Supplementary Information

Modeling Dynamic Pressure Loss by Absorption in Oleo-Pneumatic Shock Absorbers without Separator

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1 Derivation of the Hill energy from the internal energy

The Hill energy[1] L can be derived from the internal energy using the Legendre transformation with respect to the substance amount n_1 [1]

$$\begin{aligned} L &= U - \left(\frac{\partial U}{\partial n_1}\right)_{S,V} n_1 \\ \Leftrightarrow L &= TS - pV + \mu_1 n_1 - \mu_1 n_1 = TS - pV. \end{aligned} \tag{1}$$

Its total differential using the product rule yields

$$\mathrm{d}L = T\mathrm{d}S + S\mathrm{d}T - p\mathrm{d}V - V\mathrm{d}p. \tag{2}$$

The Gibbs-Duhem equation

$$-S\mathrm{d}T + V\mathrm{d}p - n_1\mathrm{d}\mu_1 = 0 \tag{3}$$

[1]For better readability, the phase symbol $[\alpha]$ is omitted in the following derivation.

converted and replaced with $S\mathrm{d}T - V\mathrm{d}p$ in Eq. (2) yields

$$\mathrm{d}L = T\mathrm{d}S - p\mathrm{d}V - n_1\mathrm{d}\mu_1. \tag{4}$$

2 Derivation of Maxwell relations based on the Hill energy

Based on Eq. (4), the differential of the Hill energy is equalized to its total differential

$$\mathrm{d}L = T\mathrm{d}S - p\mathrm{d}V - n_1\mathrm{d}\mu_1 = \left(\frac{\partial L}{\partial S}\right)_{\mu_1,V}\mathrm{d}S + \left(\frac{\partial L}{\partial V}\right)_{S,\mu_1}\mathrm{d}V + \left(\frac{\partial L}{\partial \mu_1}\right)_{V,S}\mathrm{d}\mu_1. \tag{5}$$

Schwarz's lemma states that the mixed partial derivatives, cf. Fig. S1, are equal.

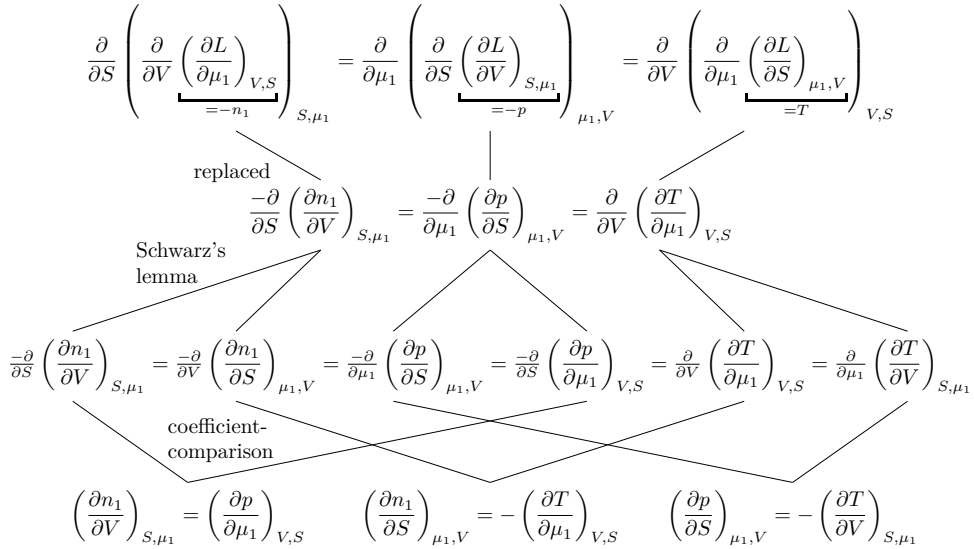

Fig. S1 Derivation of Maxwell relations based on the Hill energy

3 Derivation of the governing differential equation

It is started with the change of the internal energy of a single-component gas in an open system, which is described by the fundamental theorem

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu_1\mathrm{d}n_1, \tag{6}$$

$$\Leftrightarrow \mathrm{d}n_1 = \frac{1}{\mu_1}\mathrm{d}U - \frac{T}{\mu_1}\mathrm{d}S + \frac{p}{\mu_1}\mathrm{d}V, \tag{7}$$

assuming $\mu_1 \neq 0$. The total differential of $U(S,V,\mu_1)$

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,\mu_1} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,\mu_1} \mathrm{d}V + \left(\frac{\partial U}{\partial \mu_1}\right)_{V,S} \mathrm{d}\mu_1 \tag{8}$$

is inserted into Eq. (6), and after rearrangement

$$\mathrm{d}n_1 = \frac{1}{\mu_1}\left[\left(\frac{\partial U}{\partial S}\right)_{V,\mu_1} - T\right]\mathrm{d}S + \frac{1}{\mu_1}\left[\left(\frac{\partial U}{\partial V}\right)_{S,\mu_1} + p\right]\mathrm{d}V + \frac{1}{\mu_1}\left(\frac{\partial U}{\partial \mu_1}\right)_{V,S}\mathrm{d}\mu_1. \tag{9}$$

At constant volume V and chemical potential μ_1, Eq. (10) yields

$$\begin{aligned} \left(\frac{\partial n_1}{\partial S}\right)_{V,\mu_1} &= \frac{1}{\mu_1}\left[\left(\frac{\partial U}{\partial S}\right)_{V,\mu_1} - T\right] \\ \Leftrightarrow \left(\frac{\partial U}{\partial S}\right)_{V,\mu_1} &= T - \mu_1\left(\frac{\partial T}{\partial \mu_1}\right)_{V,S}, \end{aligned} \tag{10}$$

applying Maxwell's relation

$$\left(\frac{\partial n_1}{\partial S}\right)_{V,\mu_1} = -\left(\frac{\partial T}{\partial \mu_1}\right)_{V,S}. \tag{11}$$

At constant entropy S and chemical potential μ_1, Eq. (12) yields

$$\begin{aligned} \left(\frac{\partial n_1}{\partial V}\right)_{S,\mu_1} &= \frac{1}{\mu_1}\left[\left(\frac{\partial U}{\partial V}\right)_{S,\mu_1} + p\right] \\ \Leftrightarrow \left(\frac{\partial U}{\partial V}\right)_{S,\mu_1} &= \mu_1\left(\frac{\partial n_1}{\partial V}\right)_{S,\mu_1} - p. \end{aligned} \tag{12}$$

Finally, the term that remains at constant volume V and entropy S leads to the definition of the substance capacity

$$\begin{aligned} \left(\frac{\partial n_1}{\partial \mu_1}\right)_{V,S} &= \frac{1}{\mu_1}\left(\frac{\partial U}{\partial \mu_1}\right)_{V,S} \\ \Leftrightarrow c_{V,S1} := \frac{1}{n_1}\left(\frac{\partial U}{\partial \mu_1}\right)_{V,S} &= \frac{\mu_1}{n_1}\left(\frac{\partial n_1}{\partial \mu_1}\right)_{V,S}. \end{aligned} \tag{13}$$

In analogy to heat transfer processes, in which the isochoric heat capacity is defined as the partial derivative of the internal energy according to the temperature, the substance capacity $c_{V,S1}$ is defined. In the next step, the partial derivatives of the internal energy (Eq. (10),

Eq. (12) and Eq. (13)) are inserted into Eq. (8), which is equated with Eq. (6)

$$\begin{aligned}
&\left(T-\mu_1\left(\frac{\partial T}{\partial \mu_1}\right)_{V,S}\right)\mathrm{d}S+\left(\mu_1\left(\frac{\partial n_1}{\partial V}\right)_{S,\mu_1}-p\right)\mathrm{d}V+n_1 c_{V,S1}\mathrm{d}\mu_1 = T\mathrm{d}S-p\mathrm{d}V+\mu_1\mathrm{d}n_1\\
\Leftrightarrow&-\mu_1\left(\frac{\partial T}{\partial \mu_1}\right)_{V,S}\mathrm{d}S+\mu_1\left(\frac{\partial n_1}{\partial V}\right)_{S,\mu_1}\mathrm{d}V+n_1 c_{V,S1}\mathrm{d}\mu_1=\mu_1\mathrm{d}n_1.
\end{aligned} \tag{14}$$

Substituting $\mathrm{d}\mu_1=\dot{\mu}_1\mathrm{d}t$, $\mathrm{d}n_1=\dot{n}_1\mathrm{d}t$, $\mathrm{d}S=\dot{S}\mathrm{d}t$, $\mathrm{d}V=\dot{V}\mathrm{d}t$ for each differential in Eq. (14), dividing by $\mathrm{d}t$ and converting to $\dot{\mu}_1$ gives the differential equation in general form

$$\dot{\mu}_1=-\frac{\mu_1}{n_1 c_{V,S1}}\left(\left(\frac{\partial n_1}{\partial V}\right)_{S,\mu_1}\dot{V}-\left(\frac{\partial T}{\partial \mu_1}\right)_{V,S}\dot{S}-\dot{n}_1\right), \tag{15}$$

which describes of the change in chemical potential entirely through changes in extensive state variables. For the partial derivatives and the substance capacity in Eq. (15) there are representations which derived in Supplementary Information 4.

4 Analysis of partial derivatives

It is started with the caloric equation of state in its differential form

$$\mathrm{d}U=\left(\frac{\partial U}{\partial T}\right)_{V,n_1}\mathrm{d}T+\left(\frac{\partial U}{\partial V}\right)_{V,n_1}\mathrm{d}V+\left(\frac{\partial U}{\partial n_1}\right)_{V,n_1}\mathrm{d}n_1. \tag{16}$$

Rearranging the fundamental theorem to $\mathrm{d}S$ and applying Eq. (16) yields

$$\begin{aligned}
&\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V+\mu_1\mathrm{d}n_1\\
\Leftrightarrow&\mathrm{d}S=\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,n_1}\mathrm{d}T+\frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_{T,n_1}+p\right)\mathrm{d}V+\frac{1}{T}\left(\left(\frac{\partial U}{\partial n_1}\right)_{T,V}-\mu_1\right)\mathrm{d}n_1.
\end{aligned} \tag{17}$$

Comparing coefficients in Eq. (17), the term that remains at constant volume V and substance amount n_1 leads to the definition of the molar heat capacity

$$\begin{aligned}
\left(\frac{\partial S}{\partial T}\right)_{V,n_1}&=\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,n_1}\\
\Leftrightarrow c_{V,1}:=\frac{1}{n_1}\left(\frac{\partial U}{\partial T}\right)_{V,n_1}&=\frac{T}{n_1}\left(\frac{\partial S}{\partial T}\right)_{V,n_1}.
\end{aligned} \tag{18}$$

At constant temperature T and substance amount n_1, Eq. (19) yields

$$\begin{aligned}\left(\frac{\partial S}{\partial V}\right)_{T,n_1} &= \frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_{T,n_1} + p\right) \\ \Leftrightarrow \left(\frac{\partial U}{\partial V}\right)_{T,n_1} &= T\left(\frac{\partial S}{\partial V}\right)_{T,n_1} - p = T\left(\frac{\partial p}{\partial T}\right)_{V,n_1} - p,\end{aligned} \tag{19}$$

applying Maxwell's relation

$$\left(\frac{\partial S}{\partial V}\right)_{T,n_1} = \left(\frac{\partial p}{\partial T}\right)_{V,n_1}. \tag{20}$$

At constant temperature T and volume V, Eq. (21) yields

$$\begin{aligned}\left(\frac{\partial S}{\partial n_1}\right)_{T,V} &= \frac{1}{T}\left(\left(\frac{\partial U}{\partial n_1}\right)_{T,V} - \mu_1\right) \\ \Leftrightarrow \left(\frac{\partial U}{\partial n_1}\right)_{T,V} &= T\left(\frac{\partial S}{\partial n_1}\right)_{T,V} + \mu_1 = \mu_1 - T\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1},\end{aligned} \tag{21}$$

applying Maxwell's relation

$$\left(\frac{\partial S}{\partial n_1}\right)_{T,V} = -\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}. \tag{22}$$

Eq. (18), Eq. (19) and Eq. (21) replaced in Eq. (16), equalized to the fundamental theorem and rearrangement yields

$$\begin{aligned}\mathrm{d}U &= n_1 c_{V,1}\mathrm{d}T + \left(T\left(\frac{\partial p}{\partial T}\right)_{V,n_1} - p\right)\mathrm{d}V + \left(\mu_1 - T\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\right)\mathrm{d}n_1 \\ &= T\mathrm{d}S - p\mathrm{d}V + \mu_1\mathrm{d}n_1 \\ \Leftrightarrow \mathrm{d}T &= \frac{T}{n_1 c_{V,1}}\left(\mathrm{d}S - \left(\frac{\partial p}{\partial T}\right)_{n_1,V}\mathrm{d}V + \left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\mathrm{d}n_1\right).\end{aligned} \tag{23}$$

The partial derivative $\left(\frac{\partial p}{\partial T}\right)_{n_1,V}$ can be calculated from the ideal gas law or more complex thermal state equations. The expression $\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}$ is determined via the Gibbs energy

assuming an ideal gas

$$\begin{aligned}
&G = U - TS + pV \\
\Leftrightarrow &\mu_1 = c_{V,1}T - \frac{TS}{n_1} + \frac{pV}{n_1} \\
\Leftrightarrow &\mu_1 = c_{V,1}T - \frac{TS}{n_1} + RT \\
\Leftrightarrow &\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1} = c_{V,1} - \frac{1}{n_1}\left(T\left(\frac{\partial S}{\partial T}\right)_{V,n_1} + S\right) + R \\
\Leftrightarrow &\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1} = R - \frac{S}{n_1},
\end{aligned} \tag{24}$$

applying the definition of the isochoric heat capacity, cf. Eq. (18). As provided in Eq. (24), a differential derivation method was applied. For this purpose, the Gibbs-Duhem relation was rearranged to $\mathrm{d}\mu_1$

$$\mathrm{d}\mu_1 = \frac{V}{n_1}\mathrm{d}p - \frac{S}{n_1}\mathrm{d}T. \tag{25}$$

Applying the total differential of a thermal state equation of the form $p = p(T,V,n_1)$ to Eq. (25) yields

$$\begin{aligned}
\mathrm{d}\mu_1 &= \frac{V}{n_1}\left(\left(\frac{\partial p}{\partial T}\right)_{n_1,V}\mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_{n_1,T}\mathrm{d}V + \left(\frac{\partial p}{\partial n_1}\right)_{T,V}\mathrm{d}n_1\right) - \frac{S}{n_1}\mathrm{d}T \\
\Leftrightarrow \mathrm{d}\mu_1 &= \left(\frac{V}{n_1}\left(\frac{\partial p}{\partial T}\right)_{n_1,V} - \frac{S}{n_1}\right)\mathrm{d}T + \frac{V}{n_1}\left(\frac{\partial p}{\partial V}\right)_{n_1,T}\mathrm{d}V + \frac{V}{n_1}\left(\frac{\partial p}{\partial n_1}\right)_{T,V}\mathrm{d}n_1
\end{aligned} \tag{26}$$

Coefficient comparison in Eq. (26) leads to a general expression for the partial derivative

$$\left(\frac{\partial \mu_1}{\partial T}\right)_{n_1,V} = \frac{1}{n_1}\left(V\left(\frac{\partial p}{\partial T}\right)_{n_1,V} - S\right) \approx R - \frac{S}{n_1}, \tag{27}$$

in which, restricting to an ideal gas, the solution was obtained as shown in Eq. (24). From here, Eq. (23) is inserted into Eq. (26) for $\mathrm{d}T$ to obtain an expression for the partial derivatives $\left(\frac{\partial n_1}{\partial S}\right)_{V,\mu_1}$, $\left(\frac{\partial n_1}{\partial V}\right)_{S,\mu_1}$ and $\left(\frac{\partial n_1}{\partial \mu_1}\right)_{V,S}$

$$\begin{aligned}
\mathrm{d}\mu_1 = &\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\frac{T}{n_1 c_{V,1}}\left(\mathrm{d}S - \left(\frac{\partial p}{\partial T}\right)_{n_1,V}\mathrm{d}V + \left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\mathrm{d}n_1\right) + \frac{V}{n_1}\left(\frac{\partial p}{\partial V}\right)_{n_1,T}\mathrm{d}V \\
&+ \frac{V}{n_1}\left(\frac{\partial p}{\partial n_1}\right)_{T,V}\mathrm{d}n_1.
\end{aligned} \tag{28}$$

Rearranging to $\mathrm{d}n_1$ yields

$$\mathrm{d}n_1 = \frac{n_1}{\frac{T}{c_{V,1}}\left[\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\right]^2 + V\left(\frac{\partial p}{\partial n_1}\right)_{T,V}}\mathrm{d}\mu_1 \frac{-T\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}}{T\left[\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\right]^2 + c_{V,1}V\left(\frac{\partial p}{\partial n_1}\right)_{T,V}}\mathrm{d}S$$
$$\frac{T\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\left(\frac{\partial p}{\partial T}\right)_{n_1,V} - c_{V,1}V\left(\frac{\partial p}{\partial V}\right)_{n_1,T}}{c_{V,1}V\left(\frac{\partial p}{\partial n_1}\right)_{T,V} + T\left[\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\right]^2}\mathrm{d}V. \tag{29}$$

Coefficient comparison in Eq. (29) leads to a general representation for the substance capacity

$$c_{V,S1} := \frac{\mu_1}{n_1}\left(\frac{\partial n_1}{\partial \mu_1}\right)_{V,S} = \frac{\mu_1}{\frac{T}{c_{V,1}}\left[\left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1}\right]^2 + V\left(\frac{\partial p}{\partial n_1}\right)_{T,V}}. \tag{30}$$

Including Eq. (27) into Eq. (30) for an ideal gas, yields

$$c_{V,S1} \approx \frac{\mu_1}{\frac{T}{c_{V,1}}\left(R - \frac{S}{n_1}\right)^2 + RT} = \frac{\mu_1}{RT}\frac{1}{\frac{1}{c_{V,1}R}\left(R - \frac{S}{n_1}\right)^2 + 1}. \tag{31}$$

Finally, coefficient comparison in Eq. (29) yields

$$\left(\frac{\partial n_1}{\partial V}\right)_{S,\mu_1} \approx \frac{n_1}{V}\frac{1 + \frac{1}{c_{V,1}}\left(R - \frac{S}{n_1}\right)}{1 + \frac{1}{c_{V,1}R}\left(R - \frac{S}{n_1}\right)^2}, \tag{32}$$

and

$$\left(\frac{\partial T}{\partial \mu_1}\right)_{V,S} = -\left(\frac{\partial n_1}{\partial S}\right)_{V,\mu_1} \approx -\frac{n_1}{S}\frac{\frac{S}{n_1}\left(R - \frac{S}{n_1}\right)}{\frac{1}{{n_1}^4}\left(R - \frac{S}{n_1}\right)^2 + c_{V,1}R}, \tag{33}$$

assuming an ideal gas. Considering an special case for which $S = Rn_1$ is assumed, which simplifies Eq. (15) considerably and matches all measured data precisely. Furthermore, if an

ideal gas is assumed, the following representations hold

$$\begin{aligned} \left(\frac{\partial n_1}{\partial V}\right)_{S,\mu_1} &= \frac{n_1}{V}, & c_{V,S1} &= \frac{\mu_1}{RT}, \\ \left(\frac{\partial T}{\partial \mu_1}\right)_{V,S} &= 0, & \left(\frac{\partial \mu_1}{\partial T}\right)_{V,n_1} &= 0. \end{aligned} \tag{34}$$

Table S1 Physical properties

Parameter	Symbol	Value
ideal contraction coefficient	C_c	0.611 [2]
hydraulic resistance coefficient of the throttle	ξ	0.015
oil density (MIL-PRF-5606)	ρ_2	$867.6\,\mathrm{kg \cdot m^{-3}}$ [3]
hydraulic resistance	R_{hyd}	$11.1\,\mathrm{kg \cdot cm^{-5}}$
geometric volume of the lower chamber	V_{lc0}	$0.37\,\mathrm{dm^3}$
geometric volume of the shock absorber	V_{geo0}	$0.64\,\mathrm{dm^3}$
cross-sectional area of the throttle	A_t	$12.6\,\mathrm{mm^2}$
cross-sectional area of the piston	A_p	$1731\,\mathrm{mm^2}$
initial amount of nitrogen in phase α	$n_{10}^{[\alpha]}$	0.135 mol
oil mass	m_2	368 g
isochoric, molar heat capacity of nitrogen in phase α	$c_{V1}^{[\alpha]}$	$20.79\,\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ [4]
isochoric heat capacity of the oil (MIL-PRF-5606) in phase β	$c_{V2}^{[\beta]}$	$2093\,\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ [5]
temperature	T	283.15 K
dynamic viscosity of the oil (MIL-PRF-5606)	η_2	$1.27 \cdot 10^{-5}\,\mathrm{Pa \cdot s}$ [3]
hydrodynamic radius of nitrogen molecules	r_1	$1.85 \cdot 10^{-10}$ m (based on Vrabec et al. [6])
diffusion resistance	R_{di}	$4300\,\mathrm{J \cdot s \cdot mol^{-2}}$
amount of oil in phase β	$n_2^{[\beta]}$	0.545 mol (based on Mielke [7])

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