Chapter 1

HELIUM THERMODYNAMICS, ANALYTICAL MODEL

Yasser Safa *

Zurich University of Applied Sciences

Abstract

The thermodynamic properties of helium at wide range of temperature and pressure are analytically derived from the knowledge of the pair spherical potentials to which quantum corrections are superposed. The double Yukawa potential model is considered to describe the intermolecular attraction and repulsion energies. Low temperature quantum effects are incorporated by using the first order quantum correction of the Wigner-Kirkwood expansion. A fundamental equation of state is formulated including Helmholtz energy as an explicit function of temperature and density. The thermodynamic properties are expressed as an explicit combination of the Helmholtz energy and its derivatives. The obtained values are compared to the thermodynamic data and the Molecular Dynamic calculations, a satisfactory correspondence with simulation results is realized. The feature of helium thermodynamics in the critical region is discussed. Contrary to most previous similar works, the present theory retrieves the main features of the helium at wide temperature and pressure from analytical formulation.

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*E-mail address: yasser.safa@zhaw.ch
1. Introduction

Helium is the second most ubiquitous element in the universe, it is detected in great abundance in stars and considered as an important constituent of giant planets and interstellar gas. Helium thermodynamics is obviously an attractive research topic to garner special attention in astrophysics, it serves for dynamic models describing birth of the planets and their evolution.

Though much less abundant on earth, helium is of scientific interest both experimentally and theoretically. Indeed, the thermodynamic properties of helium are a rewarding topic for the study especially because it is exploited in a number of high-technology applications. On the other hand, helium is one of lightest elements that are ideally used for testing the quantum statistical theories of matter.

One of special properties of the most abundant form of helium ($^4\text{He}$) is its extremely low boiling point (4.2 K), which is the lowest of common cryogenic fluids. As reported in Fig. [1] helium has no triple point (the intersection on a phase diagram where three phases: solid, liquid and gas coexist in equilibrium), this because helium will not solidify even at absolute zero unless an external pressure of greater than 2.5 MPa is applied. These properties make helium ideal for a variety of industrial and research applications.

Actually, helium cryogenics is a subfield of cryogenics which cuts across many disciplines, including refrigeration, fluid mechanics and heat transfer, material science, and instrumentation [1]. Its transparency to neutrons, and its stable heat transfer regime are some of the important features of helium-coolant in power plants applications [2]. Further, helium is a monatomic molecule and has the smallest atomic size of any element. This extremely small molecular size gives rise to an important use: helium leak detection systems which are applied in many industrial fields [3].

Clearly, an advanced understanding of helium thermodynamics at different exploitation conditions is highly relevant to such a helium based technology.

Liquid helium $^4\text{He}$ can be classified in either of two phases (Fig. [1]): He I which is the normal liquid, existing between the critical point ($T_c = 5.195$ K; $P_c = 0.227$ MPa) and the lambda transition ($T_{\lambda} = 2.176$ K). He II, denoted sometimes as super-fluid helium, exists between $T_{\lambda}$ and absolute zero and has exceptional transport properties. However, helium also has a rare isotope, $^3\text{He}$, which is of particular importance to very low-temperature refrigeration, the present chapter is focused on $^4\text{He}$ feature.

The thermodynamic properties of fluid are calculated with some sort of model since it is not possible to measure each property of interest at each combination of temperature, pressure and (in the case of mixture) composition. Often, these thermodynamic values are represented by a variety of equations. Multiple equations may be used to span wide ranges of density, where one equation is often used for the liquid, one for the vapor, and possibly a third for solid (e.g. [4] ). The application of multiple equations may results in discontinuities at the borders between thermodynamic sub-domains and inconsistencies between related properties.

In order to avoid as possible these shortcomings we use a single Equation of State (EOS) of wide range applicability to represent all of the thermodynamic properties for helium. We use a fundamental equation where the Helmholtz energy is formulated explicitly as a function of density and temperature. The thermodynamic properties can thus be obtained through combinations of derivatives of the Helmholtz energy with respect to temperature or/and density.
Moreover, the strong point of method presented in this chapter is that the fundamental equation is derived analytically from the sole knowledge of the intermolecular potentials.

In an effort to limit the scope and the length of this chapter, the focus here is on a Helmholtz fundamental equation of state for helium and the related thermodynamic properties. We introduce also in details an analytical derivation of the compressibility factor and the pressure.

2. Development of fluid EOS concept and formulation

The exploitation of a fluid in an advanced technology requires the improvement of both the representation accuracy and the thermodynamic consistency in EOS formulation. This is necessary in order to insure stability during process simulation. The development of EOS formulation for the fluid arose from the need for a reasonable mathematical expression which would be usable, not only for the calculation of pressure, density and temperature values, but also for the derivation of important extensive and intensive thermodynamic properties over a wide range of values.

Originally, an equation of state is a mathematical formulation which relates the thermodynamic properties of the fluid. The quest for a simple EOS form has been persisting even since more than century, several practical equations of state have been formulated empirically and have been fitted to experimental data. Different approach have been proposed in varied forms of modeling, notably: cubic, virial and Helmholtz energy EOS.
2.1. Cubic EOS

The original equation in this class was proposed in 1873 by van der Waals [5] for fluids relating the pressure $P$, the molar volume $V$ and the temperature $T$:

$$P = \frac{RT}{V - b} - \frac{a}{V^2},$$

where $R$ is the universal gas constant. This equation introduces two corrections to the ideal-gas law: $a$ is the parameter characterizing the long range attractive force between the molecules and $b$ is an excluded volume correction depending on the hard core volume of the molecules. The volume that the molecules have to move around in is not just the molar volume $V$, but is reduced to $(V - b)$. For helium we have $a = 0.00341$ Joule m$^3$/mole$^2$ and $b = 2.37 \times 10^{-5}$ m$^3$/mole.

The shortcoming of this cubic formulation is the limited range of applicability. Therefore several developments were carried out to improve this cubic EOS, (e.g. Dieterici in 1899 and Guggenheim in 1965 and others [6]). Some improved formulations of both repulsive and attractive terms have been contributed by several researchers between 1949 and 1990 and are summarized in [7].

2.2. Virial EOS

The virial equation of state can be derived from statistical mechanics, it expresses the deviations from the ideal gas law as a power series in molar density $1/V$:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + ...$$

Here the terms $B, C, D,...$ are the virial coefficients depending on the temperature. At very low density ($1/V \to 0$) this equation reduces to the ideal gas law. Helium virial EOS was early described in [8] and [9] where values for virial coefficients are provided for a limited range of temperature $100 < T < 400$ K. Although it is possible to extract values for the low order virial coefficients from the fundamental relations, the high order terms in the virial equation are empirical and depend on the experimental data for the fitted fluid. Virial EOS is not expected to be applied to the liquid phase properties. In the case of helium, the limited region of applicability of this virial equation is discussed by [10] and [11].

2.3. Helmholtz energy (fundamental) EOS

Fundamental equations of state garnered special importance in recent years since they allow a consistent derivation of the thermodynamic properties from a single mathematical formulation.

The molecular Helmholtz energy $F$ [Joules per molecule] is introduced as a fundamental property with independent variables: number density $n$ and temperature $T$, it can be split into: $F(n, T) = F^{id}(n, T) + F^r(n, T)$. Here the term $F^{id}$ denotes the ideal gas contribution to the Helmholtz energy where the term $F^r$ represents the residual Helmholtz energy which corresponds to the influence of both intermolecular forces and quantum effects. An equation in such a format is a fundamental EOS: all the thermodynamic properties can be obtained through combinations of derivatives of the explicit Helmholtz energy function with respect to temperature or/and density. For example, from the first order derivative $n^2 \left( \frac{2kT}{m} \right)_T$ we extract the classical equation of state explicit in pressure $P = P(n, T)$. Similarly, extraction of other properties such as the speed of sound still requires only differentiations of the Helmholtz energy.
3. Main features of the presented helium model

The thermodynamic model for helium as presented in this chapter can be specified by the following features:

- The fundamental Helmholtz EOS formulation is adopted to describe the thermodynamic properties of helium.
- The inter-molecular potential model used to describe the pairwise interaction of helium molecules is the spherical pair potential containing a short range repulsion and a long range attraction components. To describe the intermolecular repulsive and attractive interaction, we use the double Yukawa potential (DY) which provides an accurate analytical expression for the Helmholtz free energy.
- The model of hard sphere system is used to represent the geometry of Helium molecules. A system of hard spheres is the simplest realistic prototype for modeling the vapor-fluid phase separation in such a fluid. The idea of representing a fluid by a system of hard spheres was originally proposed by van der Waals, his classical equation of state was derived using essentially such a simple representation.
- Until recently, most Equations of State (EOS) have resulted from mathematical approximations of experimental data and any functional connection to theory is not completely justified. The strong point of the method presented in this chapter is that the relation between pressure, temperature and density is derived analytically from the knowledge of the intermolecular potentials.
- When dealing with light species such as He and H$_2$ at low temperature, we need to take into account the quantum mechanical effects. We use the Wigner-Kirkwood expansion (see [12]) to introduce first order quantum effects of such a system.

4. Intermolecular potential energy

The estimation of the intermolecular potential energy involves some assumptions concerning the nature of attraction and repulsion between molecules. Intermolecular interaction is resulting from both short-ranged hard sphere repulsion $u^{\text{HS}}$ and long-ranged attraction (or “traction”) $u^t$. At a radial distance $r$ from molecule’s center we have

$$u(r) = u^{\text{HS}}(r) + u^t(r), \quad (1)$$

while the long-ranged attraction is treated as a perturbation and the short-ranged repulsion acts as an unperturbed reference.

The Lennard-Jones formulation is the most widely used expression to describe the intermolecular potential $u^{\text{LJ}}$ for molecular simulation. It is a simple continuous potential that provides an adequate representation of intermolecular interactions for many applications at low pressure:

$$u^{\text{LJ}}(r) = 4\epsilon \left( \left( \frac{\sigma^0}{r} \right)^{12} - \left( \frac{\sigma^0}{r} \right)^{6} \right), \quad (2)$$

where $\sigma^0$ is the position at which the potential is zero (see Fig. 2) and $\epsilon$ represents the depth of the potential minimum which is located at $r = r^M$. But the inverse-power repulsion in LJ potential is inconsistent with quantum mechanical calculations and experimental data, which show that the intermolecular repulsion has an exponential
Table 1. DY potential parameters for helium.

<table>
<thead>
<tr>
<th>$\sigma^0$ [Å]</th>
<th>$\varepsilon$ [K]</th>
<th>$\lambda$</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.634</td>
<td>10.57</td>
<td>2.548</td>
<td>12.204</td>
</tr>
</tbody>
</table>

character. Therefore, the exponential-6 (or $\alpha$-exp-6) potential can be a reasonable choice instead of the LJ potential (see [13]):

$$u_{\text{exp6}}(r) = \frac{\varepsilon}{\alpha - 6} \left( 6^\alpha \left( 1 - r/\sigma^0 \right)^\alpha - \alpha \left( \frac{r}{\sigma^0} \right)^6 \right), \tag{3}$$

the term $\alpha$ determines the softness of the repulsive part of $u_{\text{exp6}}$ with respect to the "standard" LJ potential i.e. $u_{\text{exp6}}(r) < u_{\text{LJ}}(r)$ for $r < r^M$, [14]. In the case of pure helium molecules we have $r^M = 2.97$ Å and $\alpha = 13.1$.

However, an anomalous property of the $\alpha$-exp-6 potential is observed in the region of high temperature ($T > 2000$ K). Indeed, at a small distance $r_c$, the potential reaches a maximum value and, in the limit $r \to 0$, it diverges to $-\infty$ [15].

4.1. Double Youkawa potential

The double Yukawa potential $u^{\text{DY}}$ may be considered as advantageous since it can fit many other forms of empirical potentials (see [12] and [16]), and, in addition, the related integral equation of the Helmholtz free energy and compressibility factor can be solved analytically:

$$u^{\text{DY}}(r) = \varepsilon A^{\sigma^0} \left( e^{\lambda(1-r/\sigma^0)} - e^{\nu(1-r/\sigma^0)} \right), \tag{4}$$

The terms $A$, $\lambda$, and $\nu$ control the magnitude of the repulsive ant attractive contributions of the double Yukawa potential. The parameters in Table 1 are suitably chosen to provides a close fit to the exp-6 potential proposed in [13].

In Fig. 2 the double Yukawa potential for helium molecules is introduced. At $r = r^M = 2.97$ Å, the absolute value of the potential $u^{\text{DY}}$ is equal to the potential depth $\varepsilon$. We observe a consistent representation of the repulsive and the attractive subdomains located in $r < r^M$ and $r > r^M$ respectively. At $r = \sigma^0 = 2.634$ Å, the potential is zero.

Figure 2. The double Yukawa potential for helium molecules (plotted with Mathematica 7)
5. **Fundamental Helmholtz free energy equation**

In this section we introduce an analytical derivation of the different components of the Helmholtz free energy. We proceed with an explicit formulation of the molecular energy (with unit [Joules per molecule]) which is a function of the temperature $T$ and the number density $n$ (with unit [inverse of a cubic Angström]). Here $n$ takes the value of the previously mentioned molar density $1/V$ multiplied by a factor of $Na \times 10^{-30}$ where $Na$ is the Avogadro number.

5.1. **Hard sphere free energy**

The total Helmholtz energy $F$ for a molecule of helium can be written as

$$ F = F^{id} + F^{HS} + F^t + F^Q, $$

where $F^{id}$ is the Helmholtz energy per molecule arising from the ideal gas. It is defined with

$$ \beta F^{id} = \ln \left( n \left( \frac{h^2}{2\pi kT m_a} \right)^{3/2} \right) - 1, $$

where $h$ is the Planck’s constant, $m_a$ is the atomic mass, $\beta$ is the inverse temperature $\beta = 1/kT$ and $k$ is Boltzmann’s constant.

The term $F^{HS}$ is the Helmholtz energy of hard sphere. The expression of $F^{HS}$ reads (see for example [16])

$$ \beta F^{HS} = \frac{3 \eta_3}{1 - \eta_3} + \frac{\eta_3}{(1 - \eta_3)^2}, $$

where the parameter $\eta_3$ in Eq. (7) is the packing factor related to the hard sphere diameter $\sigma$ by

$$ \eta_3 = \frac{\pi}{6} n \sigma^3. $$

The distance $\sigma$ is calculated via the integration of the correlation function

$$ \sigma = \int_0^{\sigma_H} \left( 1 - e^{-u(r)/kT} \right) dr. $$

In [17] we found Eq. (9) interpreted as a result of the minimization of the free energy difference between the reference fluid (a purely short range repulsive model) and the effective hard sphere model (including the long range attraction).

The use of Eq. (9) makes $\sigma$ temperature dependent and enables an in-depth investigation of the temperature effects on the thermodynamic behavior of the fluid.

5.2. **Attraction free energy**

At extreme values of temperature and pressure, the stiffness and the range of the intermolecular repulsion play dominant roles. In contrast, at low temperature and pressure, for predicting properly the vapor-liquid transition both the repulsive and attractive effects must be considered.

In Eq. (5), the term $F^t$ is the first order perturbation contribution due to long-ranged attraction. Statistical mechanics provides an evaluation of $F^t$ via the integral equation including the radial distribution functions $g(r)$ and the potentials $u^{DY}(r)$. We have

$$ \beta F^t = \beta n \int_0^{\sigma_H} u^{DY}(r) g^{HS}(r) 4\pi r^2 dr. $$
Using the respective Laplace transform of the function \( r g^{HS}(r) \)
\[
G(s) = \int_0^\infty r g^{HS}(r) e^{-sr} dr, \quad \forall s \in \mathbb{R},
\]
Eq. (10) can be brought to
\[
\beta F^I = \frac{2\pi n}{kT} \varepsilon G \left( \sigma^0, A \left( e^\lambda G \left( \frac{\lambda}{\sigma^0} \right) - e^\nu G \left( \frac{\nu}{\sigma^0} \right) \right) - \delta F^I, \right.
\]
where \( \delta F^I \) is the value of the integral on the interval \( [\sigma, \sigma^0] \)
\[
\delta F^I = \frac{\beta}{2} \int_\sigma^{\sigma^0} u^{DY}(r) g^{HS}(r) 4\pi r^2 dr.
\]
The details of the analytical expressions of the functions \( G(s) \) are given in [18].
The subtraction of \( \delta F^I \) is important due to the fact that the interval \( [\sigma, \sigma^0] \) is covered by Eq. (11) and does not belong to the attractive range \( [\sigma^0, \infty] \).
Regarding the intersection of the functions \( u^{DY}(r) g^{HS}(r) \) and \( u^{DY}(r) g^{HS}(\sigma) \) at \( r = \sigma \) and \( r = \sigma^0 \) respectively, by considering the close variations of these functions in the interval \( [\sigma, \sigma^0] \), we can approach the value of \( \delta F^I \) by numerical integration of the expression
\[
\delta F^I \approx \frac{\beta}{2} \int_\sigma^{\sigma^0} u^{DY}(r) g^{HS}(r) 4\pi r^2 dr,
\]
here the term \( g^{HS}(\sigma) \) refers to (RDF) the radial distribution function \( g(r) \) for a hard sphere model at the contact point \( r = \sigma \) (conventionally the term \( g^{HS}(r) \) is noted RDF and it measures the extent to which the positions of particle center deviate from those of uncorrelated ideal gas).
The contact value of RDF \( g^{HS}(\sigma) \) is the improved version of [19] and [20], denoted by \( g^{BMCSL}(\sigma) \):
\[
g^{HS}(\sigma) = g^{BMCSL}(\sigma) + g^{BS}(\sigma),
\]
the values of the terms \( g^{BMCSL}(\sigma) \) are introduced in [18] as
\[
g^{BMCSL}(\sigma) = g^{(0)}(\sigma) + g^{(1)}(\sigma),
\]
where \( g^{(0)}(\sigma) \) is the contact value of the Precus-Yevick radial distribution function (PY RDF)
\[
g^{(0)}(\sigma) = \frac{1}{1 - \eta_3} + \frac{3\eta_2}{(1 - \eta_3)^2} \frac{\sigma}{2}
\]
and \( g^{(1)}(\sigma) \) is the first-order RDF at contact point, it is given by
\[
g^{(1)}(\sigma) = \frac{2\eta_3^2}{(1 - \eta_3)^2} \left( \frac{\sigma}{2} \right)^2,
\]
where \( \eta_i \) is defined as \( \eta_i = \frac{\pi}{6} n \sigma^i, i = 0, 1, 2, 3, ... \)

5.3. Quantum free energy

The term \( F^Q \) in Eq. (5) corresponds to the first order quantum correction of the Wigner-Kirkwood expansion [21], [22]
\[
\beta F^Q = \frac{\hbar^2 B^2 N_A n}{96\pi^2} \frac{1}{m_r} \int_\sigma^\infty \nabla^2 u^{DY}(r) g^{HS}(r) 4\pi r^2 dr.
\]
Using Eq. (11) we can obtain \( F^Q \) in term of Laplace transform

\[
\beta F^Q = \frac{\hbar^2 \beta^2 N_A n}{24\pi} \frac{\varepsilon A}{m_a \sigma^2} \left( \lambda^2 e^\lambda G \left( \frac{\lambda}{\sigma^2} \right) - \nu^2 e^\nu G \left( \frac{\nu}{\sigma^2} \right) \right).
\]

(20)

After checks we find that the first order quantum correction exhibits a poor convergence for temperature \( T < 40 \text{ K} \). Although the second order correction of Wigner-Kirkwood expansion extends somewhat the convergence over colder systems, it is still by far insufficient at cryogenic temperatures, e.g., in the case of pure He with temperature \( T < 40 \text{ K} \), [23].

We recall that one may suggest the application of quantum correction to the hard sphere diameter \( \sigma \), [24], via the relation

\[
\sigma_{cor} = \sigma + \frac{\lambda}{8},
\]

(21)

where \( \lambda \) is the Broglie wavelength \( \lambda = \sqrt{\beta h^2 / 2m_a} \) and \( h = \frac{\hbar}{2\pi} \).

This correction is usable at high temperature, but insufficient for obtaining reasonable description of quantum effects at temperature \( T < 40 \text{ K} \).

6. The thermodynamic properties

The intensive or extensive properties such as temperature, density, pressure, internal energy, enthalpy, entropy, Gibbs energies, heat capacities, speed of sound, chemical potential, and the Joule-Thompson coefficient as well as phase-equilibrium properties are all considered as thermodynamic properties. On the other hand, the transport properties include viscosity, thermal conductivity, diffusion and dispersion coefficients are considered as transport properties. The term "thermophysical properties" denotes all of the thermodynamic, transport, and interfacial (surface tension) properties.

The calculation of the transport properties of helium as function of temperature and density and the dependency of helium surface tension on temperature are described in [25]. Our focus in this chapter is on the thermodynamic properties.

The properties common to engineering applications are summarized in Table 2. They are obtained by derivation of the fundamental equation with respect to the independent variables: density and temperature.

We write the dimensionless Helmholtz energy, \( \alpha = \frac{\beta F}{kT} \), as an explicit function of the independent variables: the dimensionless number density \( \delta = \frac{n}{n_r} \) and the inverse dimensionless temperature \( \tau = \frac{T}{T_r} \). The terms \( n_r \) and \( T_r \) can be chosen as the values of the critical number density \( n_c = 0.0104 \text{ Å}^{-3} \) and critical temperature \( T_c = 5.1953 \text{ K} \). The reduced Helmholtz energy, \( \alpha \), can be split into the reduced ideal gas value \( \alpha^{id} \) and the reduced residual value \( \alpha' \):

\[
\alpha(\delta, \tau) = \alpha^{id}(\delta, \tau) + \alpha'(\delta, \tau),
\]

(22)

where

\[
\alpha^{id} = \frac{F^{id}}{kT},
\]

(23)

and

\[
\alpha' = \frac{F'}{kT} = \frac{F^{HS}}{kT} + \frac{F^t}{kT} + \frac{F^Q}{kT}.
\]

(24)

In Table 2 the thermodynamic properties are introduced as function of the reduced Helmholtz energy \( \alpha \) and its derivatives with respect to reduced variables \( \delta \) and \( \tau \).
Table 2. The thermodynamic properties

<table>
<thead>
<tr>
<th>The property</th>
<th>Relation to $\alpha = \beta F$ and its derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressibility factor $Z(T, n) = n \left( \frac{\partial P}{\partial n} \right)_T$</td>
<td>$Z(T, n) = 1 + \delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T$</td>
</tr>
<tr>
<td>1st derivative at constant $T$</td>
<td>$\left( \frac{\partial P}{\partial n} \right)_T = kT \left[ 1 + 2\delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T \right.$</td>
</tr>
<tr>
<td>2nd derivative at constant $T$</td>
<td>$\left( \frac{\partial^2 P}{\partial n^2} \right)_T = kT \left[ 1 + 2\delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T + \delta^2 \left( \frac{\partial^2 \alpha}{\partial \beta^2} \right)_T \right. $</td>
</tr>
<tr>
<td>1st derivative at constant $n$</td>
<td>$\left( \frac{\partial P}{\partial T} \right)_n = kn \left[ 1 + \delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T - \delta \tau \left( \frac{\partial^2 \alpha}{\partial \beta^2} \right)_T \right] $</td>
</tr>
<tr>
<td>Entropy $S(T, n) = - \left( \frac{\partial F}{\partial T} \right)_V$</td>
<td>$\frac{S}{k} = \tau \left[ \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta + \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta \right] - \alpha^{id} - \alpha^f $</td>
</tr>
<tr>
<td>Internal energy $U(T, n) = F + TS$</td>
<td>$\frac{U}{kT} = \tau \left[ \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta + \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta \right] $</td>
</tr>
<tr>
<td>Isochoric heat capacity $C_v(T, n) = \left( \frac{\partial U}{\partial T} \right)_V$</td>
<td>$\frac{C_v}{k} = -\tau^2 \left[ \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta + \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta \right] $</td>
</tr>
<tr>
<td>Enthalpy $H(T, P) = U + kTZ$</td>
<td>$\frac{H}{kT} = 1 + \tau \left[ \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta + \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta \right] + \delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T $</td>
</tr>
<tr>
<td>Isobaric heat capacity $C_P(T, P) = \left( \frac{\partial H}{\partial T} \right)_P$</td>
<td>$\frac{C_p}{k} = -\tau^2 \left[ \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta + \left( \frac{\partial \alpha}{\partial \beta} \right)_T \delta \right] + \left[ 1 + \delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T \right.$  $ \left. - \delta \left( \frac{\partial^2 \alpha}{\partial \beta^2} \right)_T \right] \left[ 1 + \delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T \right.$  $ \left. - \delta \left( \frac{\partial^2 \alpha}{\partial \beta^2} \right)_T \right] \left[ 1 + \delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T \right.$  $ \left. - \delta \left( \frac{\partial^2 \alpha}{\partial \beta^2} \right)_T \right] $</td>
</tr>
<tr>
<td>Gibbs energy $G(T, P) = F + kTZ$</td>
<td>$\frac{G}{kT} = \alpha^{id} + \alpha^f + \delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T $</td>
</tr>
<tr>
<td>Speed of sound $W = \left( \frac{1}{m_a} \left( \frac{\partial P}{\partial n} \right) \right)^{1/2}$</td>
<td>$\frac{w^2 m_a}{kT} = 1 + 2\delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T + \delta^2 \left( \frac{\partial^2 \alpha}{\partial \beta^2} \right)_T - \left[ 1 + \delta \left( \frac{\partial \alpha}{\partial \beta} \right)_T - \delta \left( \frac{\partial^2 \alpha}{\partial \beta^2} \right)_T \right] ^2 $</td>
</tr>
</tbody>
</table>

$^a$ The pressure in this table is obtained in [Joules per cubic Angström] = $[10^{-30}]$ Pa.$^b$ The term $m_a$ denotes the atomic mass of Helium given in [Kg].
This analytical model for Helmholtz energy formulation (and subsequently the corresponding formulations of the thermodynamic properties introduced in Table 2) is valid with high accuracy for a wide range of temperature [26].

Due to the current advances in computing facilities the calculation of the thermodynamic properties can be carried out by means of numerical discretization (finite difference) of the derivatives presented in Table 2.

However the important feature of Laplace transforms Eq. (11) in this model that it allows an analytical representation of the compressibility factors as an explicit function of density and temperature. Subsequently, an explicit representation of the pressure and the Gibbs energy can be obtained analytically as a function of density and temperature.

6.1. Analytical compressibility factors

In this section the compressibility factors corresponding to the repulsive, attractive and quantum effects are derived analytically. Therefore, the equation of state where the pressure is an explicit function of temperature and density can be readily obtained, and subsequently, the Gibbs free energy.

Let us introduce the superscripts: \( \chi \in \{ \text{id}, \text{HS}, t, Q \} \) which carry the same meaning as in Eqs. (5) and (7). The compressibility factor \( Z^\chi \) is expressed via the thermodynamic relation

\[
Z^\chi = n \frac{\partial}{\partial n} \left( \frac{F^\chi}{kT} \right). \tag{25}
\]

It is easy to see that from Eqs. (25) and (6) we have the behavior of the ideal gas:

\[
Z^{\text{id}} = n \frac{\partial}{\partial n} \left( \frac{F^{\text{id}}}{kT} \right) = 1. \tag{26}
\]

With Eq. (25) and by taking into account Eq. (7), the compressibility factor \( Z^{\text{HS}} \) can be expressed as

\[
Z^{\text{HS}} = n \frac{\partial}{\partial n} \left( \frac{F^{\text{HS}}}{kT} \right) = \frac{1}{1 - \eta_3} + \frac{3 \eta_1 \eta_2}{\eta_0 (1 - \eta_3)^2} + \frac{\eta_3^3 - \eta_3}{\eta_0 (1 - \eta_3)^3}. \tag{27}
\]

By applying the partial derivative with respect to \( n \) given in (25) in the relation (12), we obtain the compressibility factor corresponding to the attractive effects:

\[
Z^t = \frac{2 \pi n}{kT} \sigma^0 A \left( e^\lambda \left( G \left( \frac{\lambda}{\sigma^0} \right) + n \frac{\partial}{\partial n} G \left( \frac{\lambda}{\sigma^0} \right) \right) \right) - e^\nu \left( G \left( \frac{\nu}{\sigma^0} \right) + n \frac{\partial}{\partial n} G \left( \frac{\nu}{\sigma^0} \right) \right) - \delta Z^t, \tag{28}
\]

where \( \delta Z^t \) corresponds to the integral in the interval \([\sigma, \sigma^0]\), which is evaluated by numerical integration of the expression

\[
\delta Z^t \approx \beta \frac{n}{2} \left( g^{\text{HS}}(\sigma) + n \frac{\partial g^{\text{HS}}(\sigma)}{\partial n} \right) \int_\sigma^{\sigma^0} u^{\text{HS}}(r) 4\pi r^2 dr, \tag{29}
\]

the term \( g^{\text{HS}}(\sigma) \) and the derivative \( \frac{\partial g^{\text{HS}}(\sigma)}{\partial n} \) can be readily obtained from Eq. (15) - (18).

The expression of the compressibility factor \( Z^Q \) corresponding to the first order quantum correction of Wigner-Kirkwood expansion is obtained from Eq. (20).
Finally, the compressibility factor is \( Z = 1 + Z' \) where \( Z' = Z_{HS} + Z_t + Z^Q \).

### 6.2. Analytical explicit pressure EOS

The pressure \( P \) can be directly obtained by summing the respective compressibility factors

\[
P = nkT \left( 1 + Z_{HS} + Z_t + Z^Q \right) .
\]  

(31)

This analytical model has been validated for the case of Helium and Hydrogen (where shape factor effect was introduced). In [26] a comparison is presented between the computed values of the pressure and the results of Monte Carlo (MC) simulation presented by Ree [13] where the intermolecular potential is the exp-6 potential. The range of the domain of comparison is \( 50 < T < 4000 \) K and \( 0.043 < P < 16 \) GPa. A reasonable agreement is observed between results. The quantum effect was not included.

Nevertheless, in the calculation based on this model, for a temperature \( T = 100 \) K, the quantum corrections as introduced raise \( P \) by about 15\%, which corresponds to the first order correction of the Wigner-Kirkwood expansion as estimated in [13]. For higher temperature the obtained values of \( P \) are not affected significantly by the quantum contribution.

Further, an other comparison is established with the results from the work of Koči et al. [27]. In this latter work the Buckingham potential is used to perform molecular dynamics (MD) simulations of He for studying the phase transitions and the melting points. In Fig. 3 the variation of the pressure with respect to the density is shown for some given values of the temperature. The squares represent the variation resulting from our computations. The cross symbols correspond to the MD results, whereas the other symbols are related to the experimental data as reported in [27].

![Figure 3. Pressure at \( T = 75 \) K compared to values from experiments and MD simulations](image.png)
Figure 4. Pressure at $T = 150$ K compared to values from experiments and MD simulations

Figure 5. Pressure at $T = 225$ K compared to values from experiments and MD simulations

Figure 6. Pressure at $T = 300$ K compared to values from experiments and MD simulations

The match of the values resulting from the model with the experimental data is almost perfect especially for the region of low pressure. In Fig. 5 and Fig. 6 the MD results exhibit a good agreement with the high pressure reference data, since the model in [27] is expected to be valid for high pressures, but not for very low pressures and low temperature (Fig. 3), where quantum effects are more important.
7. Helium at temperature bellow 40 K

To our knowledge, no physically founded equation is formulated yet to describe accurately the thermodynamic behavior of helium at temperature $0 < T < 40$ K. More efforts still needed for an analytical formulation of the quantum energy contribution especially in critical and sub-critical regions. Since the methodology in this chapter is to derive the thermodynamic properties from Helmholtz energy, it is instructive to mention the proposed formulation of Helmholtz free energy in this region of high quantum effects.

In [26] the low temperature quantum effects are represented in the formulation of $F^Q$ via cumulant approximations of the Wigner-Kirkwood expansion proposed in [28]. This is a reasonable choice since it is usable down to zero temperature. The quantum correction was introduced with an adjustable factor. The critical cryogenic region was calculated with a relatively “enough accuracy” for astrophysical study of cold interstellar medium (see Fig. 7-8). In sub-critical temperature region the resulting pressure is treated by a Maxwell construction when density $n(P,T)$ at a fixed $T$ becomes multi-valued.

The development of a new equation of state for helium had to fulfill the highest demands on the accuracy in technical applications. Thus, it is practical in this chapter to mention some advanced fitted parameters formulations for Helmholtz energy in the region of low temperature.

The temperature range $2.2 < T < 40$ K belongs to the domain of validity of the fitted formulation of Helmholtz energy proposed in [29] for helium. More precisely, for a pressure up to 100 Mpa and temperature ranging from 2.2 to 400 K (the lower temperature limit $T = 2.2$ K is the lambda transition point between helium I and helium II) the residual part of the Helmholtz free energy of the equation of state for helium is determined with the structure-optimization method (see section 4 in [29]). Further, a fitted Helmholtz energy model for helium has been established in [30] especially for temperature bellow 0.8 K.

![Figure 7](image.png)

Figure 7. The pressure of helium resulting from this analytical model without Maxwell Construction. It is plotted against log $T$ and log $n^*$ where $n^*$ is a reduced density $= (\sigma^0)^3 n$. Quantum effects are qualitatively represented via cumulant approximations of the Wigner-Kirkwood expansion. The reported critical point is located at $P_c \approx 220$ kPa and $T_c \approx 5.2$ K.
However, the detailed descriptions of the adjustable parameters of those formulations are beyond the scope of this chapter which is devoted to present an analytical “non fitted” model.

8. Conclusion

In this chapter an analytical model for helium thermodynamics was presented with a wide range of applicability. The feature of helium in a mixture is not treated in present chapter. However an analytical model for the excess Gibbs energy of mixing still is feasible by applying a suitable mixing rule and by introducing the shape factor in the case of non spheric elements such as hydrogen, nitrogen or oxygen molecules. In the region of low temperature (critical and sub critical region) the quantum effects have strong influence on the thermodynamic behavior of helium. More efforts still are need to formulate a physically founded model for an accurate representation of the thermodynamic data of cryogenic helium.

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References


