Constitutive Relations of Energy Storage in a Gas in Preferred Integral Causality

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Abstract
This paper deals with the derivation and use of the preferred integral causal form of the constitutive relations describing a three-port capacitor (C-element) that represents the energy storage in a gas that can be considered either an ideal gas (Boyle Gas-Lussac) or a Van-der-Waals gas. It will be shown under which conditions this derivation is possible and under which conditions other forms of state equations can be analytically converted to the desired form. A comparison is made between simulations in which the thermal port has integral causality and implicit simulations in which this causality is derivative.

1 Introduction
There are both computational and physical arguments to compute the (extensive) states or state variables of a dynamic model by integration with respect to time of rates of change of state (rate variables or flows). In the terminology of a port-based systems approach as expressed in bond graphs, this is called 'preferred integral causality of storage ports. For example, in an electrical capacitor or mechanical spring, the current and the velocity are integrated into an amount of electric charge and mechanical displacement respectively. Next they are related to the voltage and the force by dividing with the capacitance and the compliance respectively.

In case of the internal energy storage in a (gaseous) substance, which can be described by the extensive states entropy $S$ available volume $V$ and amount of moles $N$, and the conjugate intensive states (efforts) temperature $T$, pressure $p$ and material potential $\mu$, this means that the form $T(S,V,N)$, $p(S,V,N)$ and $\mu(S,V,N)$ is preferred. However, the common form of a so-called state equation of a gas is a relation between pressure $p$, specific volume (inverse molar density) $v$ and temperature $T$, hence a relation between intensive variables, as the extent generally does not influence the characteristic properties of a substance. By substituting the specific volume $v$ by $V/N$, this can be simply extended to the constitutive relation of the mechanical port $p(T,V,N)$, which suggests differential causality of the thermal port and indicates that still two other constitutive relations are required, viz. those of the thermal and material ports.

After a short discussion of preferred integral causality in bond graphs this paper will show what the relations are for a generic substance and under which conditions the preferred integral causal forms of the ideal gas and the Van-der-Waals gas can be derived. The use of the obtained nonlinear 3-port C-element will be demonstrated by an example similar to the case studied by Pourmovahed and Otis [1], viz. a fixed amount of nitrogen (zero-flow source at the material port) of which the available volume (cylinder-piston combination) is varied sinusoidally, while there is a heat conduction according to Fourier's law to and from the isothermal environment.

As the laborious derivations of the ideal and the Van-der-Waals cases demonstrate that there is not much hope to find analytical solutions for more realistic conditions and state equations like the virial equation and the Beattie-Bridgeman equation [2], both examples are also simulated with the thermal port in differential causality, thus requiring an implicit integration routine (BDF in this case). As only the state equation $p(T,V,N)$ is known, $S(T,V,N)$ and $\mu(T,V,N)$ have to be derived, although the latter is not important as long as $N$ is kept constant. The results of these simulations are compared with those of the preferred integral causal case and demonstrate hopeful results. Although this opens a possibility to use more realistic known relations in simulation, there remains a need for the preferred integral causal form. This, however, requires that measurement data are converted into the desired forms after which they can be approximated by constitutive relations. This remains a challenge for the future.

2 Bond graphs and preferred integral causality
The port-based approach as represented in a bond graph has demonstrated the benefits of using an integral causal form of the constitutive relations of storage ports, both for numerical simulation and the modeling process itself. In numerical simulation integration is preferred over differentiation for obvious reasons like numerical noise and proper handling of initial conditions. In the modeling process, not being able to assign integral causality to a storage port reveals a modeling decision to use a constraint that might be the result of oversimplification. For instance, if a modeler assumes a rigid connection between two ideal masses, resulting in differential causality of one of the 1-type storage ports representing the masses, this modeling decision means that a choice is made for a (physically impossible) infinite stiffness of the connection. This does not mean that the finite stiffness should be included to prevent this differential causality by definition, as a finite, but large, stiffness will induce a rather stiff system and consequently other numerical problems. However, it helps the modeler to make an explicit trade-off between numerical and conceptual complexity.

3 Generic substance
The constitutive relations in preferred integral form should have the following form for an arbitrary substance in any phase (gas, liquid or solid): $p = p(V,S,N)$, $T = T(V,S,N)$, $\mu = \mu(V,S,N)$. For the internal energy $U$ of $N$ moles of a generic substance that may be considered a three-port storage element with energy $U$ and extensive state variables $V$, $S$ and $N$, the following energy balance can be written: $dU(V,S,N) = TdS - pdV + \mu dN$. Note that the minus sign is due to the fact that the energy increases when the available volume is reduced. In intensive form this expression reduces to $d(u,v,s) = Tds - pdv + \mu dv$ with $u$, $s$ and $v$ the value of $U$, $S$ and $N$ for $N = 1$ mole. As the extensive form can be found in a straightforward manner from the intensive form, we will first use this intensive form to simplify the intermediate expressions; consequently the following holds for $du$:

$$du(v,T) = \left( \frac{\partial u}{\partial v} \right)_{d_T = 0} dv + \left( \frac{\partial u}{\partial T} \right)_{dv = 0} dT =$$

$$= \left( \frac{T \delta s}{\delta v} \right)_{d_T = 0} dv + \left( \frac{\partial u}{\partial T} \right)_{dv = 0} dT.$$  

By definition, the specific heat $c_v$ of a substance at constant volume, reads

$$c_v = \frac{1}{N} \frac{\partial}{\partial T} \frac{\partial Q}{\partial v} \bigg|_{dv = 0} \bigg|_{dT = 0} = \frac{\partial u}{\partial T} \bigg|_{dv = 0}.$$  

This means...
that \( du(v,T) = \left[ \frac{T \partial s}{\partial T} \right]_{dv=0} - p \ dv + c_v dT \) which is called the

Gibbs-Maxwell identity [3]. Maxwell reciprocity of the specific free energy \( f(x,T) \) gives

\[
\frac{\partial s}{\partial v} \bigg|_{dT=0} = \frac{\partial^2 f}{\partial v T} \bigg|_{dT=0} - \frac{\partial^2 f}{\partial v T} \bigg|_{dT=0} - c_v \frac{\partial p}{\partial T} \bigg|_{dv=0},
\]

such that

\[
du(v,T) = \left[ \frac{T \partial p}{\partial T} \right]_{dv=0} \ dv - p dv + c_v dT.
\]

Combination with \( du = T ds - p dv \) results in an important expression for \( dv \) that holds for a generic substance, independent of

its phase \( ds = \left( \frac{\partial p}{\partial T} \right)_v dv + \frac{c_v}{T} dT \). If \( c_v \) is independent of \( T \) and

\( v \) (‘perfect gas’), this can be written:

\[
T(s,v) = T_0 \exp \left[ \frac{s-s_0}{c_v} - \frac{1}{c_v} \right] \frac{\partial p}{\partial T \big|_{dv=0}} dv
\]

\[
= T_0 \exp \left[ \frac{s-s_0}{c_v} \right] \left( \frac{c_v}{v} \right) \left[ \frac{\partial p}{\partial T \big|_{dv=0}} \right] dv
\]

that the latter expression can only be worked out further if some relation between \( p \) and \( v \) is given, i.e. a state equation, which allows further evaluation of \( \partial p / \partial T \big|_{dv=0} \). Two special cases are elaborated, the simple case of the ideal gas (Boyle & Gay-Lussac) and the more complex case of the Van-der-Waals gas, both under the so-called perfect gas model assumption that \( c_v \) is constant, to give an example how constitutive relations as usually specified for gases can be converted in the integral causal form preferred for numerical simulation.

Also note that in case of any constitutive relation in which \( p \) is proportional to \( T \) for \( dv = 0 \), it holds that \( T \partial p / \partial T \big|_{dv=0} = p \), such that it can be concluded that

\[
dw = \left[ \frac{T \partial p}{\partial T} \big|_{dv=0} - p \right] dv + c_v dT = c_v dT \quad \text{when the pressure}
\]

\( p \) is proportional to the temperature \( T \) for \( dv = 0 \). In other words, in all cases where the pressure \( p \) is proportional to the temperature \( T \) for \( dv = 0 \), the specific internal energy of the substance depends only on the temperature. In case \( c_v \) is constant (perfect gas model), it then follows that \( u = u_0 + c_v T - c_v T_0 \) and, with the reasonable choice that \( u_0 = c_v T_0 \):

\[
U(V,S,N) = u(v,s) = c_v T(V',S,1). \quad \text{From the fact that the amount of}
\]

1 mol was arbitrarily chosen, it follows that the next relation for the internal energy of a generic substance should hold in case \( p \) is proportional to the temperature \( T \) for \( dv = 0 \) and \( c_v \) is constant:

\[
U(V,S,N) = N c_v T(V,S,N).
\]

4 Ideal gas

The state equation for an ideal gas is \( pV = NRT \) (Boyle & Gay-Lussac). The partial derivative \( \partial p / \partial T \big|_{dv=0} \) can be applied directly to this state equation in intensive form, \( p = RT/\nu \), such that in case of an ideal gas \( ds = R \nu \ dv + \frac{c_v}{T} dT \), which also provides a means to find the flow of the thermal port in case \( N(N=N_0) \) is constant, i.e. the port is in derivative or differential causality

\[
f_S = \frac{RN_0}{V} f_v + N_0 \frac{c_v}{T} \frac{dT}{dT}. \quad \text{In case \( N \) is not constant}
\]

\[
f_S = (S/N - R) f_N + (RN/V) f_v + (Nc_v/T) \frac{dT}{dT}, \quad \text{such that}
\]

knowledge of \( S \) is required.

Making the perfect gas model assumption that \( c_v \) is constant, the expression

\[
T(s,v) = T_0 \exp \left[ \frac{s-s_0}{c_v} - \frac{1}{c_v} \right] \frac{R}{v} dv = T_0 \left( \frac{v}{v_0} \right)^{c_v} \left( \frac{c_v}{c_v} \right) \left( \frac{v}{v_0} \right)^{-c_v} \left( \frac{c_v}{c_v} \right)
\]

obtained, i.e. the constitutive relation for the thermal port that corresponds to the preferred integral causality, but still in intensive form. The constitutive relation for the mechanical port in integral causality is an immediate result of a combination with the state equation

\[
p(s,v) = \frac{RT}{v} = \frac{R}{v} T_0 \left( \frac{v}{v_0} \right)^{c_v} \left( \frac{c_v}{c_v} \right)
\]

\[
= \frac{RT_0}{v_0} \left( \frac{v}{v_0} \right)^{c_v} \left( \frac{c_v}{c_v} \right) = p_0 \left( \frac{v}{v_0} \right)^{c_v} \left( \frac{c_v}{c_v} \right).
\]

The required extensive forms are

\[
T(S,V) = T_0 \left( \frac{V N_0}{V_0 N_0} \right)^{c_v} \left( \frac{c_v}{c_v} \right) \left( \frac{N_0}{N_0} \right)^{c_v} \left( \frac{S-N_0/N_0}{S-N_0/N_0} \right).
\]

\[
p(S,V) = p_0 \left( \frac{V N_0}{V_0 N_0} \right)^{c_v} \left( \frac{c_v}{c_v} \right)^{S-N_0/N_0} \left( \frac{c_v}{c_v} \right).
\]

Herein it is used that the difference between the specific heat at constant pressure and the specific heat at constant temperature should be equal to the work done by 1 mole of expanding gas per degree of increase of temperature, so the specific work \( pv \) divided by the temperature \( T \). For an ideal gas \( pvT \) is equal to \( R \), i.e. \( R = c_p - c_v \). As \( c_v \) is assumed constant, it also follows that

\[
U(V,S,N) = c_v T(N) = U_0 \left( \frac{V}{V_0} \right)^{c_v} \left( \frac{N_0}{N} \right)^{c_v} \left( \frac{S-N_0/N_0}{S-N_0/N_0} \right).
\]

A simple check shows that evaluation of \( \partial u/\partial s = \partial U/\partial S = T \) and \( \partial v/\partial s = \partial U/\partial S = -p \), in combination with \( v_0 = c_v T_0 \) and \( p_0 = RT_0/v_0 \) leads again —as required— to the already known relations for \( p(V,S,N) \) and \( T(V',S,N) \). Note that for the effort \( \mu \) the fact that it is conjugate to \( N \) an expression in \( V, S, N \) can be derived similarly from the expression found for \( U \) by partial derivation with respect to \( N \). However, an alternative derivation based on Gibbs’ relation yields this result in a simpler way:

\[
\mu = \frac{U}{N} = \frac{RT}{V} = \frac{c_v}{c_v} \left( \frac{c_v}{c_v} \right) \left( \frac{S-N_0/N_0}{S-N_0/N_0} \right).
\]

\[
\mu = \frac{c_v}{c_v} \left( \frac{S-N_0/N_0}{S-N_0/N_0} \right).
\]

Consequently the constitutive relation of the third port through which gas is exchanged when \( N \) is not kept constant, is also found. Note that Maxwell reciprocity of these three constitutive relations is satisfied. If \( N \) is kept constant at \( N=N_0 \) the three-port may be reduced to a two-port for which.
the extensive form of the energy and the constitutive relations has been found before [4]:
\[ U(V,S) = U_0(V/V_0) - \frac{R}{c_v} S - s_0 \quad \text{and} \quad T(V,S) = T_0(V/V_0) - \frac{R}{c_v} S - s_0 \]
and \[ p(V,S) = p_0(V/V_0)^{c_v} e^{s_0} \cdot \]

5 Conditions for analytical derivation

Note that when \( c_v \) is not constant, but depends on the temperature \( T \), the above derivation remains possible as long as both \( c_v(T) \) are integrable and while \( p \) is proportional to \( T \) for \( dv=0 \) (in order to be able to obtain \( u \)) and \( c_v(T) \) are integrable and while \( p \) is proportional to \( T \) for \( dv=0 \) (in order to be able to obtain \( u \)). Finally, it has to be possible to solve the relations for \( T \). Often the \( c_v(T) \) of certain gases is written as a polynomial in \( T \), such that the integrability condition is satisfied, for example:
\[ c_v(T) = a + bT + cT^2 \quad \text{where} \quad a, b, \text{and} \ c \text{are material constants.} \]
From this it follows that \[ \left[ c_v(T) \right]/T \right] \quad dT = d\left[ aT + bT + cT^2/2 \right] \]
such that \[ d\left[ aT + bT + cT^2/2 \right] = d\ln T - a \ln T + b + cT \]
\[ \left[ \frac{T}{T_0} + \frac{b}{c} T \right] = \ln \left[ \frac{v}{v_0} \right] - a \ln \left[ \frac{v}{v_0} \right] + b + cT \]
\[ \left[ \frac{T}{T_0} \right] = \ln \left[ \frac{v}{v_0} \right] - \frac{a}{c} T \]
In spite of the integrability, solving for \( T \) is cumbersome in this case. A Taylor expansion in \( T=T_0 \) is used. Furthermore
\[ du = c_v(T) dT = d\left[ aT + bT^2/2 + cT^3/3 \right] \]
and as long as \( T(V,S,N) \) cannot be found, \( U(V,S,N) \) cannot be found.

6 Intrinsic stability of an ideal gas

For an intrinsically stable gas it should hold that \( dp/dv < 0 \), \( dt/dv < 0 \) and the determinant of the Jacobian \( (dp/dv)(dt/dv) - (dp/dv)(dt/dv) > 0 \). When these conditions are not satisfied (e.g. \( dp/dv > 0 \)) a gas is called intrinsically unstable. There may be a phase transition for example. The values of \( v \) for which \( dp/dv = 0 \) are called the critical values. Analysis of the ideal gas relation rewritten in the form (with \( T \) as a parameter):
\[ p(v) = \frac{RT}{v} \]
shows that:
- \( v > 0 \) in order to obtain realistic values for \( p \) (\( \rho > 0 \)),
- \( \lim_{v \to 0} p = 0 \),
- \( \lim_{v \to \infty} p = \infty \),
- there are no roots \( (p = 0) \) for \( \rho > 0 \),
- the ideal gas is always intrinsically unstable and thus has no critical point(s), because \( \frac{dp}{dv} = -\frac{RT}{v} = -\frac{p^2}{RT} < 0 \).

\[ \frac{dT}{ds} = \frac{T}{c_v} + \frac{dp}{dv} \cdot \frac{dv}{ds} = \frac{dp}{dv} \cdot \frac{2}{RC_T} > 0 \quad \text{for realistic, i.e. positive, values of} \ p \text{and} \ T. \]

7 Van-\text{-}der-\text{-}Waals gas

Van der Waals proposed two corrections to the ideal gas law \( pv = RT \). He corrected:
1. the specific volume for the volume of the molecules, by replacing \( v \) by \( v - b \), and
2. the pressure with a term \( a/v^2 \) that represents the contribution of the attraction force between the molecules and that is proportional to the square of the density, so inversely proportional to the square of the specific volume. In other words, he replaced \( p \) by \( p + a/v^2 \) such that the Van-\text{-}der-\text{-}Waals state equation or Van-\text{-}der-\text{-}Waals-equation reads (in intensive form):
\[ p + \frac{a}{v^2} = RT, \quad \text{with} \ v > b, \quad p > 0 \]
and where \( a \) and \( b \) are material dependent parameters.

A gas for which this state equation holds, is called a Van-\text{-}der-\text{-}Waals gas.

The partial derivative \( \partial p/\partial T \left|_{v=\text{const}} \right. \) can be applied directly to the Van-\text{-}der-\text{-}Waals equation, such that in this case
\[ dx = \left( \frac{R}{v-b} \right) dv + \frac{c_v}{T} dT \quad \text{(cf. generic substance), which gives a means to find the flow of the thermal port in derivative or differential causality in case \( N \) is constant} \]
\[ f_i = \frac{RN}{v-bN} f_i + NC_v \frac{dT}{T} \quad \text{d} \]
In case \( N \) is not constant
\[ f_i = \left( \frac{S}{N} + \frac{1}{R - \frac{b}{v-bN}} f_i + \frac{RN}{v-bN} + \frac{C_v}{T} \right) dT \]
\[ \ln N = \ln \left( \frac{v-b}{v-b} \right) + \frac{C_v}{T} \text{ or} \ln T = T = T_0 \text{ from which in turn follows that} \]
\[ \ln \left( \frac{T-b}{v-b} \right) = \ln \left( \frac{T-b}{v-b} \right) + \frac{C_v}{T} \text{ or} \ln T = T_0 \text{ from which in turn follows that} \]
\[ \frac{T-b}{v-b} = \frac{T-b}{v-b} + \frac{C_v}{T} \text{ or} \ln T = T_0 \text{ from which in turn follows that} \]
the constitutive relation for the thermal port in preferred integral causality, but still in intensive form. Consequently, the constitutive relation for the mechanical port in preferred causality is:
\[ p(v,s) = \left( \frac{v-b}{v-b} + \frac{C_v}{T} \right) \frac{a}{v^2} + \frac{RT}{v-b} \quad \text{such that} \]
\[ dx = \left( \frac{T \frac{dp}{dT}}{v-b} \right) - p \ dv + c_v dT = \left( \frac{a}{v^2} \right) dv + c_v dT \]
\[ u - u_0 = a + c_v T - c_v T_0 \text{ and when we choose} \]
\[ u_0 = -\frac{a}{v_0} + c_v T_0 \text{, we obtain} \]
\[ U(V,S,N) = U(v,s) = c_v T - \frac{a}{v_0} + c_v T_0 \left( \frac{v-b}{v-b} + \frac{C_v}{T} \right) \text{ or} \]
resulting in \( U(V,S,N) \) for \( N=1 \) mole of Van-\text{-}der-\text{-}Waals gas. From the fact that the amount of 1 mole was arbitrarily chosen, it follows that the following should hold.
expression completely characterizes the three-port storage element that represents the storage of energy in a Van-der-Waals gas. Also in this case a simple check shows that evaluation of \(du/\partial s = \partial u/\partial \ln S = T\) and \(udv/\partial v = p\), leads again as required to the already known relations for \(P(V,S,N)\) and \(T(V,S,N)\). Like in the case of an ideal gas, a derivation of \(\mu^{\text{tot}}\) based on Gibbs’ relation yields the constitutive relation of the third port:

\[
\mu^w - u + pv - Ts = (c_v - s)T - \frac{2a}{v} + \frac{RTv}{v - b} = \left(c_v - \frac{RT}{v - bN} - \frac{S}{N} \right)T - \frac{2a}{v}.
\]

For \(N=\overline{N}_0\) the extensive form of the energy and the constitutive relations for the two-port storage element are found:

\[
U(V,S,N) = c_v\overline{N}_0 \left(\frac{V - bN_0}{V_0 - bN_0} - \frac{S - S_0}{S_0} \right)\frac{c_v e^{\overline{N}_0}}{e^{c_v \overline{N}_0} - \frac{aN_0^2}{V}}
\]

\[
T(V,S) = T_0 \left(\frac{V - bN}{V_0 - bN_0} - \frac{S - S_0}{S_0} \right)\frac{e^{c_v \overline{N}_0}}{e^{c_v \overline{N}_0} - \frac{aN_0^2}{V^2}}
\]

and

\[
p(V,S) = \left[p_0 + \frac{aN_0^2}{V_0^2} \left(\frac{V - bN}{V_0 - bN_0} - \frac{S - S_0}{S_0} \right)\frac{e^{c_v \overline{N}_0}}{e^{c_v \overline{N}_0} - \frac{aN_0^2}{V^2}}\right]
\]

8 Intrinsic stability of a Van-der-Waals gas

In a similar analysis as in the case of the ideal gas that appeared to be stable everywhere, we will show that the Van-der-Waals gas has a critical point at \(p_c, v_c\) and \(T_c\), and we will express these values in terms of \(a, b, c_v\) and \(R\). Next we sketch the normalized pressure \(p/p_c\) for a Van-der-Waals-gas as a function of the normalized specific volume \(v/v_c\) for a number of values of the normalized temperature \(T/T_c\). Analysis of \(dp/dv\) for the Van-der-Waals-equation rewritten in the form (with \(T\) as a parameter):

\[
p(v) = \frac{RT}{v - b} - \frac{a}{v^2} \begin{cases} v > b \\
\text{in order to obtain realistic values for } p > 0 \\
\lim_{v \to 0} p = 0 \\
\lim_{v \to \infty} v = b \\
\text{in that point with value } \frac{1}{128}. 
\end{cases}
\]

\[
\nu_2 = \frac{a \pm \sqrt{a^2 - 4abRT}}{2RT}
\]

Note that \(\frac{dT}{dv} = \frac{T}{v} > 0\), while evaluation of the determinant of the Jacobian is beyond the scope of this paper.

The intrinsic stability and the critical values can be found by inspecting:

\[
\frac{dp}{dv} = \frac{-RT}{v - b} + \frac{2a}{v^2} = 0
\]

\[
\Rightarrow RTv^2 - 2av^2 + 4abv - 2ab^2 = 0.
\]

Using \(RT = (p + ab^2)(v - b)\) in \(dp/dv = 0\) results in the (critical) line in the \(p-v\)-plane on which the extrema are located for various values of \(T\):

\[
p = \frac{a(v - 2b)}{2v^2}
\]

Figure 1: \(p/p_c(v/v_c)\) for various values of \(T/T_c\)

In order to find the critical point — i.e. that there is intrinsic instability (\(dp/dv > 0\)) in only one point instead of a whole interval — the maximum of this line should be derived. In order to do so the derivative is put to zero, \(\frac{dp}{dv} = \frac{6ab - 2av}{v^3} = 0\), such that the maximum lies at \(v = 3b\) \(\frac{d^2p}{dv^2} = \frac{-6a}{243b^3} < 0\), the so-called critical value \(v_c\) of \(v\). Substitution in the previously derived relations results in the critical pressure \(p_c = a/27b^2\) and the critical temperature \(T_c = 8a(27bR)\).

In figure 1 the normalized pressure \(p/p_c\) is plotted against \(v/v_c\) for various values of the normalized temperature \(T/T_c\). Practice has shown that the Van-der-Waals-equation is not very accurate in \(v\), but that it is accurate in \(p\) and \(T\), such that \(a, b, c_v\) and \(R\) for a specific gas are to be computed from

\[
a = 27(4T_c)^2/(64p_c) \quad \text{and} \quad b = RT_c/(8p_c). \quad \text{For large values of } T\times T_c \Rightarrow \frac{dp}{dv} = \frac{3}{v/v_c} \frac{1}{128} \quad \text{intrinsic instability, } p = RT(v - b)\]

(hyperbola) with asymptotes \(v = b\) and \(p = 0\).

The critical line relation can now be expressed in the critical values:

\[
p/p_c = 3(v/v_c)^2 - 2(v/v_c)^6.
\]

Apart from the already found maximum in \(v/v_c = 1\), putting the second derivative to zero results in a flexure in \(v/v_c) = 4/3\) or \(v/v_c = 3/4\) with \(p/p_c(4/3) = 27/32\) and a derivative in that point with value \(-1/128\). Furthermore we find that for this critical line that

\[
\lim_{v/v_c \to 0} p/p_c = 0 \quad \text{and} \quad \lim_{v/v_c \to \infty} p/p_c = \infty
\]

zero in \(v/v_c = 2/3\), i.e. \(v = 2\sqrt{3} = 3\). At this critical line \(dp/dv = 0\), while below this line \(dp/dv > 0\), such that the gas is intrinsically unstable in this area, which displays itself in the form of a phase transition.

Note that by the introduction of the reduced pressure \(p_{\text{red}} = p/p_c\), the reduced temperature \(T_{\text{red}} = T/T_c\) and the reduced specific volume \(v_{\text{red}} = v/v_c\), the material dependent parameters \(a, b, c_v, R\) as well as the gas constant \(R\) can be eliminated from the Van-der-Waals-equation:

\[
(p_{\text{red}} + 3/v_{\text{red}}^2)(3v_{\text{red}} - 1) = 8T_{\text{red}}, \quad \text{such that this}
\]
-equation: \( (p_v + 3/v_t^2)(3v_t - 1) = 8T_v \), such that this form of the equation is identical for all gases, in other words, a gas is in this case not characterized by \( a \) and \( b \), but by \( p_v \) and \( T_v \) and consequently by \( pR \) and \( TR \) (with \( \lim_{v_t \to \infty} pR = 0 \) and \( \lim_{v_t \to \infty} pR = \infty \)).

9 Simulations

In order to illustrate the use of the derived relations in numerical simulation, a three-port C for an ideal gas and one for a Van-der-Waals gas have been implemented in the form of submodels in [5]. Using these submodels, a cylinder filled with a constant amount gas, which is assumed to be nitrogen in the Van-der-Waals case, in a cylinder of which the volume is varied by a sinusoidal motion of a piston and which has heat conduction to and from the isothermal environment (Figure 2; note that the direct sum junction is necessary to connect three individual ports to a three dimensional multiport). The heat conduction is modeled by a two-port RS-element that represents Fourier’s law

\[ J_Q = \lambda \Delta T = \lambda (T_1 - T_2) = T_1 f_S = T_2 f_S, \]

where \( f_S \) is the heat flow and \( \Delta T \) the temperature difference. Consequently the constitutive relations of such a two-port RS in flow-out causality are

\[ f_S = \lambda (T_1 - T_2)/T_1 \]

and

\[ T_2 = \lambda (T_1 - T_2)/T_2 . \]

As we will also simulate with a thermal port with derivative causality, this requires effort-out causality of one of the ports (the second):

\[ f_S = \lambda S_2 (\lambda + f_{S_2}) \quad \text{and} \quad T_2 = T_1 \lambda (\lambda + f_{S_2}) . \]

Using these models a realistic cycle process has been simulated using 20-sim [2000], with the following data:

- \( R=8314.5 \text{ J mole}^{-1} \text{K}^{-1} \), \( V=15 \text{ liter} \), \( N_0=0.07 \text{ mole} \),
- \( T_0=75 \text{ K} \) (Fig. 3), \( T_p=300 \text{ K} \) (Fig. 4), Nitrogen (N):
- \( p_v=3.3 \text{ MPa} \) (33 bar), \( T_v=127 \text{ K} \),
- Fourier conductance: \( \lambda=25 \text{ J/KA} \), mechanical input: amplitude: \( dP/dt = 5e-5 \text{ m/s} = 50 \text{ m/s} \), frequency: \( \omega = 0.015 \text{ rad/sec} \) (cycle time = 7 min.).

For temperatures above the critical temperature, the results of the ideal and the Van-der-Waals gas are similar (Figure 4), but for temperatures well below the critical point, the difference is considerable: the thermal losses predicted by the Van-der-Waals gas are considerably higher than those predicted by the ideal gas (cf. the enclosed areas in the 20-sim results in Figure 3a-d). If the thermal port is left in differential causality, the analysis becomes much simpler, especially in the case the \( N \) is constant as in this experiment. Note that the results are similar (Figure 3), although in the derivative case only an implicit integration technique can be used, the backward differential formula (BDF) in this case. The results for the experiment at \( T_0=300 \text{ K} \) (Figure 4) are even closer, such that they are not shown separately.

10 Conclusion

The paper shows that the constitutive relations for a C-element representing the energy storage in a gas can be analytically derived for both an ideal gas and a Van-der-Waals gas in case of the prefect gas model (constant specific heat). The use of the derived relations has been shown in some illustrative simulations of a test bed involving nitrogen (figure 2). As to be expected the results largely differ for temperatures (e.g. \( 75 \text{ K} \)) lower than the critical temperature (for nitrogen \( T_c = 127 \text{ K} \)), but are similar for temperatures (e.g. \( 300 \text{ K} \)) well above the critical point. It is also shown that the analysis is large simplified if derivative causality of the thermal port is accepted, by using an implicit numerical integration scheme. The latter opens the possibility to use known more realistic state equations that cannot be written in integral causal form, like the virial equation or the Beattie-Bridgeman equation [2]. However, this can only be an intermediate solution as the ultimate goal should be to propose new constitutive relations that are in integral causal form and fit measurement data reliably.

References

[5] 20-sim, modeling and simulation software, see: www.20sim.com for more information and demo version (free download, does not allow implicit integration), contact the author for models used in this paper.
Figure 3: Results of the example experiment for $T_0 = 75$ K (solid lines pressure $p(V)$, dashed lines temperature $T(V)$)

3a: Ideal (integral causality)

3b: Ideal (thermal port in derivative causality)

3c: Van der Waals (integral causality)

3d: Van der Waals (thermal port in derivative causality)

Figure 4: Results of the example experiments for $T_0 = 300$ K (solid lines pressure $p(V)$, dashed lines temperature $T(V)$)

4a: Ideal (integral causality)

4b: Van der Waals (integral causality)

Figure 5: Multiple run for $T_0 = 75, 150, 225, 300$ K

5a: Ideal gas

5b: Van der Waals gas