sec. III, we develop in more detail the example depicted in Fig. 1(a) and obtain some unexpected results.

III. STRAIGHT LINE WITH NEGATIVE SLOPE

In this section, we illustrate the previous discussion with the straight-line process already discussed in Sec. II, assuming that the substance involved is an ideal gas. This path is given by

$$M = \frac{P - P_0}{V - V_0}, \quad (9)$$

where M is a negative constant, as depicted in Fig. 2(a). Even though this process has more academic than practical interest, it provides significant insights about conceptual aspects of thermodynamics.⁷⁻¹⁰ In this section, we present additional perspectives on this process. Furthermore, understanding the specific heat in this process is useful since any smooth path in a PV diagram can be locally treated as a straight line. For ideal gases and employing the sign convention that work is positive when the gas expands, we have $\vec{d}Q = dU + \vec{d}W = n c_V dT + PdV$ and $PV = nRT$, so $PdV + VdP = nRdT$. From Eq. (9), we obtain $dP = MdV$ and then

$$PdV = \frac{nRdT}{1 + \frac{MV}{P}}. \quad (10)$$

Substituting this result into the first law of thermodynamics, we find

$$\vec{d}Q = \left[n c_V + \frac{nR}{1 + \frac{MV}{P}} \right] dT. \quad (11)$$

One can readily verify that the particular cases $M = 0$ (isobaric path) and $M = \infty$ (isochoric path) yield the expected specific heats. Also, for $M < 0$ there is always a pair (P, V) for which the specific heat diverges, corresponding to the point where the straight line is tangent to the isotherm. This can be readily checked, since at divergence, we have $M = -P/V$ (from Eq. (11)) and also $M = dP/dV$ from Eq. (9). Combining these gives $VdP + PdV = 0$ and, thus, from the

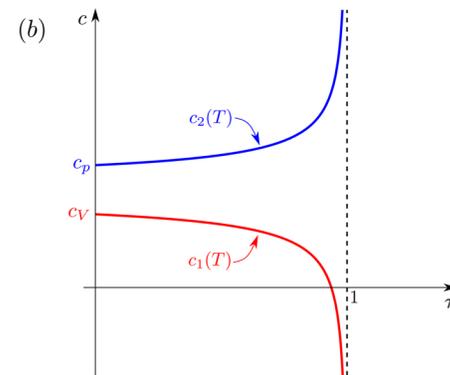


Fig. 2. (a) A straight-line process with negative slope. (b) The two branches $c_1(T)$ and $c_2(T)$ of the specific heat for an ideal gas expressed as a function of the ratio $\tau = T/T_0$ for the process depicted in part (a).

equation of state, $dT=0$, showing that the divergence is indeed on the point where the path is tangent to an isotherm. Our discussion in Sec. II revealed that this point is of special interest in the study of specific heat, and therefore, we choose the pair (P_0, V_0) in Eq. (9) as the tangency point, that is,

$$P_0 = -MV_0. \quad (12)$$

Denoting the temperature of this isotherm by T_0 , we find, by employing the ideal gas equation of state,

$$V_0 = \sqrt{\frac{nRT_0}{|M|}}. \quad (13)$$

Substituting Eqs. (12) and (13) into Eq. (9), the equation defining the straight line process can be rewritten as

$$P = MV + 2\sqrt{|M|nRT_0} = \frac{MnRT}{P} + 2\sqrt{|M|nRT_0}. \quad (14)$$

This yields a quadratic equation in P whose solution is

$$P(T) = \sqrt{|M|nRT_0} \pm \sqrt{|M|nR(T_0 - T)}. \quad (15)$$

As expected, there are two different pressures corresponding to the same temperature so long as $T < T_0$. Employing the definition given in Eq. (4) and substituting Eq. (12) and the equation of state $V = nRT/P$ into Eq. (11), we obtain (after a lengthy calculation)

$$c_1(T) = c_V - \frac{R(1 - \sqrt{1 - \tau})}{2\sqrt{1 - \tau}}, \quad (16)$$

$$c_2(T) = c_V + \frac{R(1 + \sqrt{1 - \tau})}{2\sqrt{1 - \tau}}, \quad (17)$$

where $\tau = T/T_0$. $c_1(T)$ corresponds to the specific heat for pressures below P_0 , and $c_2(T)$ to that for pressures above P_0 . For ideal gases, these expressions are exact. We plot these expressions in Fig. 2(b). To this end, we shall assume that c_V does not depend on temperature. This is a reasonable assumption, valid whenever the equipartition theorem holds, which is usually assumed in introductory courses.¹⁶ The divergence of the specific heat near the tangency point $\tau = 1$ goes as $\tau^{-1/2}$ and, therefore, yields a finite value upon integration and consequently a finite heat exchange. The total heat exchanged is given by $Q = \int_0^{T_0} n[c_1(T') - c_2(T')]dT'$ and corresponds to the negative of the area between the curves displayed in Fig. 2(b). The most impressive feature of Eqs. (16) and (17) is that the specific heat does not depend on M ! Actually, this result could have been foreseen by dimensional analysis: Since the pair M, T_0 uniquely defines the straight line, the specific heat $c(T)$ can depend only on R, T, T_0 , and M and, therefore, must be of the form $Rf(T/T_0)$, which is exactly what we obtained (note that R is contained in c_V). This suggests a counter-intuitive geometrical theorem. Consider two straight lines with different slopes tangent to the same isotherm T_0 . If we take their initial and end points to lie on the same isotherm of temperature of T_1 , they will undergo the same internal energy variation. Since the heat exchange does not depend on the slope (it does not depend on M), then the work performed by the gas is the same in each process, showing that the areas of the two trapezoids

depicted in Fig. 3(b) are the same! If $T_1 = 0$, the trapezoids become triangles. We leave as a challenge to the reader to verify this theorem by direct evaluation of the areas.

The results that we have obtained so far in this section are equivalent those derived by Calvo-Hernandez.⁹ However, he expressed specific heat as a function of volume instead of temperature. While that choice allows for a rich physical discussion, we argue here that considering specific heat as a function of temperature [in Eqs. (16) and (17)], important additional features come to light. First, we must employ a bivalued specific heat function. When one expresses the specific heat as a function of volume in this process, a single-valued function is found because the volume varies monotonically. Nonetheless, if one wishes to apply the specific heat to evaluate the heat exchanged (which is the main purpose for defining specific heat), we must integrate c along the temperature. To do so, we must either express c as a function of temperature or change the variable of integration, which would in turn lead to a separation of the integration in two different parts, one before the tangency between the path and the isotherm T_0 and another thereafter. The bivalued nature of specific heat for this process becomes evident when c is written as a function of the temperature. Expressing the specific heat as a temperature-dependent bivalued function also reveals several insights not available otherwise. For example, all straight lines tangent to the same isotherm have the same specific heat function, a feature hidden when expressing c as a function of V . We remark that, even though $c(V)$ for this process does depend on M , this does not contradict the fact that Eqs. (16) and (17) do not: changing M for a fixed V gives straight lines tangent to different isotherms. A careful discussion of this last point can be found in Arenzon's paper.¹²

Furthermore, note that the specific heat depends on the temperature only through the dimensionless parameter T/T_0 . In the limit $T_0 \rightarrow \infty$, tangent lines to the isotherm approach either isochors or isobars. The isochors are of lower pressure than P_0 , while the opposite is true for the isobars. Hence, we expect $c_1(T) \rightarrow c_V$ and $c_2(T) \rightarrow c_P$ in the limit $\tau \rightarrow 0$, in agreement with Eqs. (16) and (17). This limit is equivalent to taking $T \rightarrow 0$. In this case, for pressures lower than P_0 , we must have $P \rightarrow 0$, which in turn implies $\delta W = -PdV \rightarrow 0$ and, hence, $\delta Q \rightarrow dU = nc_V dT$. For pressures higher than P_0 , we must have $V \rightarrow 0$ in the limit $T \rightarrow 0$, in which case, $\delta W = -PdV \rightarrow -nRdT$, where we employed the equation of state; this yields $\delta Q \rightarrow dU + nRdT = nc_P dT$.

It is important to emphasize that our results are useful even for more generic processes. For example, suppose we wish to analyze the specific heat at some point A of a generic path Π in a PV diagram. This is the same as the specific heat of a straight-line, which is tangent to Π at A . If we assume that the slope of Π at A is negative, then our Eqs. (16) and (17) apply because a straight-line with negative slope can be uniquely specified by furnishing the slope and the temperature T_0 of the isotherm tangent to it. If the volume at A is greater than V_0 given in Eq. (13), then the specific heat of Π at A is given by Eq. (17). If the temperature at A is much smaller than T_0 , then the results obtained previously for the limit $T \rightarrow 0$ are valid, showing that this limit can be physical in some situations.

Equations (16) and (17) possess other features worth mentioning. First, as shown in Fig. 2, the specific heat may assume any value except those between c_V and c_P , a property already discussed in the literature.⁹ For pressures greater

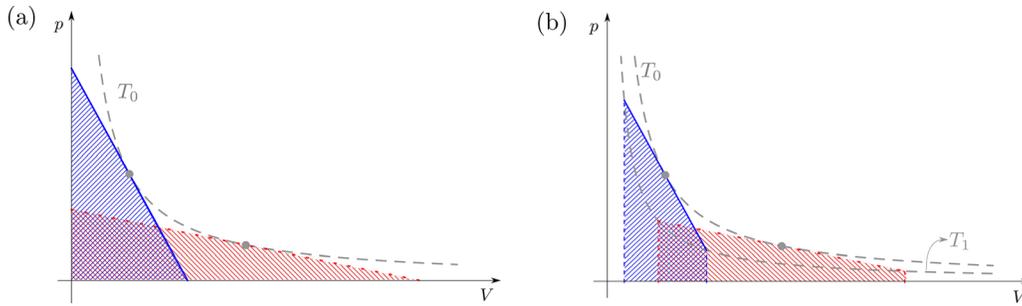


Fig. 3. The fact that the specific heat does not depend on M for a fixed T_0 leads to a geometric theorem: The blue and red patterned areas have the same numerical values. In part (a), the two triangles are delimited by a segment of line tangent to an hyperbola and the axis. In part (b), the trapezoids are delimited by this segment and vertical lines passing through the extreme points of the segment and the horizontal axis.

than P_0 , an increase in temperature is always accompanied by an increase in volume, thus demanding that heat be absorbed and implying positive specific heat, explaining why $c_2 > 0$ for all temperatures: It starts from c_p for low temperatures and increases without bound near T_0 . For pressures lower than P_0 , an increase in temperature comes with a decrease in volume. Near the tangency point, a small increase in internal energy amounts to large work performed on the gas and, thus, much heat must be lost, which explains why $c_1(T)$ must be negative and with a large absolute value close to the tangency point. On the

other hand, for very low pressures the opposite happens: Negligible work entails an appreciable gain in internal energy, requiring heat to enter the system and explaining the positive values of c_1 for small temperatures. By continuity, there is a point where $c_1 = 0$. This point corresponds to the tangency point between the line and an adiabatic curve and is indicated by letter B in Fig. 4(a). Since this point belongs to the branch with specific heat c_1 , B must always have a lower pressure than the tangency point between the same line and an isotherm, which is denoted by the letter C in Fig. 4(a).¹⁰

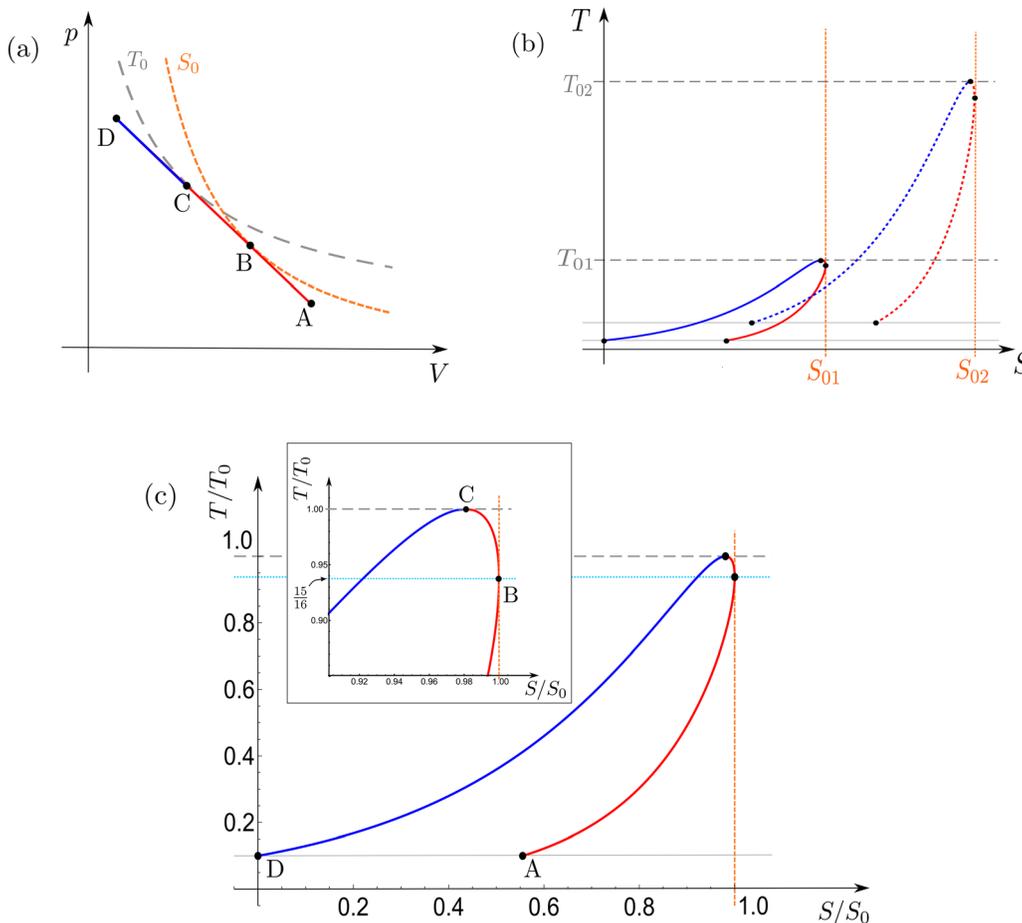


Fig. 4. The process studied in Sec. III a represented in (a) a PV diagram where it is a straight line with negative slope, and (b) and (c) in a TS diagram. In (b), we present plots for two different examples, which are tangent to two different isotherms denoted by T_{01} and T_{02} . The tangency isotherms (adiabats) are represented by horizontal (vertical) lines. In (c) we plot the entropy as a function of the dimensionless parameter T/T_0 . The span from B to C (inset) the specific heat is negative. Points A and D are chosen so that their temperature is $0.1T_0$.

The temperature for which the specific heat vanishes can readily be determined. Whenever the equipartition theorem is valid, we may write the isochoric molar specific heat as $c_v = rR/2$, where r is the number of degrees of freedom for each molecule of the ideal gas. From Eq. (16), we see that the specific heat vanishes when $\tau = \tau_B$ given by

$$\tau_B = 1 - \frac{1}{(r+1)^2}. \quad (18)$$

This result shows that a given straight line process with negative slope is tangent to an isotherm and to an adiabat at temperatures whose ratio is independent of the line, i.e., the ratio is independent of both T_0 and M . For a monatomic gas ($r=3$), $\tau_B = 15/16$. Increasing r implies $\tau_B \rightarrow 1$, that is, points B and C would coincide. This is expected since for $r \gg 1$, $c_p/c_v \rightarrow 1$ and adiabats becomes isotherms. Physically, this is due to the fact that for $r \gg 1$ almost all heat exchange goes into internal energy.

Valuable insights can also be gained if we analyze our process in a entropy versus temperature diagram.¹⁷ In the remainder of this section, we shall assume a monatomic ideal gas. The entropy as a function of temperature can be obtained from $\vec{d}Q = TdS = cdT$, and hence, the entropy variation between the initial point, denoted by A , and a point with temperature T is given by $\Delta S(T) = \int_{T_A}^T \frac{c(T')}{T'} dT'$. Since we have two branches for the specific heat, we will also have two branches for the entropy. An alternative way to obtain $S(T)$ is to employ the Sackur–Tetrode expression for the entropy of an ideal gas as a function of temperature and volume and then use the ideal gas equation and Eq. (15) to express S as a function of T for the straight-line path: The entropy diverges in the limit $T \rightarrow 0$.¹⁵ We have chosen to plot $S(T)$ from point A and point D , both with temperature $0.1T_0$, one in each branch. Without loss of generality, we set the entropy at point D to be zero; this is the state with minimum entropy. In Fig. 4(b), we represent $S(T)$ for two different values of T_0 . They are independent of M (as long as $M < 0$), as expected from Eqs. (16) and (17). In the TS diagram, it can be directly seen that we need two branches to express S (and therefore the specific heat) as a function of temperature. The branches are separated by the point C where the process is tangent to an isotherm, depicted by a horizontal line in this diagram. At point B , the process achieves its maximum entropy, denoted by S_0 in Fig. 4(a). In the TS diagram this point corresponds to the tangency between the process and a vertical line, which denotes the adiabat of tangency. Both processes presented in Fig. 4(b) collapse to the same curve if we plot S/S_0 as a function of the dimensionless parameter T/T_0 , as presented in Fig. 4(c). Recalling that the sign of the specific heat can be obtained from the sign of the slope of the process in the ST diagram, we re-obtain the result commented earlier that the specific heat is negative between B and C and positive otherwise.

IV. FINAL REMARKS

The convenience of defining specific heat is that it allows for a direct computation of the heat exchanged in going from the initial to the final temperature of a process. In this work, we have analyzed what conditions a general process must satisfy in order for us to be able to assign a single-valued specific heat to it. The answer is that it is only required that

the path in question not be tangent to any isotherm (assuming that the path is smooth). However, this point is not usually discussed in texts, sometimes leading the students to imagine that it is always possible to assign a specific heat function for an arbitrary thermodynamic process.

We have used the implicit function theorem to provide a rigorous derivation of the conditions that a path must satisfy in order to present a single-valued specific heat function. Our treatment is restricted to the case where the state of the gas is uniquely defined by furnishing just two variables, but only minor changes are required in the general case; one just has to introduce more generalized variables. Finally, while our discussion here has centered on the specific heat, it applies analogously for other response functions as well on replacing the temperature by the appropriate variable.

As our main example, we analyzed the specific heat of a straight line process with a negative slope in the PV diagram. Since this path has one tangency point with one isotherm (with temperature denoted by T_0), we had to assign to it a bivalued specific heat. We have shown that these functions depend only on the dimensionless parameter T/T_0 . The fact that the specific heat is independent of the slope of the line (for a given T_0) enabled us to enunciate a theorem relating the areas of triangles and trapezoids delimited by hyperbolas. Connecting mathematical theorems to physical insights can be a powerful teaching tool, and we invite readers to create new examples of this across the breadth of physics.¹⁸

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APPENDIX: IMPLICIT FUNCTION THEOREM

Here, we are concerned with the conditions, which must be satisfied in order that we can (locally) invert the equation $h(T, V) = M$ and express it as $V = g(T, M)$, where g is some function. The physical intuition developed in the text suggests that the condition must be that the path not be tangent to any isotherm in the point where we want to invert the function, that is,

$$\left(\frac{\partial T}{\partial V}\right)_h \neq 0. \quad (A1)$$

However, what the implicit theorem function states is different, requiring instead that¹³

$$\left(\frac{\partial h}{\partial V}\right)_T \neq 0. \quad (A2)$$

We argue that these conditions are equivalent for reasonable physical processes. To do so, we assume without loss of generality that $dV \neq 0$, that is, that the point of interest is not tangent to an isochor. If $dV=0$, we could use pressure instead of the volume and the demonstration below would be the same.

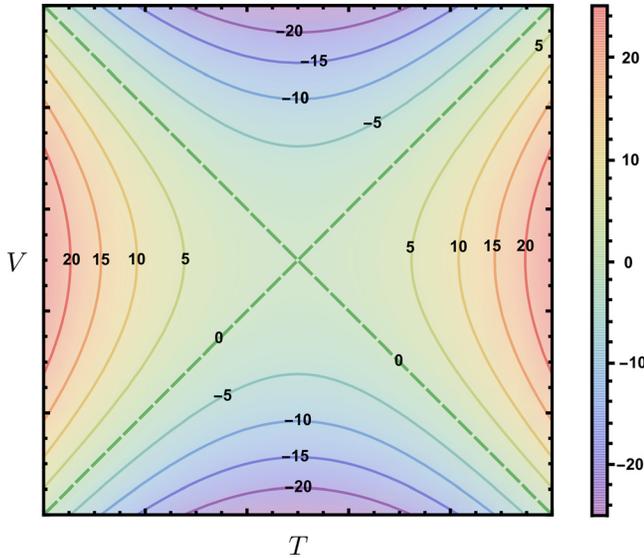


Fig. 5. Density plot and level curves close to a saddle point for an arbitrary $h(T, V)$ (with a saddle point). Numerical values indicate different (and also arbitrary) values of M . Note that while in the vertical direction M decreases from the saddle point, in the horizontal direction it increases, as expected for a saddle point. The dashed green line represents the level curve $h(T, V) = 0$, i.e., the only path in this example, which contains the saddle point for a given M .

We first summarize some properties among partial derivatives and implicit functions, which will be useful so that we can establish our main point. More details can be found in Callen's text.¹⁹ In an infinitesimal displacement along the path, we have $dh = 0$, and therefore,

$$\begin{aligned} \left(\frac{\partial h}{\partial V}\right)_T dV + \left(\frac{\partial h}{\partial T}\right)_V dT = 0 &\Rightarrow \left(\frac{\partial h}{\partial V}\right)_T \\ &= -\left(\frac{\partial h}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_h. \end{aligned} \quad (\text{A3})$$

If the point in question is not a critical point of h , then $\left(\frac{\partial h}{\partial V}\right)_T$ and $\left(\frac{\partial h}{\partial T}\right)_V$ cannot be both zero and, hence,

$$\left(\frac{\partial h}{\partial V}\right)_T = 0 \iff \left(\frac{\partial T}{\partial V}\right)_h = 0, \quad (\text{A4})$$

which is the result that we wished to establish. If we have a critical point then we may be unable to invert the function even if condition (A1) is satisfied. However, this is an issue of more mathematical than physical interest since a critical point does not appear in any reasonable physical process. Indeed, if the critical point is either a local maximum or a local minimum of h , then we know that the level curve consists of only a single point and it cannot describe any

physical process.¹³ On the other hand, if the critical point is a saddle point of h , then near the saddle point the level curve locally corresponds to the intersection of two lines as illustrated in Fig. 5, and a physical process could locally correspond only to one of them in which case we would have no problem inverting it.

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¹Stephen G. Brush, *The Kind of Motion We Call Heat: A History of the Kinetic Theory of Gases in the Nineteenth Century. Volume 1: Physics and the Atomists* (North Holland, Amsterdam, 1986).

²A. T. Petit and P. L. Dulong, "Recherches sur quelques points importants de la Théorie de la Chaleur," *Ann. Chim. Phys.* **10**, 395–413 (1819).

³Robert Fox, "The background to the discovery of Dulong and Petit's law," *Br. J. Hist. Sci.* **4**, 1–22 (1968).

⁴Roberto Piazza, "The strange case of Dr. Petit and Mr. Dulong," [arXiv:1807.02270](https://arxiv.org/abs/1807.02270) (2018).

⁵L. Boltzmann, "Über die Natur der Gasmoleküle," *Wien. Ber.* **74**, 553–560 (1876).

⁶A. Einstein, "Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme," *Ann. Phys.* **22**, 180–190 (1906).

⁷Jack Willis and Donald F. Kirwan, "The 'sadly cannot' thermodynamic cycle," *Phys. Teach.* **18**, 51–52 (1980).

⁸R. H. Dickerson and J. Mottmann, "On the thermodynamic efficiencies of reversible cycles with sloping, straight-line processes," *Am. J. Phys.* **62**, 558–562 (1994).

⁹A. Calvo Hernández, "Heat capacity in a negatively sloping, straight-line process," *Am. J. Phys.* **63**, 756–756 (1995).

¹⁰M. Bucher, "Graphical determination of heat reversal along a linear PV process," *Am. J. Phys.* **67**, 93 (1999).

¹¹S. Velasco, A. González, J. A. White, and A. Calvo Hernández, "Heat capacity of an ideal gas along an elliptical PV cycle," *Am. J. Phys.* **70**, 1044–1048 (2002).

¹²J. J. Arenzon, "Unconventional cycles and multiple adiabatic points," *Eur. J. Phys.* **39**, 065103 (2018).

¹³Jerrold E. Marsden and Anthony Tromba, *Vector Calculus* (W.H. Freeman, New York, NY, 2011).

¹⁴S. G. Canagaratna, "A critique of the definitions of heat," *Am. J. Phys.* **37**, 679–683 (1969).

¹⁵Ryogo Kubo, *Thermodynamics: An Advanced Course with Problems and Solutions* (North Holland, Amsterdam, 1968).

¹⁶The equipartition theorem is valid within classical statistical mechanics and assumes that the energy of the system contains only quadratic terms. By employing the equipartition theorem we are assuming temperatures high enough that quantum effects are negligible and at the same time sufficiently low so that the vibrations may be treated within the harmonic approximation (only for molecular gases, since monatomic gases do not have vibrational degrees of freedom). This last approximation is easily met by real gases at room temperatures; the first one must be more carefully analyzed in each case. For monoatomic gases it holds very well.

¹⁷Harvey S. Leff, "Entropy and heat along reversible paths for fluids and magnets," *Am. J. Phys.* **63**, 814–817 (1995).

¹⁸M. Levi, *The Mathematical Mechanic: Using Physical Reasoning to Solve Problems* (Princeton U. P., Princeton, NJ, 2009).

¹⁹Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (John Wiley & Sons, New York, NY, 1985), pp. 473–478.