

THE HELMHOLTZ FREE ENERGY OF PURE FLUID SUBSTANCES AND FLUID MIXTURES

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Abstract

The Helmholtz free energy is essential to the modelling of multiphase flow with the diffuse interface formalism. In models where it is a good approximation to let the temperature be constant and uniform, a simplified calculation of the Helmholtz free energy is performed, that leaves a number of functions of temperature unspecified (one per chemical component, in case of mixtures). If the model is to include the energy balance equation, i.e., account for flow with variable temperature, then the Helmholtz free energy must include these temperature dependent terms. This paper is an exposition of the determination of such terms, where three types of molecules are considered: (i) single conformation, (ii) multiple conformation, and (iii) polar. A specific example for each case is included: methane, n-pentane, and water. The Helmholtz free energy of fluid mixtures is also considered.

Nomenclature

Abbreviations

EOS Equation of state
Species Chemical component

Convention

$(X)^p$ X to the power p

Latin letters. An asterisk indicates that the symbol always appears with a superscript indicating the chemical component (and the conformation if relevant).

a	[Pa m ⁶ /mol ²]	*EOS constant
A, \bar{A}	[Pa m ⁶]	EOS constant
b	[m ³ /mol]	*EOS constant
B, \bar{B}	[m ³]	EOS constant
c	[m/s]	Speed of light
C	[J/mol]	*Chemical potential
D	[J]	*Depth of potential well at ground state
F	[J]	Helmholtz free energy
\mathcal{F}	[J/m ³]	Helmholtz free energy per unit volume
h	[J s]	Planck constant
I_1, I_2, I_3	[kg m ²]	*Principal moments of inertia of a molecule

k	[J/K]	Boltzmann constant
$k^{\alpha\beta}$	[.]	Binary interaction coefficients
ℓ	[.]	*Number of atoms in a molecule
L, \bar{L}	[.]	See equations (44) and (49)
m	[.]	*EOS constant. See equation (2)
m_v	[.]	*Number of vibrational modes of a molecule
M	[kg]	*Molecular mass
n	[mol]	Number of molecules
N	[.]	*Number of molecules
N_A	[1/mol]	Avogadro's number
P	[Pa]	Pressure
q	[.]	*Canonical ensemble partition function
Q	[.]	*Canonical ensemble partition function
R	[J/(mol K)]	Universal gas constant
S	[J/K]	Entropy
T	[K]	Temperature
\bar{T}	[.]	Dimensionless temperature
v	[m ³ /mol]	Molar volume
V	[m ³]	Volume
V^*	[m ³]	Infinite volume
\mathcal{V}	[m ³ /mol]	*A function of T , and of molecular mechanical parameters
Y	[.]	*See equation (50)
z	[K]	*See equation (38)
Z	[K]	*See equations (22) and (35)

Greek letters. For the meaning of the asterisk see "Latin letters" above.

β_{ab}	[.]	In water EOS. "Association volume."
ϵ_{ab}	[J]	In water EOS. "Association energy."
η	[.]	*Probability of a given conformation
ϑ	[K]	*See equation (30)
κ	[.]	Water EOS function of T . See equation (42)
ν	[.]	Number of chemical components in a mixture
ν_i	[1/cm]	*Molecular vibrational frequency of mode i
ρ	[mol/m ³]	*Molar density
σ	[.]	*Symmetry number of a molecule
τ	[K]	*See equations (25) and (37)
ω_{e1}	[.]	*Degeneracy of electronic ground state

Superscripts

α, β	[.]	Indicate the chemical component
1, 2, 3		Indicate methane, n-pentane, water, respectively
A, \dots		Indicate molecular conformation
ig		Ideal gas

Subscripts

a		Indicates association term
c		Indicates value at critical point
e		"Effective" or "electronic", depending on context
pol		Polynomial
r		Refers to rotational degrees of freedom
t		Refers to translational degrees of freedom
v		Refers to vibrational degrees of freedom

1 Introduction

The diffuse interface model presented in [9], for multiphase flow in porous media of a multicomponent fluid, is in principle valid for variable temperature. Its applicability was however restricted to constant and uniform temperatures by the fact that a number of functions of temperature, one for each chemical component, were left unspecified in the Helmholtz free energy density. These functions drop out by differentiation if temperature is assumed constant and uniform. The manner in which these functions can be determined is presented in the present paper.

The Helmholtz free energy F of a fluid is usually calculated via the equation expressing pressure P in terms of volume V , temperature T , and mole numbers n^1, n^2, \dots, n^ν , assuming there are ν chemical components.¹ This equation, called the "equation of state" or EOS, is well known for most mixtures of industrial interest, for example hydrocarbons. For the different types of EOS see [3]. The one used here is known as the Redlich-Kwong EOS, and has the following form for one mole of fluid consisting of just one species α .

$$P = \frac{RT}{v - b^\alpha} - \frac{a^\alpha}{v(v + b^\alpha)} + P_a(T, V), \quad (1)$$

where R is the universal gas constant, v is the molar volume, b^α is a constant, and

$$a^\alpha = a_c^\alpha [1 + m^\alpha (1 - \sqrt{T/T_c^\alpha})^2], \quad (2)$$

where a_c^α , m^α , and T_c^α are constants. P_a is the *association term*, which is only present for polar molecules. The EOS of a mixture is [4]

$$P = \frac{nRT}{V - B} - \frac{A}{V(V + B)} + P_a(T, V, n^1, \dots, n^\nu), \quad (3)$$

where

$$n = \sum_{\alpha=1}^{\nu} n^\alpha, \quad (4)$$

$$A = \sum_{\alpha, \beta=1}^{\nu} n^\alpha n^\beta \sqrt{a^\alpha a^\beta} (1 - k^{\alpha\beta}), \quad (5)$$

$$B = \sum_{\alpha=1}^{\nu} b^\alpha n^\alpha. \quad (6)$$

In equation (3), P_a is the *association term* [4], only present if there are polar species (e.g. water or methanol) in the mixture. It must go to 0 faster than $1/V$ as $V \rightarrow \infty$, as a consequence of the requirement that equation (3) must reduce to the EOS of an ideal gas, $PV = nRT$, as $V \rightarrow \infty$. It follows that F_a , defined by

$$F_a(T, V, n^1, \dots, n^\nu) = \lim_{V^* \rightarrow \infty} \int_V^{V^*} P_a(T, V', n^1, \dots, n^\nu) dV', \quad (7)$$

exists.

In equation (5), the $k^{\alpha\beta}$ are the binary interaction coefficients, having the properties $k^{\alpha\alpha} = 0$ and $k^{\alpha\beta} = k^{\beta\alpha}$. These and the other constants characterising species α can be found in published tables.

The Helmholtz free energy F is calculated from the EOS by integration of

$$dF = -SdT - PdV + \sum_{\alpha=1}^{\nu} C^\alpha dn^\alpha, \quad (8)$$

where S is entropy and the C^α are the chemical potentials. Assuming constant temperature and constant mole numbers we get

$$F(T, V, n^1, \dots, n^\nu) = \lim_{V^* \rightarrow \infty} \left[F(T, V^*, n^1, \dots, n^\nu) + \int_V^{V^*} P(V') dV' \right], \quad (9)$$

where $P(V)$ is the right-hand side of equation (3), with T and the n^α taken as constant parameters. On the right-hand side of equation (9), the limit as $V^* \rightarrow \infty$ of $F(T, V^*, \dots)$ is the Helmholtz free energy of an ideal mixture of ideal gases (chapter 6 in [5], chapter 2 in [8]), i.e.,

$$\lim_{V^* \rightarrow \infty} F(T, V^*, n^1, \dots, n^\nu) = \lim_{V^* \rightarrow \infty} \sum_{\alpha=1}^{\nu} F^{\text{ig}}(T, V^*, n^\alpha), \quad (10)$$

and the Helmholtz free energy of an ideal gas of species α has the general expression [6]

$$F^{\text{ig}}(T, V^*, n^\alpha) = n^\alpha RT \ln \frac{n^\alpha \mathcal{V}^\alpha(T)}{eV^*}. \quad (11)$$

Here $e = \exp(1)$ and the $\mathcal{V}^\alpha(T)$ are the functions of T that were left unspecified in [9]. Their calculation is the main subject of this paper.

The integral on the right-hand side of (9) can be performed, and one gets

$$\lim_{V^* \rightarrow \infty} \int_V^{V^*} P(V') dV' = -nRT \ln(V - B) + \frac{A}{B} \ln \frac{V}{V + B} + nRT \ln V^* + F_a. \quad (12)$$

Gathering results (10)–(12) we see that (9) becomes

$$F(T, V, n^1, \dots, n^\nu) = \sum_{\alpha=1}^{\nu} n^\alpha RT \ln \frac{n^\alpha \mathcal{V}^\alpha(T)}{e(V - B)} + \frac{A}{B} \ln \frac{V}{V + B} + F_a, \quad (13)$$

¹A superscript will indicate the chemical component, throughout in this paper. Also, *species* will be used instead of *chemical component*.

the infinities, $\ln V^*$, having cancelled each other.

In the model described in reference [9] the equations describing multiphase flow are written in terms of the entropy (T -derivative of F) and of the spatial gradient of the chemical potential (n^α -derivative of F). Equation (13) then shows that one actually needs the first order T -derivatives of the $T \ln \mathcal{V}^\alpha(T)$ -functions, for $(\alpha = 1, \dots, \nu)$, and not the functions themselves. Any constants appearing in any of the $T \ln \mathcal{V}^\alpha(T)$ disappear. We return to this during the calculations of the \mathcal{V}^α .

The determination of \mathcal{V}^α is given below, for three molecular types: (i) non polar single conformation (section 2), non polar multiple conformation (section 3), and polar single conformation (section 4).

The numbering, i.e., the allocation of numerical values to the α 's, depends on the mixture and is done in this paper as follows: the non polar species are considered first and numbered by order of increasing molecular mass; the polar species are then appended and numbered by order of increasing molecular mass: thus for a mixture of methane (CH_4), pentane (C_5H_{12}), water (H_2O), and methanol (CH_3OH), (where the last two are polar), α is respectively 1, 2, 3, and 4. Since specific examples will be considered in this paper, it is convenient to have a particular mixture in mind. This is the mixture of methane, n-pentane, and water. Quantities pertaining to these three species will be identified by setting $\alpha = 1, 2, 3$ respectively.

2 Single conformations

2.1 Generalities

What follows is the determination of the $\mathcal{V}^\alpha(T)$ -function for a species α whose molecules are polyatomic, non polar, and have a single conformation.

The Helmholtz free energy of an ideal gas of species α has the general expression (see [6], especially chapters 8 and 9):

$$F^{\text{ig}}(T, V^*, N^\alpha) = -kT \ln Q^\alpha, \quad (14)$$

where k is the Boltzmann constant, N^α is the number of particles, and Q^α is the canonical ensemble partition function for the species. The numerical value of α identifies the species in a numbering scheme like the one indicated at the end of section 1.

If the molecules are indistinguishable, and if the number of available molecular states is much larger than N^α [6], one can write

$$Q^\alpha = \frac{(q^\alpha)^{N^\alpha}}{N^{\alpha!}}, \quad (15)$$

so that, using Stirlings formula for the factorial (assuming $N^\alpha \gg 1$) equation (14) becomes

$$F^{\text{ig}}(T, V^*, N^\alpha) = N^\alpha kT \ln \frac{N^\alpha}{eq^\alpha}. \quad (16)$$

If the Hamiltonian of a molecule can be assumed to be separable, then

$$q^\alpha = q_t^\alpha q_r^\alpha q_v^\alpha q_e^\alpha \quad (17)$$

where

$$q_t^\alpha = \left(\frac{2\pi M^\alpha kT}{h^2} \right)^{\frac{3}{2}} V^*, \quad (18)$$

$$q_r^\alpha = \frac{\sqrt{\pi}}{\sigma^\alpha} \left(\frac{8\pi^2 kT}{h^2} \right)^{\frac{3}{2}} (I_1^\alpha I_2^\alpha I_3^\alpha)^{\frac{1}{2}}, \quad (19)$$

$$q_v^\alpha = \prod_{i=1}^{m_v^\alpha} \frac{e^{-h\nu_i^\alpha/(2kT)}}{1 - e^{-h\nu_i^\alpha/(kT)}}, \quad (20)$$

$$q_e^\alpha = \omega_{e1}^\alpha e^{D^\alpha/(kT)}. \quad (21)$$

Partition function q_t^α accounts for the three translational degrees of freedom of the molecule, considered as a point. M^α is the molecular mass and h is Planck's constant.

The second partition function, q_r^α , accounts for the rotational degrees of freedom, and I_1^α , I_2^α , and I_3^α are the principal moments of inertia of the molecule. The constant σ^α is the symmetry number, defined as "the number of different ways in which the molecule can achieve, by rotation, the same (i.e., counting like atoms as indistinguishable) orientation in space." [6] For CO_2 , H_2O , and CH_4 , $\sigma = 2, 2$, and 12 , respectively.

The third partition function, q_v^α , accounts for the energies of small vibrations of the atoms around their equilibrium positions, ν_i^α being the frequency of vibration of mode i . For a molecule of type α with ℓ^α atoms, there are m_v^α modes of vibration, where $m_v^\alpha = 3\ell^\alpha - 6$ for non-linear molecules, and $m_v^\alpha = 3\ell^\alpha - 5$ for linear molecules. (By definition, the mass centers of the atoms in a *linear molecule* are on a straight line. CO_2 is an example.)

In the fourth partition function, the constants D^α and ω_{e1}^α are due to the nuclear and electronic configuration of the molecule. Taking the state of zero energy to be the one where nuclei and electrons are free, $-D^\alpha < 0$ is the energy needed to assemble the molecule at ground state, from its constituent nuclei and electrons. D^α is the depth of the potential well of the ground state, and ω_{e1}^α is the degeneracy of the ground state. For most cases, only the ground state needs be considered since a jump to the next electronic level usually needs temperatures of about 10^4 K [6]. For saturated molecules ($\text{C}_n\text{H}_{2n+2}$ for hydrocarbons), $\omega_{e1} = 1$.

According to the last but two paragraph in section 1, constants appearing in $T \ln \mathcal{V}^\alpha(T)$ are not needed, at least in models similar to [9]. It is useful, in view of this, and referring to equations (20) and (21), to isolate such constants in

$$Z^\alpha = -\frac{D^\alpha}{k} + \sum_{i=1}^{m_v^\alpha} \frac{h\nu_i^\alpha}{2k}. \quad (22)$$

The expression for \mathcal{V}^α can now easily be found by identifying the two expressions of F^{ig} , (11) and (16). Incidentally, the dimension of \mathcal{V}^α is volume per mole so that $\mathcal{V}^\alpha/b^\alpha$ is

dimensionless (b^α being the constant with dimension of volume per mole appearing in the pure component EOS, see equation (1)). Keeping in mind that $N^\alpha = N_A n^\alpha$, where N_A is Avogadro's number, one gets:

$$\frac{\mathcal{V}^\alpha(T)}{b^\alpha} = \frac{N_A V^*}{b^\alpha q^\alpha} = e^{Z^\alpha/T} \frac{\mathcal{V}_e^\alpha(T)}{b^\alpha}, \quad (23)$$

where

$$\frac{\mathcal{V}_e^\alpha(T)}{b^\alpha} = \left(\frac{\tau^\alpha}{T}\right)^3 \prod_{i=1}^{m_v^\alpha} \left(1 - e^{-h\nu_i^\alpha/(kT)}\right), \quad (24)$$

and

$$\tau^\alpha = \frac{h^2}{4k} \left(\frac{N_A \sigma^\alpha}{\pi^5 b^\alpha \omega_{e1}^\alpha}\right)^{\frac{1}{3}} \frac{1}{(M^\alpha)^{\frac{1}{2}} (I_1^\alpha I_2^\alpha I_3^\alpha)^{\frac{1}{6}}}. \quad (25)$$

The Helmholtz free energy of a fluid consisting of a single species, with polyatomic, non polar, and single-conformation molecules is

$$F(T, V, n^\alpha) = n^\alpha RT \ln \frac{n^\alpha \mathcal{V}^\alpha(T)}{e(V - b^\alpha)} + \frac{a^\alpha}{b^\alpha} \ln \frac{V}{V + b^\alpha}, \quad (26)$$

according to equation (13), and keeping in mind that F_a is identically equal to zero. For models that are similar to the model of reference [9], \mathcal{V}_e^α can be substituted to \mathcal{V}^α in equation (26).

2.2 The example of methane

The constants appearing in equations (24) and (25) can be found in the literature [1, 6, 10]. Superscript 1 is used below to indicate methane.

$$\begin{aligned} M^1 &= 0.016042/N_A \text{ kg}, \\ \sigma^1 &= 12, \\ \omega_{e1}^1 &= 1, \\ b^1 &= 0.2979 \times 10^{-4} \text{ m}^3/\text{mol}, \\ I_1^1 = I_2^1 = I_3^1 &= 0.533 \times 10^{-46} \text{ kg m}^2, \\ m_v^1 &= 9, \\ \nu_i^1 &= 2914, 1526 (2), 3020 (3), 1306 (3). \end{aligned}$$

The ν_i^1 are the frequencies appearing in equation (24), with their multiplicities in parentheses, and in units of cm^{-1} . One obtains $h\nu_i^1/k$ in K by multiplying ν_i^1 in cm^{-1} with $100ch/k \approx 1.438776$, where c is the speed of light in m/s. One also finds

$$\tau^1 = 6.17509 \text{ K}.$$

A plot of \mathcal{V}_e^1/b^1 versus T (in K) is shown in figure 1.

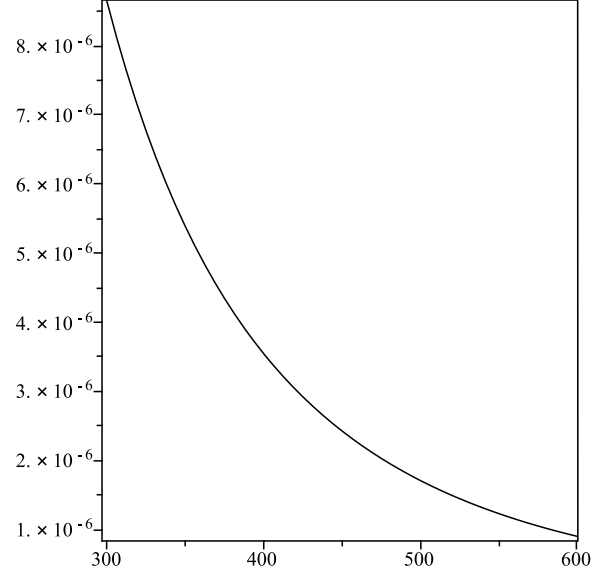


Figure 1: Plot of \mathcal{V}_e^1/b^1 (methane) versus T in K.

3 Multiple conformations

3.1 Generalities

What follows is the determination of the $\mathcal{V}^\alpha(T)$ -function for a species α whose molecules are polyatomic, non polar, and have many conformations.

We begin with some definitions. Some species exist as mixtures of a usually small number of *conformations*, where the molecule of conformation A differs from the molecule of conformation B by rotations about single bonds. The notation in this paper is as follows: a conformation is identified by a capital letter superscript, and the letters are allocated in the order of decreasing potential-well depths: $D^{\alpha A} > D^{\alpha B} > \dots$

In general, if species α exists in conformations A, \dots, J, \dots , a straightforward generalization of equation (15) is

$$Q^\alpha = \left[\frac{(q^{\alpha A})^{N^{\alpha A}}}{N^{\alpha A}!} \right] \dots \left[\frac{(q^{\alpha J})^{N^{\alpha J}}}{N^{\alpha J}!} \right] \dots, \quad (27)$$

where $N^{\alpha J}$ is the numbers of particles of species α in conformation J . The $q^{\alpha J}$ are given by expressions similar to expressions (17)–(21), where superscript α is replaced by αJ , thus including the conformation. We can write, quite generally

$$N^{\alpha J} = N^\alpha \eta^{\alpha J}, \quad (28)$$

where N^α is the number of molecules of species α , and $\eta^{\alpha J}$ is the probability of a molecule of species α being in conformation J . If $D^{\alpha J}$ denotes the depth of the potential well of the ground state of species α in conformation J , we can write

$$\eta^{\alpha J} = \frac{e^{D^{\alpha J}/(kT)}}{e^{D^{\alpha A}/(kT)} + \dots + e^{D^{\alpha J}/(kT)} + \dots}. \quad (29)$$

The $D^{\alpha J}/k$ are large, of the order of 10^7 K, while their differences are at most of the order of 10^3 K. Referring to the

convention stated in the second paragraph of the present section, it is natural to define $\vartheta^{\alpha J}$ by

$$k\vartheta^{\alpha J} = D^{\alpha J} - D^{\alpha A}, \quad (30)$$

so that

$$\eta^{\alpha J} = \frac{e^{\vartheta^{\alpha J}/T}}{1 + \dots + e^{\vartheta^{\alpha J}/T} + \dots}. \quad (31)$$

Using equations (27) and (28) in (14), and keeping in mind that $\sum_J \eta^{\alpha J} = 1$, one obtains the following generalization of (16):

$$F^{\text{ig}}(T, V^*, N^\alpha) = N^\alpha kT \ln \left[\frac{N^\alpha}{e} \left(\frac{\eta^{\alpha A}}{q^{\alpha A}} \right)^{\eta^{\alpha A}} \dots \left(\frac{\eta^{\alpha J}}{q^{\alpha J}} \right)^{\eta^{\alpha J}} \dots \right]. \quad (32)$$

The expression of \mathcal{V}^α is found by identifying the two expressions of F^{ig} , equations (32) and (11). Again using $\sum_J \eta^{\alpha J} = 1$, one gets

$$\frac{\mathcal{V}^\alpha}{b^\alpha} = \prod_J \left(\frac{\mathcal{V}^{\alpha J}}{b^\alpha} \eta^{\alpha J} \right)^{\eta^{\alpha J}}, \quad (33)$$

where, generalizing equations (22) to (25):

$$\frac{\mathcal{V}^{\alpha J}}{b^\alpha} = e^{Z^{\alpha J}/T} \frac{\mathcal{V}_e^{\alpha J}}{b^\alpha} \quad (34)$$

with

$$Z^{\alpha J} = -\frac{D^{\alpha J}}{k} + \sum_{i=1}^{m_v^\alpha} \frac{h\nu_i^{\alpha J}}{2k}. \quad (35)$$

$$\frac{\mathcal{V}_e^{\alpha J}}{b^\alpha} = \left(\frac{\tau^{\alpha J}}{T} \right)^3 \prod_{i=1}^{m_v^\alpha} \left(1 - e^{-h\nu_i^{\alpha J}/(kT)} \right), \quad (36)$$

$$\tau^{\alpha J} = \frac{h^2}{4k} \left(\frac{N_A \sigma^{\alpha J}}{\pi^5 b^\alpha \omega_{e1}^{\alpha J}} \right)^{\frac{1}{3}} \frac{1}{(M^\alpha)^{\frac{1}{2}} (I_1^{\alpha J} I_2^{\alpha J} I_3^{\alpha J})^{\frac{1}{6}}}. \quad (37)$$

In analogy with the single-conformation case, we can isolate terms in \mathcal{V}^α that drop out from the flow equations. Keeping in mind that $\sum_J \eta^{\alpha J} = 1$, we define

$$z^{\alpha J} = Z^{\alpha J} - Z^{\alpha A}, \quad (38)$$

and re-write equations (33) and (34) as follows:

$$\frac{\mathcal{V}^\alpha}{b^\alpha} = e^{Z^{\alpha A}/T} \frac{\mathcal{V}_e^{\alpha A}}{b^\alpha}, \quad (39)$$

where

$$\frac{\mathcal{V}_e^{\alpha A}}{b^\alpha} = \prod_J \left(e^{z^{\alpha J}/T} \frac{\mathcal{V}_e^{\alpha J}}{b^\alpha} \eta^{\alpha J} \right)^{\eta^{\alpha J}}. \quad (40)$$

Note that in the present case, the isolation of terms that drop out from the flow equations can be done in infinitely many ways. All, however, lead to the same expression for the T -derivatives of $T \ln \mathcal{V}^\alpha(T)$.

The Helmholtz free energy of a fluid consisting of a single species, with polyatomic, non polar, and multiple-conformation molecules is given by equation (26) where $\mathcal{V}^\alpha(T)$ is given by expression (39). For models that are similar to the model of reference [9], \mathcal{V}_e^α (expression (40)) can be used instead.

3.2 The example of n-pentane

A fluid of n-pentane molecules exists as a mixture of 3 conformations, called *tt*, *gt*, and *gg* [13]. In tables 1 and 2 superscript 2 indicates n-pentane, and *A*, *B*, *C* are used instead of *tt*, *tg*, *gg*. This agrees (see the values of D^{2A} , D^{2B} , and D^{2C} in table 1) with the convention stated in the second paragraph of section 3.1.

The following constants are independent of the conformation:

$$\begin{aligned} M^2 &= 0.07215/N_A \text{ kg}, \\ b^2 &= 0.100701 \times 10^{-3} \text{ m}^2/\text{mol}, \\ m_v^2 &= 45, \\ \omega_{e1}^{2A} &= \omega_{e1}^{2B} = \omega_{e1}^{2C} = 1. \end{aligned}$$

Symmetry numbers and principal moments of inertia [12] are given in table 1, together with the potential well depths [11], and the resulting $\tau^{\alpha J}$ and $z^{\alpha J}$. The vibrational frequencies [11] are given in table 2. A plot of \mathcal{V}_e^2/b^2 versus T (in K) is shown in figure 2.

4 Polar molecules

4.1 Generalities

What follows is the determination of the $\mathcal{V}^\alpha(T)$ -function for a species α whose molecules are polyatomic, polar, and have a single conformation. The $\mathcal{V}^\alpha(T)$ -function is independent of the ability of polar molecules to form clusters since it is determined under the assumption that the fluid is an ideal gas or, technically, that $V \rightarrow \infty$. In fact, the association term vanishes at that limit. See the example of water in section 4.2 below. It follows that the $\mathcal{V}^\alpha(T)$ -function for the case of polar molecules has the same form as the $\mathcal{V}^\alpha(T)$ -function of methane (assuming single conformation): equations (22)–(25) are thus applicable.

4.2 The example of water

According to the numbering scheme stated in the last paragraph of section 1, superscript 3 indicates water.

J	A	B	C
σ^{2J}	2	1	1
I_1^{2J}	0.439	0.382	0.243
I_2^{2J}	0.463	0.409	0.350
I_3^{2J}	0.0494	0.0726	0.132
D^{2J}	519061.8638	519058.0492	519054.6312
ϑ^{2J}	0	-458.79	-869.88
τ^{2J}	0.167815	0.130515	0.130740
z^{2J}	0	503.14	972.57

Table 1: Symmetry numbers, principal moments of inertia, potential well depths, and some derived quantities. See the main text for the latter.

i	ν_i^{2A}	ν_i^{2B}	ν_i^{2C}
1	4437.46	4446.08	4443.93
2	4436.97	4437.01	4441.56
3	4431.21	4431.93	4433.57
4	4428.81	4430.52	4431.62
5	4380.97	4384.73	4384.88
6	4355.85	4368.64	4375.19
7	4346.35	4351.58	4360.02
8	4344.74	4348.44	4350.22
9	4331.88	4344.87	4348.70
10	4329.61	4328.90	4344.79
11	4320.37	4322.69	4333.15
12	4304.72	4307.10	4314.80
13	2179.77	2175.63	2180.18
14	2167.30	2169.29	2166.41
15	2158.64	2161.31	2162.95
16	2157.42	2157.72	2162.70
17	2154.34	2151.95	2148.28
18	2142.26	2144.50	2146.24
19	2138.15	2136.06	2134.15
20	2036.96	2040.17	2040.74
21	2036.76	2033.72	2033.41
22	2012.37	2011.44	2003.19
23	1975.51	1984.32	1996.17
24	1918.68	1932.38	1966.79
25	1909.26	1915.99	1915.18
26	1868.47	1867.23	1848.16
27	1826.71	1826.45	1824.87
28	1740.44	1719.51	1687.37
29	1673.89	1667.64	1668.15
30	1545.71	1557.04	1576.54
31	1499.00	1488.59	1471.48
32	1494.99	1479.48	1467.74
33	1433.55	1442.39	1443.70
34	1331.17	1315.93	1304.29
35	1258.38	1254.55	1240.22
36	1249.59	1214.31	1211.68
37	1104.10	1107.40	1101.35
38	1055.57	1061.79	1051.64
39	571.27	675.13	677.94
40	570.99	473.53	550.29
41	356.18	410.28	389.15
42	346.54	347.08	386.93
43	256.43	299.39	311.87
44	159.34	179.19	215.23
45	154.29	117.82	90.95

Table 2: The 45 vibrational frequencies of conformations tt (A), tg (B), and gg (C) of the n-pentane molecule [11].

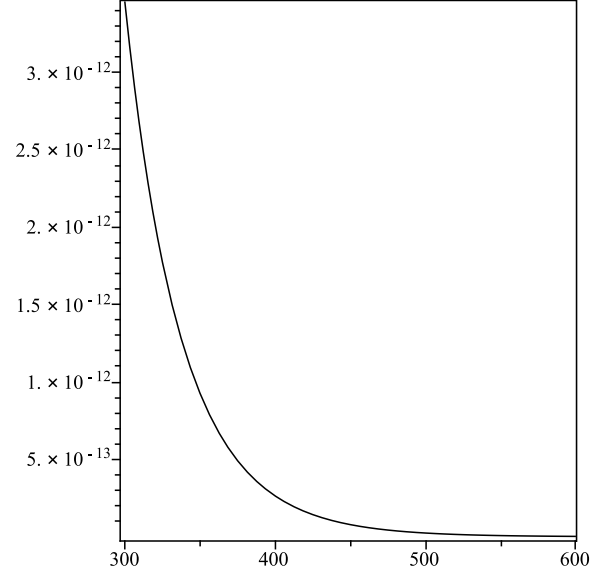


Figure 2: Plot of \mathcal{V}_e^2/b^2 (n-pentane) versus T in K.

The EOS of water is written here for completeness, since it is not needed for the determination of the $\mathcal{V}^3(T)$ -function. For an arbitrary number n^3 of moles of water in volume V , and in the framework of the theory presented in reference [4], the EOS is

$$P(T, V, n^3) = \frac{n^3 RT}{V - b^3 n^3} - \frac{(n^3)^2 a^3(T)}{V(V + b^3 n^3)} - \frac{RT}{b^3 \kappa(T)} \left[1 + \frac{b^3 n^3 \kappa(T)}{2(V - 0.475 b^3 n^3)} - \sqrt{1 + \frac{b^3 n^3 \kappa(T)}{V - 0.475 b^3 n^3}} \right], \quad (41)$$

where

$$\kappa(T) = 8\beta_{ab}[\exp(\epsilon_{ab}/(RT)) - 1], \quad (42)$$

ϵ_{ab} and β_{ab} being the *association energy* and *association volume* between a site of type a and a site of type b on the water molecule. They are known constants [4].

It is easily seen that the association term P_a , given by the second and third lines on the right-hand side of equation (41), behaves as $1/(V)^2$ when $V \rightarrow \infty$, which agrees with the statement made in the second sentence following equation (6). The integration of P_a (see equation (7)) is easily done, and equation (13) becomes, when specialised to the case of just one species, water ($\alpha = 3$):

$$F(T, V, n^3) = n^3 RT \ln \frac{n^3 \mathcal{V}^3(T)}{e(V - b^3 n^3)} + \frac{a^3 n^3}{b^3} \ln \frac{V}{V + b^3 n^3} - 4n^3 RT \left[\frac{1}{L} + \ln \frac{L}{2} - \frac{1}{2} \right], \quad (43)$$

where

$$L = 1 + \sqrt{1 + \frac{b^3 n^3 \kappa(T)}{V - 0.475 b^3 n^3}}. \quad (44)$$

The water constants necessary to the determination of $\mathcal{V}_e^3(T)$ are [2, 7]):

$$\begin{aligned} M^3 &= 0.018015/N_A \text{ kg}, \\ \sigma^3 &= 2, \\ \omega_{e1}^3 &= 1, \\ b^3 &= 0.145 \times 10^{-4} \text{ m}^3/\text{mol}, \\ I_1^3 &= 0.10220 \times 10^{-46} \text{ kg m}^2, \\ I_2^3 &= 0.19187 \times 10^{-46} \text{ kg m}^2, \\ I_3^3 &= 0.29376 \times 10^{-46} \text{ kg m}^2, \\ m_v^3 &= 3, \\ \nu_i^3 &= 3755.93, 3657.05, 1594.75 \text{ cm}^{-1}. \end{aligned}$$

Then

$$\tau^3 = 7.029204 \text{ K},$$

and a plot of \mathcal{V}_e^3/b^3 versus T (in K) is shown in figure 3.

The Helmholtz free energy of fluid water is given by equation (43) where, for models that are similar to the model of reference [9], \mathcal{V}_e^3 can be used instead of \mathcal{V}^3 .

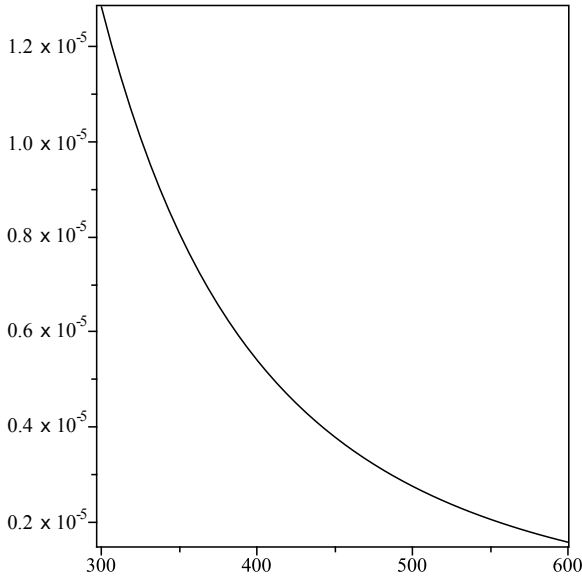


Figure 3: Plot of \mathcal{V}_e^3/b^3 (water) versus T in K.

5 Fluid mixtures

We consider here the Helmholtz free energy for the specific example mentioned at the end of section 1, namely a fluid mixture of methane, n-pentane, and water. The general expression of the Helmholtz free energy is already written

down, see equation (13). It is here specialized to $\nu = 3$. Also, since fluid mechanics is the final area of application it is most useful to introduce the Helmholtz free energy density $\mathcal{F} = F/V$, as a function of T and the molar densities ρ^1, ρ^2, ρ^3 defined by

$$\rho^\alpha = n^\alpha/V. \quad (45)$$

(The familiar mass densities are cumbersome in the present context because they introduce the molar mass as an extra factor [9, 10].) It is easily found that

$$\begin{aligned} \mathcal{F}(T, \rho^1, \rho^2, \rho^3) &= \sum_{\alpha=1}^3 RT \rho^\alpha \ln \frac{\mathcal{V}^\alpha(T)}{b^\alpha} \\ &+ \sum_{\alpha=1}^3 RT \rho^\alpha \ln \frac{b^\alpha \rho^\alpha}{e(1-\bar{B})} \\ &+ \frac{\bar{A}}{\bar{B}} \ln \frac{1}{1+\bar{B}} - 2RT \rho^3 \left[\frac{1}{\bar{L}} + \ln \frac{\bar{L}}{2} - \frac{1}{2} \right], \end{aligned} \quad (46)$$

where

$$\bar{A} = \sum_{\alpha, \beta=1}^3 \rho^\alpha \rho^\beta \sqrt{a^\alpha(T) a^\beta(T) (1 - k^{\alpha\beta})}, \quad (47)$$

$$\bar{B} = \sum_{\alpha=1}^3 b^\alpha \rho^\alpha, \quad (48)$$

$$\bar{L} = 1 + \sqrt{1 + \frac{b^3 \rho^3 \kappa(T)}{1 - 0.475 \bar{B}}}. \quad (49)$$

As already mentioned, for models that are similar to the one of reference [9] one can replace the \mathcal{V}^α with the corresponding \mathcal{V}_e^α . In addition, it is of interest to find effective methods for calculating

$$Y^\alpha \equiv \frac{d}{dT} \left(T \ln \frac{\mathcal{V}_e^\alpha(T)}{b^\alpha} \right), \quad (\alpha = 1, 2, 3). \quad (50)$$

This is especially relevant for large molecules having many conformations, as in the example of n-pentane above, where the numerical calculation of \mathcal{V}_e^3 is relatively time consuming. Figures 1 to 3 show that the \mathcal{V}_e^α are convex and monotonically decreasing, at least in the range of temperatures considered. It is thus easy to calculate polynomial approximations to the functions Y^α defined by (50). The following expressions, denoted Y_{pol}^α , are second degree polynomial interpolations, approximating Y^α for $300 \text{ K} \leq T \leq 600 \text{ K}$, and passing through the points $(T_i, Y^\alpha(T_i))$, where $T_i = 300, 450, 600 \text{ K}$. They are expressed in terms of a dimensionless temperature $\tilde{T} = T/T_c^3$, where $T_c^3 = 647.096 \text{ K}$ is the critical temperature of water:

$$Y_{\text{pol}}^1 = 1.2774 \tilde{T}^2 - 7.9459 \tilde{T} - 11.293, \quad (51)$$

$$Y_{\text{pol}}^2 = 2.7894 \tilde{T}^2 - 30.976 \tilde{T} - 20.749, \quad (52)$$

$$Y_{\text{pol}}^3 = 2.9243 \tilde{T}^2 - 8.7813 \tilde{T} - 10.823. \quad (53)$$

Conclusions

The Helmholtz free energies for three pure species, and for a mixture of these species, have been presented. The expressions include the functions of temperature that usually drop out when modelling flows at constant and uniform temperatures. The determination of the complete temperature dependence depends on the knowledge of the following nuclear parameters, for each species α : the molecular mass, the symmetry number (σ^α), the degeneracy of the ground state electronic energy (ω_{e1}^α), the principal moments of inertia of the molecule ($I_1^\alpha, I_2^\alpha, I_3^\alpha$). Most importantly, one also needs the frequencies of the molecular vibrations, and the energies ($-D^\alpha < 0$) that are necessary to assemble the molecules at their ground states from their constituent nuclei and electrons. For models that are similar to the model presented in reference [9], the D^α are only needed for multiple-conformation molecules, and then only their differences are necessary, taking the most stable conformation as reference, for example.

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