

CHEMICAL POTENTIAL OF A LENNARD JONES FLUID

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SUMMARY: The aim of this paper is to present results of analytical calculation of chemical potential of a Lennard Jones (LJ) fluid performed in two ways: by using the thermodynamical formalism and the formalism of statistical mechanics. The integration range is divided into two regions. In the small distance region, which is $r < \sigma$ in the usual notation, the integration range had to be cut off in order to avoid the occurrence of divergences. In the large distance region, the calculation is technically simpler. The calculation reported here will be useful in all kinds of studies concerning phase equilibrium in a LJ fluid. Interesting kinds of such systems are the giant planets and the icy satellites in various planetary systems, but also the (so far) hypothetical quark stars.

Key words. Equation of state

1. INTRODUCTION

The aim of this paper is to present a calculation of chemical potential of a fluid consisting of neutral atoms or molecules. Interest in such systems has considerably increased towards the end of the last century, as a consequence of progress in planetary science. Until the end of October 2010, according to data at <http://exoplanet.eu>, as much as 493 planets outside the Solar system have been detected. It has been shown that 423 of them have masses $M \leq 5M_J$ where M_J is the mass of Jupiter. The major part (398) of the stars with planets have masses equal to or smaller than the solar mass, and 151 planet has the semi-major axis of the orbit between 1 and 3 astronomical units.

Judging by the experience from our Solar System, it is expectable that this interval of distances from a star corresponds to temperatures under which fluids consisting of neutral atoms and molecules can exist. It is known that giant planets have huge atmospheres and dense fluid interiors. Another class

of planetologically interesting systems, in which fluids are important, are the icy satellites in our planetary system. For example, it has been concluded from data accumulated in the course of the Galileo mission, that Jovian satellites Europa and possibly Callisto almost certainly have fluid oceans beneath their surfaces.

Calculations to be discussed in this paper can also find applications in theoretical studies of quark stars. These are (so far hypothetical) phases of extremely dense matter, expected to occur in interiors of neutron stars. In a recent study, aiming to constrain the parameters of solid quark matter by using data on the binary pulsar *PSR J1614 – 2230*, the Lennard-Jones model was used to describe the cold quark matter in quark stars (Lai and Xu 2010). It was shown there that if the number of quarks in a quark cluster is $N_q < 10^3$ there is enough parameter space for the existence of quark stars with masses higher than 2 solar masses.

Modelling theoretically the internal structure of celestial objects ranging from the icy satellites and/or giant planets to quark stars, demands the

a knowledge of chemical potential of the fluid in their interiors.

A necessary preparatory step in such a study must be the determination of interparticle interaction potential. Obviously, for a fluid or any other kind of a system to be in equilibrium, the interparticle potential must be a combination of an attractive and a repulsive term.

It is known that there exists an attractive force - called the van der Waals (vdW) force (for example Margenau 1939 or Dzyaloshinskii, Lifchitz and Pitaevskii 1961) between a pair of neutral atoms or molecules at a mutual distance larger than their respective dimensions. The potential corresponding to the vdW force is proportional to r^{-6} , where r is the interparticle distance. As shown by F. London, the physical origin of the vdW force is the interaction of instantaneous multipoles, while the repulsive contribution is of electrostatic origin.

The vdW forces are anisotropic, which renders them additionally complicated (Dzyaloshinskii, Lifchitz and Pitaevskii 1961). However, their isotropic part is often approximated by the so called Lennard-Jones (LJ) potential. All the calculations in what follows will deal with this particular model potential. The LJ model potential has the form:

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]. \quad (1)$$

The symbol ϵ denotes the depth of the potential well, while σ is the diameter of the molecular "hard core". Obviously, $\lim_{r \rightarrow 0} u(r) = \infty$. It can simply be shown that $\lim_{r \rightarrow \sigma} u(r) = 0$ and that $(\partial u(r)/\partial r) = 0$ for $r_{\min} = 2^{1/6}\sigma$. The depth of the potential well is $u(r_{\min}) = -\epsilon$.

An example of the LJ potential drawn for the particular case of CH_4 , with values of ϵ and σ from (Reichl 1988), is represented in Fig. 1. This particular molecule is interesting in two research fields: the planetary science, because it is present in the atmospheres of the giant planets, but also in studies of the interstellar medium. In the figure, the distance is expressed in units of σ and the potential divided by the Boltzmann constant k_B given in units of K .

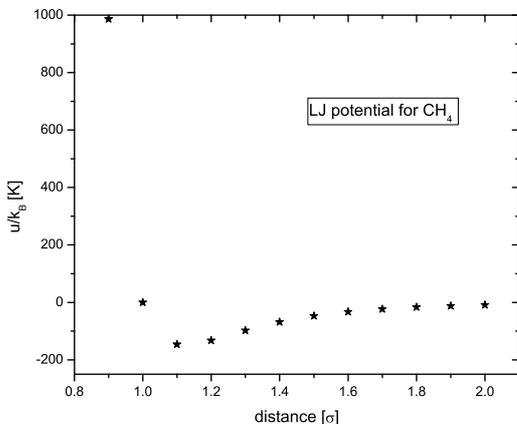


Fig. 1. The LJ potential for methane (CH_4).

2. THE METHOD OF CALCULATION OF THE CHEMICAL POTENTIAL

Chemical potential of a fluid (or any other system) can be calculated in two different ways: by using the general thermodynamical formalism, or by the general formalism of statistical mechanics.

2.1. The thermodynamical formalism

In this approach the calculation starts from the definition of the Gibbs potential:

$$G = U - TS + PV \quad (2)$$

where all the symbols have their standard meanings. Using the virial expansion, the pressure can be expressed as (Landau and Lifchitz 1976):

$$P \cong P_{ID} \left(1 + \frac{N}{V} B\right) \quad (3)$$

where N is the number of particles in the system and V the volume. The symbol B denotes the second virial coefficient, given by:

$$B = \frac{1}{2} \int_0^\infty (1 - \exp^{-u(r)/T}) dV \quad (4)$$

and P_{ID} is the pressure of the ideal gas. The symbol $u(r)$ denotes the interaction potential. Inserting Eq. (3) into Eq. (2), it follows that

$$G = U - TS + PV = G_{ID} + NP_{ID}B. \quad (5)$$

Chemical potential is defined as $\mu = (\partial G/\partial N)_{P,T}$, which implies that:

$$\mu = \left(\frac{\partial G_{ID}}{\partial N}\right)_{P,T} + P_{ID}B + NB \left(\frac{\partial P_{ID}}{\partial N}\right)_{P,T} \quad (6)$$

or

$$\mu = \mu_{ID} + P_{ID}B + NB \left(\frac{\partial P_{ID}}{\partial N}\right)_{P,T}. \quad (7)$$

The equation of state of ideal gas is $P_{ID}V = NT$ which finally leads to

$$\mu = \mu_{ID} + 2P_{ID}B. \quad (8)$$

For the particular case of the LJ potential, it can be shown that the second virial coefficient is given by (Reichl 1988):

$$B(T) = -(b_0/2) \sum_{n=0}^{\infty} \frac{1}{n!} \Gamma\left(\frac{2n-1}{4}\right) \left(\frac{\epsilon}{T}\right)^{\frac{2n+1}{4}} \quad (9)$$

where $b_0 = 2\pi\sigma^3/3$ and Γ denotes the Gamma function. Inserting Eq. (9) into Eq. (8) it follows that:

$$\mu = \mu_{ID} - b_0 p_{ID} \sum_{n=0}^{\infty} \frac{1}{n!} \Gamma\left(\frac{2n-1}{4}\right) \left(\frac{\epsilon}{T}\right)^{\frac{2n+1}{4}} \quad (10)$$

which is the result for chemical potential. Limiting the sum in this expression to terms up to and including $n = 1$, it follows that:

$$\mu \cong \mu_{ID} + 2p_{ID}b_0 \left[2.45083 - 1.8128\left(\frac{\epsilon}{T}\right)^{1/2} \right] \times \left(\frac{\epsilon}{T}\right)^{1/4}. \quad (11)$$

2.2. The formalism of statistical mechanics

The chemical potential of a fluid is given by (Hill 1987):

$$\frac{\mu}{k_B T} = \ln(\rho \lambda^3) + \frac{\rho}{k_B T} \int_0^1 d\gamma \int_0^{\infty} dr \times 4\pi r^2 u(r) g(r) \quad (12)$$

where γ denotes the "coupling parameter" (Hill 1987), ρ is the particle number density, $u(r)$ the interaction potential and $g(r)$ is the radial distribution function. The symbol \hbar is the Planck constant divided by 2π , m is the particle mass and λ is the thermal wavelength given by

$$\lambda = \left(\frac{2\pi\hbar^2}{mk_B T}\right)^{1/2}.$$

Expression (10) is valid under the condition $\rho \lambda^3 > 1$, which leads to:

$$\rho \geq \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}. \quad (13)$$

The radial distribution function is a "bridge" relating macroscopic thermodynamic properties with interparticle interactions in any kind of a substance. In the theory of liquids, $g(r)$ can be determined from first principles (Hill 1987) just by assuming a suitable form of intermolecular potential (Morsali et al. 2005). In what follows, the result for $g(r)$ obtained in Morsali et al. (2005) will be used. Changing the variable from r to $x = r/\sigma$, and performing the integration over γ , it follows that:

$$\frac{\mu}{k_B T} = \ln(\rho \lambda^3) + 4\pi\sigma^3 \frac{\rho}{k_B T} \int_0^{\infty} dx x^2 u(x) g(x). \quad (14)$$

The domain of integration can be divided into two subdomains $x \in [0, 1]$ and $x \in [1, \infty]$

$$\begin{aligned} I &= \sigma^3 \int_0^{\infty} dx x^2 u(x) g(x) = \\ &\sigma^3 \left[\int_0^1 dx x^2 u(x) g_1(x) + \int_1^{\infty} dx x^2 u(x) \times g_2(x) \right] \\ &= \sigma^3 \times [I_1 + I_2]. \quad (15) \end{aligned}$$

The divergence of the LJ potential which occurs when $x \rightarrow 0$ can be bypassed either by introducing a suitable change of the range of integration $x \in [x_0, 1]$ instead of $x \in [0, 1]$ with $x_0 \neq 0$, or by changing the form of the potential in the domain $x \in [0, 1]$. For $x \in [0, 1]$ the function $g(r)$ has the form

$$g_1(x) = s \exp[-(mx + n)^4] \quad (16)$$

and for $x \in [1, \infty]$ the radial distribution function is

$$\begin{aligned} g_2(x) &= 1 + \frac{1}{x^2} \exp[-(ax + b)] \sin[(cx + d)] + \\ &\frac{1}{x^2} \exp[-(gx + h)] \cos[(kx + l)] \quad (17) \end{aligned}$$

where $a, b, c, d, g, h, k, l, m, n$ and s are functions of pressure, temperature and density given in Morsali et al. (2005).

The appropriate boundary conditions, that the radial distribution function should tend to 1 in the limits of zero density and infinite distance, and the consequences of these conditions are also discussed there. As a consequence, the functions b, d, h and l are functions of density only, n is the function of temperature only and the other functions depend on the temperature and density (Morsali et al. 2005).

3. THE CALCULATION

3.1. The case $x \in [0, 1]$

With the change of variables $x = r/\sigma$, the LJ potential gets the form:

$$u(x) = 4\epsilon[x^{-12} - x^{-6}]. \quad (18)$$

Inserting Eqs. (16) and (18) into the expression for I_1 in Eq. (15), it follows that:

$$\begin{aligned} I_1 &= 4s\epsilon \sum_{l=0}^{\infty} \frac{(-1)^l}{(l!)} \int_{x=x_0}^1 \left(\frac{1}{x^{10}} - \frac{1}{x^4}\right) \\ &\quad (mx + n)^{4l} dx. \quad (19) \end{aligned}$$

Performing the integrations, after some algebra, it finally follows that:

$$\begin{aligned} I_1 &\cong \frac{8}{9} s\epsilon \times \left[1 + \frac{27}{5} m^4 - \right. \\ &\left. \frac{27}{10} m^8 - \frac{9m^{12}}{54} + \dots + \frac{1}{2x_0^9} - \frac{n^4}{2x_0^9} + \dots \right]. \quad (20) \end{aligned}$$

3.2. The case $x \in [1, \infty]$

In this case, the calculation of chemical potential is more straightforward. Inserting Eqs. (17) and (18) into the expression for I_2 in Eq. (15), and performing the integration, gives the following approximate result for the integral I_2 :

$$I_2 \cong -\frac{8\epsilon}{9} + \pi\epsilon \cos[d] \cosh[b] \left[\frac{a^5}{120} - \frac{a^3 c^2}{12} + \frac{ac^4}{24} - \frac{c}{5} \cos[c] \cos[d] + \dots \right]. \quad (21)$$

3.3. The chemical potential

According to Eqs. (14) and (15) chemical potential is given by:

$$\mu = k_B T \ln(\rho \lambda^3) + 4\pi \rho \sigma^3 (I_1 + I_2) \quad (22)$$

where the first terms of I_1 and I_2 are given by Eqs. (20) and (21).

Inserting Eqs. (20) and (21) into Eq. (22), one gets a simple analytical approximation for chemical potential of a LJ fluid.

4. DISCUSSION AND CONCLUSIONS

In this paper, we have obtained an approximate analytical expression for chemical potential of a Lennard Jones fluid. Two ways in which such an expression can be obtained have been presented, and both of these approaches have been applied.

The approach based on the general thermodynamic formalism gives a result, expressed as Eq. (10), which is both mathematically and physically simpler. It contains just two variables which characterize the material under consideration - these are σ - the diameter of the molecular "hard core", and ϵ - the depth of the potential well. Note that the chemical potential obtained in this way for a certain value of the ratio ϵ/T reduces to the value μ_{ID} .

The formalism of statistical mechanics is both mathematically and physically more complex. The general conclusion is that the chemical potential depends on thermodynamic parameters of the fluid through the functions a - s , which are in turn functions of the pressure and/or density and/or temperature (Morsali et al. 2005), but also on the interaction parameters. The approximate expression for chemical potential of a LJ fluid is:

$$\begin{aligned} \mu \cong & k_B T \ln(\rho \lambda^3) + \frac{32}{9} \pi \rho \epsilon \sigma^3 s \left[1 + \frac{27m^4}{5} \right. \\ & + \dots + \frac{1}{2x_0^9} + \dots + \frac{a^3}{s} \cos[d] \cosh[b] \left(\frac{3a^2}{320} - \frac{3c^2}{32} \right) \\ & \left. + \dots \right]. \quad (23) \end{aligned}$$

All the symbols in this expression have their standard meanings, or were introduced in Morsali et al. (2005). Mathematically, the symbol x_0 denotes the cut off radius of the LJ potential introduced in calculations in order to avoid the occurrence of divergences. Physically, this quantity represents the inter-particle distance at which the pressure ionisation occurs. Qualitatively speaking, the pressure excitation and/or ionisation occur because electronic energies change under the influence of the external pressure field. For details about this process see, for example, Kothari (1938).

The calculation presented in this paper was motivated by recent advances in planetary science. As a consequence of numerous discoveries of giant exoplanets, modellisation of their internal structure has regained importance. These planets consist mostly of fluids, and accordingly an obvious need for a theoretical "preparation of the ground" for the modellisation of their interiors has occurred. Studies of phase equilibrium and phase transitions demand an explicit knowledge of chemical potential. Some preliminary results in that direction have recently been obtained (Celebonovic 2009) in the limit of small density and without taking into account chemical potential. Another interesting problem, which becomes accessible for study with the results obtained in this paper is the behaviour of chemical potential of a LJ fluid with changes of its thermodynamical parameters. Some aspects of both of these problems will be discussed in a future work.

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ХЕМИЈСКИ ПОТЕНЦИЈАЛ ЛЕНАРД-ЏОНСОВОГ ФЛУИДА

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Претходно саопштење

У овом раду изведен је на два начина аналитички израз за хемијски потенцијал Ленард-Џонсовог флуида. Израчунавање је изведено користећи термодинамички формализам, као и формализам статистичке механике. Област интеграције је подељена на две под-области. Добијени резултати биће корисни у свим истраживањима везаним за равнотежу фаза и фазне прелазе у Ленард-

Џонсовом флуиду. Примери таквих система значајних у астрономији су велике планете у нашем планетарном систему, али и ван њега, као и велики сателити за које се сматра да садрже океане испод површина. Нова истраживања показују да би Ленард-Џонсов флуид могао да има примену и у проучавањима звезда које се састоје од кваркова.