

Specific heats of saturated water vapor and liquid

Albrecht Elsner

Am Mühlbach 14, 85748 Garching, Germany

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This paper introduces a modification of the expression for the specific heat of saturated vapor attributed to Clausius and widely used in the literature. The proposed formula contains an additional term which avoids the often-criticized negative value of the specific heat of saturated vapor. Results are given for the case of water.

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I. INTRODUCTION

Data on the specific heat of saturated water vapor have been published ever since James Watt developed the steam engine, and Clausius the appropriate theory [1]. Whereas Watt assumed the value of the specific heat of water vapor to be about zero, Clausius calculated negative values. The latter's ideas were adopted by Helmholtz [2], Planck [3], and others (e.g., [4]), but Helmholtz in particular was somewhat doubtful in that he considered "the odd result of a negative specific heat for saturated water vapor" to be in contradiction to the behavior of various other vapors. A recently published textbook [5] asks the question, "Can a heat capacity be negative?" and gives the answer, "In a canonical state, the heat capacity cannot be negative, because increasing the mean energy in the system implies a positive heat capacity." Other authors [6], for their part, are of the opinion that "there is no occasion to measure or use the specific heat for the vapor." This statement is confronted by published tables of specific heats of saturated vapors and liquids with both negative [7] and positive [8] values for the saturated vapor.

Whereas the heat capacity of the complete fluid system can be directly measured, the specific heats of the saturated vapor and condensate can only be calculated from other measured data, such as the specific heat capacity of the fluid system in conjunction with the vapor pressure, internal energies, and densities of the fluid. The connection between these state parameters will now be look at once more.

II. HEAT CAPACITY OF A SATURATED FLUID AND SPECIFIC HEATS OF THE EQUILIBRIUM PHASES

The heat capacity C of a fluid system is generally a function of the fluid mass M , the system volume V , and the fluid energy U :

$$C = C(M, V, U) . \quad (1)$$

The heat capacity in relation to the mass M represents an averaged value that no longer depends on M and is called

the specific heat capacity or, in short, the specific heat of the fluid system:

$$C/M = C(1, V/M, U/M) . \quad (2)$$

Depending on the test condition under which the system is subjected to a change of state, one makes a distinction between specific heats and characterizes them by means of the state parameters that are kept fixed in the test. We are concerned here solely with the change of state of a fluid with fixed system parameters both M and V . Under this condition, i.e., $V/M = \text{const}$, a fluid at a temperature below the critical value assumes the pressure of saturation (vapor pressure), and is called a saturated fluid. The specific heat capacity of the fluid system is then $C_{V/M}/M = C_{V/M}(1, V/M, U/M)$, which is referred to as C_σ/M (saturation σ) by many authors in the literature. For a given fluid-density value V/M , the heat capacity is a function of the fluid energy U/M only.

Let us now take the average of a system parameter by dividing its value by the mass M , and let us characterize such a specific system parameter by means of a bar:

$$\bar{v} \equiv V/M, \quad \bar{u} \equiv U/M, \quad \bar{c} = \bar{c}(\bar{v}, \bar{u}) \equiv C(1, \bar{v}, \bar{u}) . \quad (3)$$

Since we are dealing with the properties of a saturated fluid in the following we will omit, for brevity, the saturation-state indices \bar{v} or σ and write for the vapor pressure simply p instead of $p_{\bar{v}}$ or p_σ and for a specific system parameter simply \bar{x} instead of $\bar{x}_{\bar{v}}$ (energy $x = u$, entropy $x = s$, heat capacity $x = c$).

In the case of a saturated fluid a system parameter is additively composed of the phase parameters, which are characterized by an index for the respective phase [v for vapor and l for liquid (condensate)]:

$$M = M_v + M_l, \quad V = V_v + V_l, \quad (4)$$

$$U = U_v + U_l, \quad C = C_v + C_l .$$

Next we introduce the so-called specific phase parameters, which should not be confused with the specific system parameters defined by Eq. (3). They represent quantities that refer to the masses $M_{v,l}$ present in the volumes $V_{v,l}$ and describe the state of the phases. They are pure

temperature functions and are likewise characterized by a phase index. They include, for example, the specific volumes $v_{v,l}$, the specific internal energies $u_{v,l}$, and the specific heats $c_{v,l}$ of the vapor and condensate phases in equilibrium:

$$v_{v,l} \equiv V_{v,l}/M_{v,l}, \quad u_{v,l} \equiv U_{v,l}/M_{v,l}, \quad c_{v,l} \equiv C_{v,l}/M_{v,l}. \quad (5)$$

The specific system parameters and the specific phase parameters are related as follows:

$$\begin{aligned} \bar{v}M &= v_v M_v + v_l M_l, & \bar{u}M &= u_v M_v + u_l M_l, \\ \bar{c}M &= c_v M_v + c_l M_l. \end{aligned} \quad (6)$$

In particular, the third equation establishes a definite relation between the specific heat capacity of the saturated fluid and the specific heats of its equilibrium phases.

The specific heat capacity of the saturated fluid (composed of the coexisting vapor and condensate phases) can be described thermodynamically as a consequence of the change of the fluid energy due to heat input under the condition $\bar{v} = \text{const}$ that maintains the state of saturation, as follows:

$$\begin{aligned} \bar{c} &= \left(\frac{\partial \bar{u}}{\partial T} \right)_{\bar{v}} = \frac{\partial}{\partial T} \left(\frac{U}{M} \right)_{V/M}, \\ U &= -V \frac{d(p/T)}{d(1/T)} + M \frac{d(\mu/T)}{d(1/T)}. \end{aligned} \quad (7)$$

As usual, T denotes the system temperature, p the vapor pressure, and μ the chemical potential of the fluid. Relations (7) allow the specific heats of the saturated vapor and the saturated liquid to be given explicitly from Eqs. (6). As shown in the Appendix, calculation yields

$$\begin{aligned} c_{v,l} &= \frac{du_{v,l}}{dT} + \frac{dv_{v,l}}{dT} \frac{d(p/T)}{d(1/T)} \\ &= \left[\frac{ds_{v,l}}{dT} - \frac{dv_{v,l}}{dT} \frac{dp}{dT} \right] T \\ &= \left[v_{v,l} \frac{d^2 p}{dT^2} - \frac{d^2 \mu}{dT^2} \right] T. \end{aligned} \quad (8)$$

Here $s_{v,l}$ are the specific entropies of the vapor and condensate.

In the literature, relations (8) are apparently not used to calculate the specific heats of saturated vapor and liquid. Other expressions, which are discussed below, are used instead.

III. EXPRESSIONS FOR THE SPECIFIC HEATS OF SATURATED VAPOR AND SATURATED LIQUID FOUND IN THE LITERATURE

The literature contains various expressions for $c_{v,l}$. Very often (e.g., [4,7,9,10]) the following expressions are found:

$$c_{v,l} = \frac{ds_{v,l}}{dT} T = \frac{du_{v,l}}{dT} + \frac{dv_{v,l}}{dT} p. \quad (9)$$

The first equation, $c_{v,l} = T ds_{v,l}/dT$, will have to be looked

at more closely, whereas the second one then follows direct from the Gibbs-Duhem equations

$$\frac{du_{v,l}}{dT} + \frac{dv_{v,l}}{dT} p - \frac{ds_{v,l}}{dT} T = 0. \quad (10)$$

The first expression is substantiated according to, for example, Ref. [4] by the fact that the specific heat of the system can be calculated from the fluid entropy $S/M \equiv \bar{s}$ in accordance with $\bar{c} = T(\partial \bar{s}/\partial T)_{\bar{v}}$. By analogy, $c_{v,l} = T ds_{v,l}/dT$ is then written for the phases. This conclusion is not justified, however, because the entropy of a saturated fluid is a function of s_v and s_l with temperature-dependent coefficients, $\bar{s} = (M_v/M)s_v + (M_l/M)s_l$, and reads (expressed in terms of the measurable parameters density and vapor pressure) $\bar{s} = \bar{v} dp/dT - v_l/(v_v - v_l)s_v + v_v/(v_v - v_l)s_l$. By the same right, from $\bar{c} = (\partial \bar{u}/\partial T)_{\bar{v}}$ it can neither be postulated that $c_{v,l} = du_{v,l}/dT$, which would contradict Eq. (10), too.

A diagram (Fig. 1) may help clarify the situation. On a plot of specific entropies versus $\ln T$ and specific energies

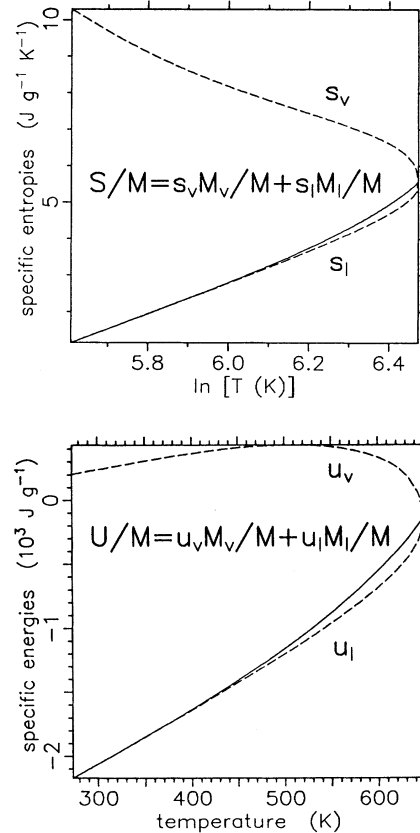


FIG. 1. Specific entropies and energies of water. The solid curves give the specific entropy S/M and energy U/M for a fluid system with critical density and the dashed curves give the specific values $s_{v,l}$ and $u_{v,l}$ of saturated vapor and liquid. The data on the saturation curves are taken from [15] with the reference values at the critical point $u_c = 0$ and at the triple point $s_v(T_t) = s(\text{ideal gas}) = k[\frac{5}{2} + \ln v_v(T_t)/v_q(T_t)]$, where $v_q(T_t) = h^3/(2\pi m k T_t)^{3/2}$ and m is the particle mass, h the Planck constant, and k the Boltzmann constant. For a saturated fluid it holds that $s_l \leq S/M \leq s_v$ and $u_l \leq U/M \leq u_v$.

versus T we can draw the system entropy \bar{s} and system energy \bar{u} as full curves (case $\bar{v}=v_c$), and the specific saturated values s_v, s_l and u_v, u_l as dashed curves (which fit continuously at the critical point). The slope of the solid curves is the specific heat capacity of the fluid with critical density v_c , i.e.,

$$\bar{c}_v = C(M, v_c M, U)/M = C(1, v_c, \bar{u}_{v_c}).$$

A comparison of the entropy and energy plots shows that it is not possible to interpret the slopes of the saturation curves, $T ds_{v,l}/dT$ and $du_{v,l}/dT$, as the specific heats $c_{v,l}$ of the saturated vapor and liquid.

Since $ds_v/dT < 0 < ds_l/dT$, relations (9) immediately lead to the relations

$$c_v < 0 < c_l, \quad C_v < 0 < C_l. \quad (11)$$

Accordingly, the vapor would thus have a negative heat capacity, and the heat capacity of the fluid would always be smaller than that of the condensate, $C < C_l$.

A formulation used earlier (e.g., [1-4,11]) is

$$c_v = c_l + \frac{d(s_v - s_l)}{dT} T, \quad c_l \approx [c_p]_l, \quad (12)$$

where $[c_p]_l > 0$ denotes the specific heat of the condensate at constant pressure. Negative numerical values of c_v are likewise given for water.

If one takes the difference $c_v - c_l = (ds_v/dT - ds_l/dT)T$ according to Eqs. (9) and (12), one obtains a negative value:

$$c_v - c_l < 0, \quad (13)$$

this being in contradiction to the known thermodynamic equations [12]

$$\begin{aligned} v_v - v_l > 0, \quad \left[\frac{\partial \bar{c}}{\partial \bar{v}} \right]_T &= \frac{c_v - c_l}{v_v - v_l}, \\ \left[\frac{\partial \bar{c}}{\partial \bar{v}} \right]_T &= \left[\frac{\partial^2 p}{\partial T^2} \right]_{\bar{v}} T = \frac{d^2 p}{dT^2} T > 0. \end{aligned} \quad (14)$$

In a table for water [8] one finds

$$0 < c_v < c_l \quad (15)$$

in the temperature region 273–583 K. These data are likewise in contradiction to requirement (14).

Occasionally, integral expressions for the specific heats are linked with other state parameters, e.g., in the relations [13]

$$\mu = v_{v,l} p - \int_T^{T_c} c_{v,l} dT + T \int_T^{T_c} \frac{c_{v,l}}{T} dT, \quad (16)$$

where the index c refers to the critical state. Taking the second derivative here yields

$$\begin{aligned} c_{v,l} &= \left[v_{v,l} \frac{d^2 p}{dT^2} - \frac{d^2 \mu}{dT^2} + \frac{d}{dT} \left[\frac{dv_{v,l}}{dT} p \right] + \frac{dv_{v,l}}{dT} \frac{dp}{dT} \right] T \\ &= \left[\frac{ds_{v,l}}{dT} + \frac{d}{dT} \left[\frac{dv_{v,l}}{dT} p \right] \right] T. \end{aligned} \quad (17)$$

In order to put Eqs. (8) and (17) into accord, the conditions

$$d[(dv_{v,l}/dT)p]/dT + (dv_{v,l}/dT)(dp/dT) = 0$$

have to be satisfied in (17), but this is not possible with a condensable gas. Indeed, to describe the behavior of a real gas correctly, relations (16) have to be extended as follows:

$$\begin{aligned} \mu &= u_c - s_c T + v_{v,l} p + \int_{v_{v,l}}^{v_c} \frac{d(p/T)}{d(1/T)} dv_{v,l} \\ &+ T \int_{v_{v,l}}^{v_c} \frac{dp}{dT} dv_{v,l} - \int_T^{T_c} c_{v,l} dT + T \int_T^{T_c} \frac{c_{v,l}}{T} dT. \end{aligned} \quad (18)$$

Of the relations (9)–(18) only Eqs. (10), (14), and (18) are in agreement with the thermodynamic laws.

The foregoing reveals that the specific heats of saturated vapor and saturated liquid have not been calculated uniformly in the literature. Figure 2 shows published data $c_{v,l}$ for water, including results for c_l from Monte Carlo–simulation calculations [14]. For calculating the values of $c_{v,l}$ according to Eqs. (8), (9), (12), and (17), temperature functions for the parameters p , $v_{v,l}$, and $s_{v,l}$ [15] were used.

IV. SPECIFIC HEATS OF SATURATED WATER VAPOR AND LIQUID

By means of relations (8) we will first show that the value of the specific heat of vapor is positive and is always larger than that of the condensate. This follows direct from the third relation (8) if it is borne in mind that $v_v > v_l$, $d^2 p/dT^2 > 0$, and $-d^2 \mu/dT^2 > 0$. Thus for any temperature it holds that

$$0 < c_l < c_v, \quad c_v - c_l = (v_v - v_l) \frac{d^2 p}{dT^2} T. \quad (19)$$

Figure 3 shows the specific heats according to Eqs. (8) for water in the temperature range from the triple point up to the vicinity of the critical point ($\lim_{T \rightarrow T_c} c_{v,l} \rightarrow \infty$).

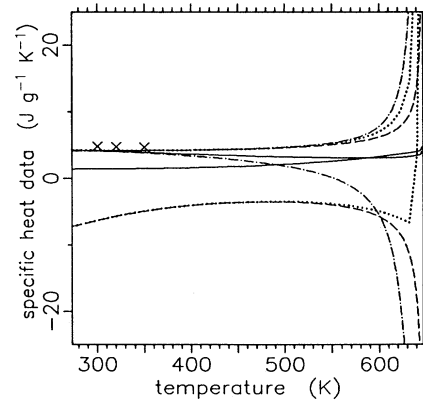


FIG. 2. Specific-heat data c_v and c_l for water as given in the literature. The various data refer to Ref. [14] (crosses), Ref. [8], and Eq. (15) (solid curves), Eqs. (9) (dashed curves), Eqs. (12) with $[c_p]_l$ data from Ref. [15] (dotted curves), and Eqs. (17) (dash-dotted curves).

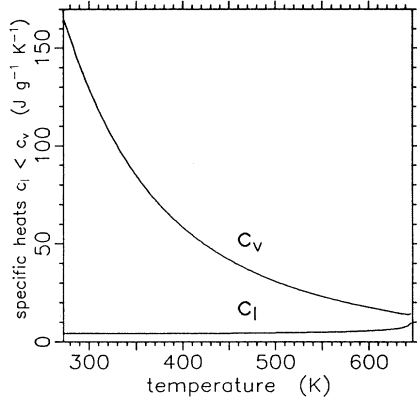


FIG. 3. Specific-heat data c_v and c_l for water calculated from Eqs. (8).

The difference to the data in Fig. 2 is of a fundamental character. The values $c_{v,l}$ in Eqs. (8) and (9), for example, differ exactly by the terms $-(dv_{v,l}/dT)(dp/dT)T$, i.e., in the case of vapor by large positive amounts and in the case of liquid by smaller negative amounts. In other words, the c_v values calculated according to Eqs. (9) are much too small and the c_l values somewhat too large.

Let us now consider the heat capacities of the fluid and its individual phases. In order to specify them one has to calculate the mass distribution M_v/M in the partial volume V_v and M_l/M in V_l from Eqs. (3)–(5); in accordance with the lever rule one obtains

$$\frac{M_v}{M} = \frac{V/M - v_l}{v_v - v_l}, \quad \frac{M_l}{M} = \frac{v_v - V/M}{v_v - v_l}. \quad (20)$$

Together with the last line of Eqs. (8) this yields the relations

$$C_v = \frac{M(V/M - v_l)}{1 - v_l/v_v} \left[\frac{d^2p}{dT^2} - \frac{1}{v_v} \frac{d^2\mu}{dT^2} \right] T$$

and

$$C_l = \frac{M - V/v_v}{1 - v_l/v_v} \left[v_l \frac{d^2p}{dT^2} - \frac{d^2\mu}{dT^2} \right] T$$

and hence (for $T < T_c$ and $V/M = v_c$)

$$0 < C_v < C_l, \quad C = \left[v \frac{d^2p}{dT^2} - M \frac{d^2\mu}{dT^2} \right] T. \quad (21)$$

These relations state that (for a system with critical mass density) the heat capacity of the saturated vapor is smaller than that of the saturated liquid. As Fig. 4 shows, the heat capacity of the vapor outside the critical region is negligible in relation to that of the liquid; the heat capacity of the fluid is governed almost solely by the heat capacity of the condensate. This applies all the more the closer one comes to absolute zero. At absolute zero the heat capacity of each phase vanishes, which is in agreement with Nernst's view:

$$C_v = M(V/M - v_l) \frac{d^2p}{dT^2} T \rightarrow 0$$

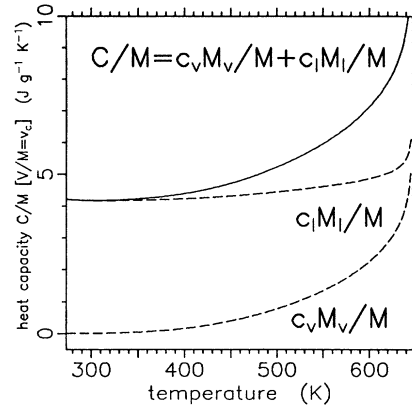


FIG. 4. Specific heat capacity of water for a fluid system with critical density. The solid curve gives the specific heat capacity of the system and the dashed curves give the specific heat capacities of the vapor and liquid phases.

and

$$C_l = M \left[v_l \frac{d^2p}{dT^2} - \frac{d^2\mu}{dT^2} \right] T \rightarrow 0.$$

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APPENDIX

We begin our specific-heat calculation by mentioning the well-known equilibrium state relations between the specific phase parameters $v_{v,l}$, $s_{v,l}$, and $u_{v,l}$ and the potentials p and μ , i.e., the equations for the saturated fluid:

$$\frac{(s_v - s_l)T - (u_v - u_l)}{v_v - v_l} = p,$$

$$\frac{(s_v v_l - s_l v_v)T - (u_v v_l - u_l v_v)}{v_v - v_l} = \mu,$$

$$\frac{s_v - s_l}{v_v - v_l} = \frac{dp}{dT}, \quad \frac{s_v v_l - s_l v_v}{v_v - v_l} = \frac{d\mu}{dT},$$

$$\frac{u_v - u_l}{v_v - v_l} = -\frac{d(p/T)}{d(1/T)}, \quad \frac{u_v v_l - u_l v_v}{v_v - v_l} = -\frac{d(\mu/T)}{d(1/T)},$$

$$\frac{d}{dT} \frac{u_v - u_l}{v_v - v_l} = \frac{d^2p}{dT^2} T, \quad \frac{d}{dT} \frac{u_v v_l - u_l v_v}{v_v - v_l} = \frac{d^2\mu}{dT^2} T,$$

$$\frac{du_{v,l}}{dT} - \frac{dv_{v,l}}{dT} \frac{u_v - u_l}{v_v - v_l} = \left[v_{v,l} \frac{d^2p}{dT^2} - \frac{d^2\mu}{dT^2} \right] T.$$

We shall now see that the expressions on both sides of the last equation are equal to the specific heats of saturated vapor and saturated liquid ($c_{v,l}$). These can be calculated with the help of Eqs. (6), (7), and (20) in two different ways.

(1) We obtain two similar expressions for \bar{c} as linear combinations of M_v/M and M_l/M :

$$\bar{c} = c_v \frac{M_v}{M} + c_l \frac{M_l}{M},$$

$$\begin{aligned} \bar{c} &= \frac{d}{dT} \left[u_v \frac{M_v}{M} + u_l \frac{M_l}{M} \right]_{v,M} \\ &= \left[\frac{du_v}{dT} + \frac{dv_v}{dT} \frac{d(p/T)}{d(1/T)} \right] \frac{M_v}{M} \\ &\quad + \left[\frac{du_l}{dT} + \frac{dv_l}{dT} \frac{d(p/T)}{d(1/T)} \right] \frac{M_l}{M}. \end{aligned}$$

We can deduce that the coefficients $c_{v,l}$ and $du_{v,l}/dT + (dv_{v,l}/dT)d(p/T)/d(1/T)$ are equal since they are pure temperature functions, whereas $M_{v,l}/M$ depend on both temperature and fluid density. This yields the first line of Eqs. (8).

Since $(1/T)d\bar{u}/dT = d\bar{s}/dT$ we can also proceed from an entropy formulation of the problem:

$$\begin{aligned} \frac{\bar{c}}{T} &= \frac{d}{dT} \left[s_v \frac{M_v}{M} + s_l \frac{M_l}{M} \right]_{v,M} \\ &= \left[\frac{ds_v}{dT} - \frac{dv_v}{dT} \frac{dp}{dT} \right] \frac{M_v}{M} + \left[\frac{ds_l}{dT} - \frac{dv_l}{dT} \frac{dp}{dT} \right] \frac{M_l}{M}. \end{aligned}$$

Again, the coefficients in front of $M_{v,l}/M$ yield the expressions for $c_{v,l}/T$ [second line of Eqs. (8)], which, moreover, could also have been obtained from the first line of Eqs. (8) by means of the Gibbs-Duhem relations (10).

(2) From Eqs. (6), (7), and (20) we also obtain

$$\bar{c} = \frac{V}{M} \frac{c_v - c_l}{v_v - v_l} - \frac{c_v v_l - c_l v_v}{v_v - v_l},$$

$$\bar{c} = \frac{V}{M} \frac{d^2 p}{dT^2} T - \frac{d^2 \mu}{dT^2} T.$$

Again, by comparing the coefficients on the right-hand side of the above equations we find the two relations

$$\frac{c_v - c_l}{v_v - v_l} = \frac{d^2 p}{dT^2} T, \quad \frac{c_v v_l - c_l v_v}{v_v - v_l} = \frac{d^2 \mu}{dT^2} T$$

and from these we immediately derive the third line of Eqs. (8).

Because of

$$\begin{aligned} \frac{c_v v_l - c_l v_v}{v_v - v_l} &= v_v \frac{c_v - c_l}{v_v - v_l} - c_v = v_l \frac{c_v - c_l}{v_v - v_l} - c_l \\ &= v_v \frac{d^2 p}{dT^2} T - c_v \\ &= v_l \frac{d^2 p}{dT^2} T - c_l \end{aligned}$$

we can also write

$$\bar{c} = c_v - \left[v_v - \frac{V}{M} \right] \frac{d^2 p}{dT^2} T = c_l + \left[\frac{V}{M} - v_l \right] \frac{d^2 p}{dT^2} T.$$

Finally, with the above results we confirm that

$$\begin{aligned} \frac{d}{dT} \frac{u_v - u_l}{v_v - v_l} &= \frac{c_v - c_l}{v_v - v_l}, \\ \frac{d}{dT} \frac{u_v v_l - u_l v_v}{v_v - v_l} &= \frac{c_v v_l - c_l v_v}{v_v - v_l}. \end{aligned}$$

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