

Exact asymptotic expansions for the thermodynamics of hydrogen gas in the Saha regime

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys. A: Math. Theor. 42 214031

(<http://iopscience.iop.org/1751-8121/42/21/214031>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.154

The article was downloaded on 03/06/2010 at 07:49

Please note that [terms and conditions apply](#).

Exact asymptotic expansions for the thermodynamics of hydrogen gas in the Saha regime

A Alastuey¹ and V Ballenegger²

¹ Laboratoire de Physique, ENS Lyon, CNRS, 46 allée d'Italie, 69364 Lyon Cedex 07, France

² Institut UTINAM, Université de Franche-Comté, CNRS, 16 route de Gray, 25030 Besançon Cedex, France

Received 30 October 2008, in final form 13 January 2009

Published 8 May 2009

Online at stacks.iop.org/JPhysA/42/214031

Abstract

We consider the hydrogen quantum plasma in the Saha regime, where it almost reduces to a partially ionized atomic gas. We briefly review the construction of systematic expansions of thermodynamical functions beyond Saha theory, which describes an ideal mixture of ionized protons, ionized electrons and hydrogen atoms in their ground state. Thanks to the existence of rigorous results, we first identify the simultaneous low-temperature and low-density limit in which Saha theory becomes asymptotically exact. Then, we argue that the screened cluster representation is well suited for calculating corrections, since that formalism accounts for all screening and recombination phenomena at work in a more tractable way than other many-body methods. We sketch the corresponding diagrammatical analysis, which leads to an exact asymptotic expansion for the equation of state. That scaled low-temperature expansion improves the analytical knowledge of the phase diagram. It also provides reliable numerical values over a rather wide range of temperatures and densities, as confirmed by comparisons to quantum Monte Carlo data.

PACS numbers: 52.25.Kn, 52.25.Jm

1. Introduction

Obtaining asymptotically exact formulae for the equation of state of quantum Coulomb matter is important, both at a theoretical level and for practical applications. They provide a better understanding of basic phenomena like molecular recombination and screening in the framework of statistical mechanics. Such formulae are free from any intermediate phenomenological modelization and uncontrolled approximation. They provide moreover reliable and accurate data in some range of thermodynamical parameters. Exact expansions are of particular interest for hydrogen described as a gas of quantum protons and electrons interacting via the Coulomb potential. Indeed, thanks to its relative simplicity, analytical

calculations can be carried out further than for heavier species. In practice, the corresponding expansions are quite useful since hydrogen is the most abundant element in the universe. Astrophysicists need accurate equations of state over a wide range of temperatures and densities, including the so-called Saha regime where hydrogen reduces to a partially ionized atomic gas.

In the 1950s [1], a first kind of asymptotic expansion was derived for an electron gas at high densities, which behaves as a free Fermi gas in a first approximation. Corrections can be computed in a systematic way in the framework of standard many-body perturbation theory [2], where the small-expansion parameter is the charge of the electrons. A second kind of asymptotic expansions, namely the familiar virial expansions, were constructed in the 1960s [3], for two- or more component systems, including quantum hydrogen. In such expansions, temperature T is fixed at a non-zero value, and numerical densities ρ_α for species α are driven to zero. For hydrogen, we set $\rho = \rho_p = \rho_e$. At lowest order, the system behaves as an ideal mixture of nuclei and electrons, as rigorously proved in [4]. Corrections are represented by series involving integer and half-integer powers of the ρ_α 's, as well as logarithmic terms. Corresponding calculations have been first performed up to order ρ_α^2 [5], by using the effective-potential method introduced by Morita [6]. Further corrections of order $\rho_\alpha^{5/2}$ have been derived in the 1990s within another formalism based on the path integral representation [7], and retrieved later by the Ebeling–Morita method [8].

The above expansions are suited for regimes where the systems are almost fully ionized. They cannot describe the Saha regime for hydrogen, where a finite fraction of electrons and protons recombine into atoms in their ground state. Then, according to the familiar Saha theory [9], the system is expected to behave as an ideal mixture of ionized protons, ionized electrons and H atoms. The construction of suitable asymptotic expansions requires first the identification, if it exists, of a regime of thermodynamical parameters where Saha theory becomes asymptotically exact. As described in section 2, that regime is obtained by setting $T \rightarrow 0$, while the ratio ρ/ρ^* is kept fixed with temperature-dependent density ρ^* given by expression (4).

Once the proper limit which defines the Saha regime has been identified, the construction of systematic expansions beyond Saha theory requires a formalism which accounts for all recombination and screening phenomena at work. For that purpose, the screened cluster diagrammatical representation [10] is particularly suitable, as briefly described in section 3. The corresponding analysis of all involved graphs provides the so-called SLT expansion of pressure P , i.e

$$\beta P/\rho^* = \beta P_{\text{Saha}}/\rho^* + \sum_{k=1}^{\infty} b_k(\rho/\rho^*)\alpha_k(\beta), \quad (1)$$

where Saha pressure P_{Saha} is given by formula (5) in section 2. Functions $b_k(\rho/\rho^*)$ only depend on the ratio ρ/ρ^* , while the temperature-dependent functions $\alpha_k(\beta)$ decay exponentially fast when T vanishes, $\alpha_k(\beta) \sim \exp(-\beta\delta_k)$ except for possible multiplicative powers of β . Expansion (1) is ordered with respect to the decaying rates $0 < \delta_1 < \delta_2 < \dots$ of the $\alpha_k(\beta)$ functions. The first five corrections computed in [11] are schematically presented in section 4. They account for non-ideal phenomena such as plasma polarization, shift in the atomic energy levels, interactions between ionized charges and atoms and also formation of H_2 molecules or H^- and H_2^+ ions. Further corrections $k \geq 6$ decay exponentially faster than $\exp(\beta E_{\text{H}})$, where $E_{\text{H}} = -me^4/(2\hbar^2)$ is the atomic ground-state energy and $m = m_p m_e/(m_p + m_e)$ is the reduced mass for the two-body electron–proton problem. Along a given low-temperature isotherm, we also study the behaviour of the $b_k(\rho/\rho^*)$ functions. The SLT expansion (1) then appears as a partial infinite resummation of ordinary virial expansions at low densities $\rho \ll \rho^*$.

Expansion (1) remains valid at intermediate ($\rho \sim \rho^*$) and large ($\rho > \rho^*$) densities, but breaks down at too large densities $\rho \gg \rho^*$ because molecular recombination becomes then prominent.

As usual for asymptotic series, keeping only the first few terms of the SLT expansion (1) should lead to an accurate equation of state, provided that thermal energy $k_B T$ is smaller than the Rydberg energy $|E_H|$. In section 5, we give a flavour of numerical calculations based on the truncation of (1) up to term $k = 5$ included [12]. Because of the relatively large temperature scale $|E_H|/k_B \simeq 150\,000$ K, and of the occurrence of exponentially decaying factors, that truncated equation of state is reliable over a rather wide range of thermodynamic parameters, as confirmed by comparisons to quantum Monte Carlo simulations by Militzer and Ceperley [13]. This allows us to introduce a semi-empirical criterion for the convergence of SLT expansions, which provides the validity domain of the SLT EOS in the temperature–density plane. Our formulae should be particularly useful in physical situations where deviations to Saha theory play an important role even if they remain small. For instance, a very accurate EOS is needed for interpreting recent seismology measurements in the Sun [14]. Our SLT EOS should be useful since, according to usual models, the Sun adiabat lies in the previous validity domain (see figure 1). However, note that an accurate description of that adiabat requires us to take into account heavier species such as helium, carbon, nitrogen and oxygen. If exact calculations become much more complicated, a simple account of obvious ideal contributions, in particular for less abundant species, should be sufficient for significantly improving a pure-hydrogen EOS.

We stress that our approach is based solely on first principles, and does not necessitate the definition of bound and ionized charge densities, nor of an ionization rate. In fact, an unambiguous definition of such phenomenological concepts cannot be made within the exact many-body problem. This does not cause any trouble as far as thermodynamical quantities are concerned, as commented in section 4. Other quantities like conductivity or opacity cannot be obtained directly within the present formalism. Usually, such quantities are computed within the framework of the chemical picture, where atoms and molecules are introduced phenomenologically as preformed entities. A first-principles description is of course possible in principle, but it becomes quite cumbersome since it would require a rigorous introduction of either real-time evolution or coupling to radiation.

2. The hydrogen gas in the Saha regime

2.1. The physical picture

Within the physical picture, a hydrogen gas is viewed as a system of quantum point particles which are either protons or electrons, interacting via the instantaneous Coulomb potential $v(r) = 1/r$. Protons and electrons have respective charges, masses, and spins, $e_p = e$ and $e_e = -e$, m_p and m_e , $\sigma_p = \sigma_e = 1/2$. In the present non-relativistic limit, the corresponding Hamiltonian for $N = N_p + N_e$ particles reads

$$H_{N_p, N_e} = - \sum_{i=1}^N \frac{\hbar^2}{2m_{\alpha_i}} \Delta_i + \frac{1}{2} \sum_{i \neq j} e_{\alpha_i} e_{\alpha_j} v(|\mathbf{x}_i - \mathbf{x}_j|), \quad (2)$$

where $\alpha_i = p, e$ is the species of the i th particle and Δ_i is the Laplacian with respect to its position \mathbf{x}_i . The system is enclosed in a box with volume Λ , in contact with a thermostat at temperature T and a reservoir of particles that fixes the chemical potentials equal to μ_p and μ_e for protons and electrons respectively. Because the infinite system maintains local neutrality $\rho_p = \rho_e$ in any fluid phase, the bulk equilibrium quantities depend in fact solely on the mean

$$\mu = (\mu_p + \mu_e)/2, \quad (3)$$

while the difference $v = (\mu_e - \mu_p)/2$ is not relevant as rigorously proved in [15].

2.2. Identification of the scaled limit

In the so-called Saha regime, a finite fraction of protons and electrons combine into hydrogen atoms, forming a partially ionized hydrogen gas. That regime is attained when several conditions are met. The temperature must be sufficiently low so that atoms can form, namely $kT \ll |E_H|$. The density must be sufficiently low as well so that atoms maintain their individuality thanks to $a \gg a_B$, where a is the mean inter-particle distance and a_B is the Bohr radius. If the density becomes too low, atoms dissociate by entropy, while if it becomes too large, they recombine into H_2 molecules. According to those simple considerations, both T and ρ must go to zero in a related way. The precise form of that relation can be inferred from a rigorous analysis in the grand-canonical ensemble devised by Macris and Martin [16], who extended Fefferman's work on the atomic phase of the hydrogen plasma [17]. They introduce a scaling limit where the temperature T goes to zero, while the average chemical potential μ of protons and electrons approaches the ground-state energy E_H with a definite slope [16]. Then, they proved that pressure P , within that scaling limit, tends to its Saha expression P_{Saha} , which describes an ideal mixture of hydrogen atoms, ionized protons and ionized electrons, with an ionization rate determined by the chosen slope.

In terms of temperature and density, the previous scaling limit can be rephrased as a low-temperature expansion at a fixed ratio ρ/ρ^* (see equation (1)), where ρ^* is the temperature-dependent density,

$$\rho^* = \frac{\exp(\beta E_H)}{2(2\pi\lambda_{pe}^2)^{3/2}} \quad \text{with} \quad \lambda_{pe} = (\beta\hbar^2/m)^{1/2}. \quad (4)$$

Note that density vanishes exponentially fast when T tends to zero. This ensures the proper energy–entropy balance which keeps a finite ionization rate that is entirely determined by the fixed ratio ρ/ρ^* . Pressure P in units of $\rho^*k_B T$ tends to the Saha formula

$$\beta P_{\text{Saha}}/\rho^* = \rho/\rho^* + (1 + 2\rho/\rho^*)^{1/2} - 1 \quad (5)$$

apart from exponentially small terms when $T \rightarrow 0$. The respective behaviours of Saha pressure (5), $P_{\text{Saha}} \sim 2\rho$ for $\rho \ll \rho^*$, and $P_{\text{Saha}} \sim \rho$ for $\rho \gg \rho^*$ clearly illustrate that ρ^* is a cross-over density between full ionization and full recombination.

3. Construction of SLT expansion

3.1. Introduction of a suitable formalism

Corrections to Saha pressure (5) involve interactions between ionized charges and atoms, as well as formation of ions and molecules. Standard many-body theory is not well suited for taking into account recombination, since that mechanism is not perturbative with respect to the charge. For instance, an infinite number of Feynman ladder graphs must be resummed for describing a single atom H.

The effective-potential method, which amounts to introducing a classical equivalent system of point particles with many-body effective interactions, is *a priori* more efficient for dealing with recombination. Indeed, n -body effective interactions are inferred from n -body quantum Gibbs factors which do account for recombination of n particles at short distances. The contributions of two-body effective interactions can be analysed within standard methods of classical statistical mechanics. In particular, that feature has been exploited for computing virial expansions up to order ρ^2 [3], where atomic contributions appear. Ionic and molecular recombination are embedded in three- and four-body effective interactions. Unfortunately, the

analysis of the corresponding contributions becomes rather cumbersome, in particular because no standard classical tool is available.

The above drawbacks of both standard many-body theory and effective-potential method clearly emphasize the need for a formalism more appropriate to deal with the Saha regime. The ACTEX method, introduced by Rogers [18] in the 1970s, is intended to account for the formation of chemical species in the framework of the physical picture. The approach starts from the usual activity expansion of thermodynamical quantities in the grand-canonical ensemble. Despite its rather successful predictions at moderate densities and temperatures, the approach cannot be applied here as it stands, because ACTEX series are not exactly reorganized via a systematic treatment of both recombination and screening. In fact, quantum Gibbs factors involved in activity series do not factorize as products of two-body counterparts, like in the case of classical charges. Resummations, which are crucial for taking into account screening effects, are very hard to handle in the usual quantum activity series.

The difficult task of controlling simultaneously recombination and screening effects in quantum activity series can be accomplished, thanks to the Feynman–Kac path integral representation. Within that formalism, the genuine quantum system of point protons and electrons is shown to be equivalent to a classical gas of extended loops [19]. Thermodynamic quantities of hydrogen are then represented by activity series in the world of loops, which can be suitably rearranged as described below.

3.2. The screened cluster representation

Since loops are classical objects with two-body interactions, standard Mayer diagrammatical methods can be applied. In particular, the one-body loop density is represented by a series of Mayer-like graphs in the grand-canonical ensemble. Usual points are replaced by loops, loop fugacities are simply related to particle fugacity $z = \exp(\beta\mu)$, while Mayer bonds are built with the loop–loop interaction potential. Since that potential behaves as the Coulomb interaction at large distances, Mayer graphs are plagued with long-range divergences. Such divergences are systematically removed via chain resummations, which amount to introducing a screened potential [20]. In contrast to the familiar classical Debye potential which decays exponentially fast, the quantum potential decays only as $1/r^3$ at large distances r . However, at low densities, it reduces to its classical Debye counterpart plus small corrections. At the same time, the whole series is reorganized in terms of particle clusters. Eventually, the particle density ρ , obtained by integrating loop density over all possible shapes, is exactly rewritten as the following diagrammatical series [10]:

$$\rho = \text{graph}_1 + \text{graph}_2 + \text{graph}_3 + \text{graph}_4 + \text{graph}_5 + \text{graph}_6 + \dots \tag{6}$$

The corresponding graphs are constructed with topological rules close to that of ordinary Mayer graphs, except for some exclusion constraints avoiding double counting. Usual points are now replaced by particle clusters. The statistical weight of a given cluster involves particle fugacities, as well as screened interactions. Two clusters can be connected by a single bond, which is either $-\beta\Phi$, $\beta^2\Phi^2/2$, or $-\beta^3\Phi^3/6$, where Φ is the screened interaction between those clusters.

Expansion (6) accounts, in a fully consistent way, for all effects of interactions in the system at a finite density and a finite temperature. The various phenomena at work are embedded in well-defined graphs. For instance, the first graphs shown in (6) account, respectively, for a single ionized proton, formation of an atom H and of a molecule H₂

and interactions between two atoms. As the scaling limit defines quite diluted conditions, only a few simple graphs in the screened cluster expansion are expected to contribute to the first corrections to Saha theory.

3.3. Behaviour of graphs in the scaling limit

The scaling limit defined in section 2.2 within the grand-canonical ensemble can be rephrased as follows. Starting from particle fugacity z and temperature T , we introduce a new couple (γ, T) of independent thermodynamic parameters defined through the relation z equal to a constant times $\gamma \exp(\beta E_H)$. Then, we set $T \rightarrow 0$ at fixed γ . The parameter γ determines hence the slope at which the chemical potential tends to the ground-state energy E_H as $T \rightarrow 0$. The behaviours of graphs in representation (6) result from the competition between three mechanisms, which can be roughly described as follows:

- *Screening.* Contributions of bonds $-\beta\Phi$, $\beta^2\Phi^2/2$ and $-\beta^3\Phi^3/6$ are controlled by the inverse Debye screening length $\kappa = (8\pi\beta e^2\rho^*\gamma)^{1/2}$ for ionized protons and ionized electrons with density $\rho^*\gamma$. They behave as positive or negative powers of κ , which itself decays exponentially fast as $\exp(\beta E_H/2)$.
- *Recombination.* For a particle cluster made with N_p protons and N_e electrons, the behaviour of its statistical weight gives raise to a cluster partition function $Z(N_p, N_e)$ in the vacuum. Each $Z(N_p, N_e)$ is a truncated trace of Gibbs operator $\exp(-\beta H_{N_p, N_e})$ involving only bare Coulomb Hamiltonians, which converges thanks to a truncation inherited from screening by ionized charges [10]. In $Z(N_p, N_e)$, contributions of all possible recombined entities made with $M_p \leq N_p$ protons and $M_e \leq N_e$ electrons are mixed together. Remarkably, the contribution of a given chemical species made with N_p protons and N_e electrons naturally emerges through Boltzmann factor $\exp(-\beta E_{N_p, N_e}^{(0)})$, where $E_{N_p, N_e}^{(0)}$ is the ground-state energy of Hamiltonian H_{N_p, N_e} . That factor increases exponentially fast since $E_{N_p, N_e}^{(0)} < 0$.
- *Entropy.* In a given cluster, the presence of $N = N_p + N_e$ particles generates activity powers z^N , which decay exponentially fast as $\exp(N\beta E_H)$.

The behaviour of a graph in the scaling limit is obtained, roughly speaking, by taking the product of the exponential factors generated by each of the above mechanisms. Then, every graph is found to decay exponentially fast. The leading contributions arise from the first two graphs in representation (6). They do reduce to the ideal terms ρ_p^{id} and ρ_H^{id} predicted by Saha theory. Further corrections decay exponentially faster than ρ^* in agreement with rigorous bounds [16]. Dividing all terms by ρ^* , the SLT expansion of ρ/ρ^* reads [11]

$$\rho/\rho^* = \gamma + \frac{\gamma^2}{2} + \sum_{k=1}^{\infty} \gamma^{n_k} h_k(\beta), \quad (7)$$

where the first two terms account for contributions from ionized particles and hydrogen atoms in their ground state. The remaining terms involve functions $h_k(\beta)$ that decay exponentially fast when $T \rightarrow 0$, while γ^{n_k} is an integer or half-integer power of γ (which may be multiplied by integer powers of $\ln \gamma$ when $k \geq 6$). Expansion (7) is ordered with respect to increasing decay rates of the h_k s. The corresponding hierarchy follows from subtle inequalities between the ground-state energies of all Coulomb Hamiltonians H_{N_p, N_e} . For instance, the molecular contribution, which determines the leading low-temperature behaviour of h_2 , indeed decays exponentially fast thanks to $E_{H_2} > 3E_H$: this ensures that molecules H_2 are very scarce in the Saha regime compared to atoms H, even though they are more stable energetically, i.e. $E_{H_2} < 2E_H$.

4. Equation of state beyond Saha theory

4.1. Scaled low-temperature expansion of pressure

Representation (7) expresses the density in terms of variables T and γ , or equivalently T and μ since there is a one-to-one correspondence between those sets of variables. As the natural thermodynamical parameters are the temperature and the density, it is quite useful to invert the SLT expansion (7) to determine $\gamma(\rho, T)$, in order to compute all thermodynamical quantities as functions of T and ρ . In the present scaling limit, this can be done in a perturbative way using the Saha expression

$$\gamma_{\text{Saha}}(\rho, T) = \sqrt{1 + 2\rho/\rho^*} - 1, \tag{8}$$

easily obtained by keeping only the first two terms in (7). Each correction to that form reduces to a product of an algebraic function of ρ/ρ^* times a temperature-dependent function which decays exponentially fast.

The standard thermodynamical relation, which expresses density in terms of the partial derivative of pressure with respect to z at fixed T , can be rewritten here as

$$\rho = \frac{\gamma}{2} \frac{\partial \beta P}{\partial \gamma}(\beta, \gamma). \tag{9}$$

After inserting the SLT expansion (7) of ρ into (9), a straightforward integration with respect to γ provides the SLT expansion of P in terms of γ and T . The corresponding expansion (1) of $\beta P/\rho^*$ in terms of ρ/ρ^* and T , then follows by using the inversion relation $\gamma(\rho, T)$ determined above [11]. The physical content of first five corrections in (1), as well as the expressions and values of the corresponding decay rates are summarized in the following table.

Correction (k)	Physical content	δ_k (in eV)
1	Plasma polarization around ionized charges	$ E_{\text{H}} /2 \simeq 6.8$
2	Formation of molecules, atom–atom interactions	$ 3E_{\text{H}} - E_{\text{H}_2} \simeq 9.1$
3	Atomic excitations, charge–charge interactions	$3 E_{\text{H}} /4 \simeq 10.2$
4	Formation of ions, atom–charge interactions	$ 2E_{\text{H}} - E_{\text{H}_2^+} \simeq 11.0$
5	Fluctuations of plasma polarization	$ E_{\text{H}} \simeq 13.6$

The first correction $k = 1$ is equivalent to a modification of Saha ionization equilibrium [21] derived within Green functions techniques (see also [5]), where rate $\delta_1 = |E_{\text{H}}|/2$ arises from the behaviour $\kappa \sim \exp(-\beta|E_{\text{H}}|/2)$ in the scaling limit. All further corrections are entirely new, as well as the structure of the SLT expansion (1). Beyond their leading behaviours $\alpha_k(\beta) \sim \exp(-\beta\delta_k)$, the functions $\alpha_k(\beta)$ include further corrections which decay exponentially faster. For instance, if the leading behaviour of $\alpha_3(\beta)$ is controlled by the first atomic excited state, all the other contributions of excited states are incorporated into $\alpha_3(\beta)$. Similarly, $\alpha_2(\beta)$ includes not only the contribution of the molecular ground state, but also all contributions of molecular excited states. As mentioned above about recombination, the sums of all those contributions are indeed finite. Also, we stress that such contributions of recombined entities, like H atoms in $k = 3$ or H_2 molecules in $k = 2$, are entangled with that of their dissociation products. Thus, purely atomic or molecular contributions cannot be unambiguously defined. This does not cause any trouble here, since only full contributions embedded in $k = 3$ and $k = 2$ are relevant for thermodynamics. In other approaches based on the chemical picture, that ambiguity has been the source of many controversies since the introduction of the Planck–Larkin formula (see e.g. [22–24]). Eventually, note that

the contributions to expansion (1) of more complex entites, such as H_2^- , H_3^+ or H_3 , decay exponentially faster than $\exp(-\beta|E_{\text{H}}|)$ as detailed in [11].

4.2. Low-temperature isotherms

Let us consider now a small fixed temperature T and study the behaviour of various corrections to the Saha pressure in (1) when the density ρ is varied. The corresponding low ($\rho \ll \rho^*$) and large ($\rho \gg \rho^*$) density behaviours are summarized below:

k	$\rho \ll \rho^*$	$\rho \gg \rho^*$
1	$\rho^{3/2}$	$\rho^{3/4}$
2	ρ^4	ρ^2
3	ρ^2	$\rho^{1/2}$
4	ρ^3	$\rho^{3/2}$
5	ρ^2	$\rho^{1/2}$

At low densities $\rho \ll \rho^*$, the leading correction of order $\rho^{3/2}$ is given by plasma polarization (term $k = 1$), while at large densities $\rho \gg \rho^*$ the leading correction of order ρ^2 arises from both molecules H_2 and atom–atom interactions (term $k = 2$). We have checked that the familiar virial expansion at low densities is indeed recovered up to order ρ^2 included, since all terms $k \geq 6$ provide powers higher than ρ^2 . We stress that at too large densities, expansion (1) breaks down because various corrections, in particular those due to molecular recombination, prevail over the Saha pressure which grows only as ρ . In fact, a semi-empirical criterion based on that observation allows us to infer a validity domain for the SLT expansion, as described below.

5. Numerical applications and comparisons to Monte Carlo data

The truncated EOS obtained by keeping the first five terms in the SLT expansion (1) can be computed numerically. The b_k s are easily computed since they reduce to simple algebraic functions of the ratio ρ/ρ^* . Numerical values for the temperature-dependent functions α_1 , α_3 and α_5 are also readily inferred from explicit analytic expressions. No similar expressions for α_2 and α_4 are available, since analytical results on the three- and four-body quantum problem are very scarce. Then, we use simple modelizations of those functions which account for their exact low-temperature forms on the one hand, and incorporate familiar phenomenological descriptions of ions H^- and H_2^+ and of molecule H_2 on the other hand [12].

Various isotherms corresponding to increasing temperatures have been considered. For temperatures below 2000 K, the Saha regime defines extremely diluted conditions which do not make physical sense: this explains why the Earth or Brown Dwarfs atmospheres only involve H_2 molecules. Temperature can be increased up to $T = 30\,000$ K, which is still small compared to the characteristic temperature scale $|E_{\text{H}}|/k_B \simeq 150\,000$ K. At a given temperature, calculations within the truncated EOS are not reliable above some density ρ_c , for which corrections to the Saha pressure become too large, in agreement with previous estimations for $\rho \gg \rho^*$. This breakdown is due to molecular recombination below $T \simeq 16\,000$ K, and to atom–atom interactions for higher temperatures.

At relatively low temperatures, i.e. below $T = 10\,000$ K, PIMC calculations [13] have been performed at rather high densities $\rho \gg \rho_c$ for which H atoms are mainly recombined into

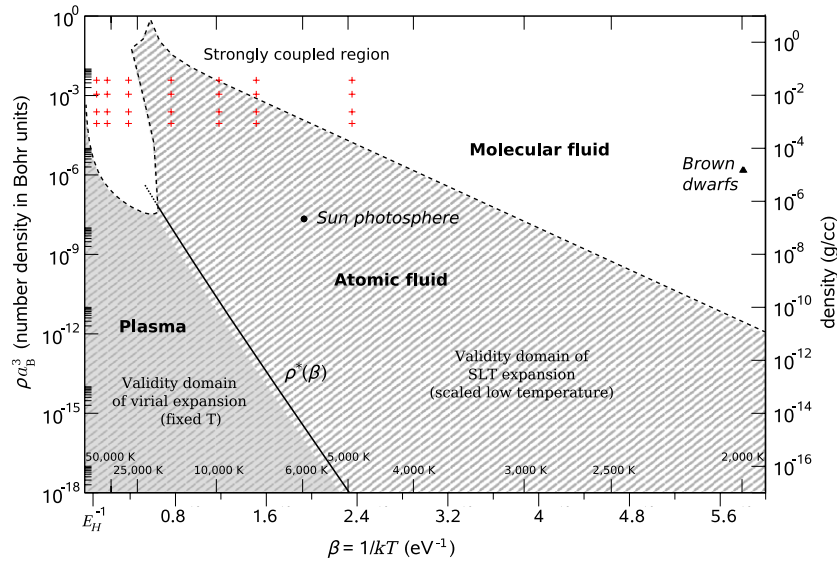


Figure 1. Validity domain of truncated SLT equation of state. Crosses indicate state points where PIMC simulation results are available [13].

H₂ molecules. In the Saha regime, statistics in PIMC results are poor because the corresponding densities are too diluted. In fact, under such conditions, our analytical results might serve as testbeds for simulation methods. For higher temperatures, i.e. above $T = 10\,000$ K, there exists a density range (see PIMC crosses displayed in figure 1), where comparisons between our results and PIMC data [13] are instructive. A good agreement is observed in some density range, which can be inferred from a semi-empirical criterion: corrections cannot exceed a few per cent of Saha pressure. This defines, at a heuristic level, the validity domain of the SLT expansion shown in figure 1. In the whole domain, weak-coupling and weak-degeneracy conditions are fulfilled. The tongue structure of the domain between $T \simeq 10\,000$ K and $T \simeq 25\,000$ K results from the increase of the strength of interactions between ionized charges and atoms. Note that the whole domain is restricted to rather low densities in general, so high-density phenomena, like the celebrated plasma phase transition, remain beyond the scope of our approach.

Eventually, we emphasize that our numerical calculations will be detailed in a forthcoming paper [12], where simple representations of functions $\alpha_k(\beta)$ ($k = 1, \dots, 5$) will be given, while the corresponding functions $b_k(\rho/\rho^*)$ can already be found in [11]. Our results will be compared to PIMC data, and also to phenomenological calculations. Applications to the Sun adiabat should be considered later.

References

- [1] Gellmann M and Brueckner K A 1957 Correlation energy of an electron gas at high density *Phys. Rev.* **106** 364-8
 Montroll E W and Ward J C 1958 Quantum statistics of interacting particles: general theory and some remarks on properties of an electron gas *Phys. Fluid* **1** 55
- [2] Fetter A L and Walecka J D 1971 *Quantum Theory of Many-Particle Systems* (San Francisco: McGraw-Hill)
 Martin Ph A and Rothen F 2004 *Many-Body Problems and Quantum Field Theory: An Introduction* 2nd edn (Berlin: Springer)

- [3] Ebeling W 1967 *Ann. Phys. Leipz.* **19** 104
- [4] Lebowitz J and Pena R 1973 Low density form of the free energy of real matter *J. Chem. Phys.* **59** 1362–4
- [5] Kraeft W D, Kremp D, Ebeling W and Ropke G 1986 *Quantum Statistics of Charged Particle Systems* (New York: Plenum)
- [6] Morita T 1959 Equation of state of high temperature plasma *Prog. Theor. Phys.* **22** 757
- [7] Alastuey A and Perez A 1992 Virial expansion of the equation of state of a quantum plasma *Europhys. Lett.* **20** 19–24
- [8] Kahlbaum T 2000 The quantum-diffraction term in the free energy for Coulomb plasma and the effective-potential approach *J. Physique IV* **10** 455
- [9] Saha M 1920 *Philos. Mag.* **40** 472
- [10] Alastuey A, Ballenegger V, Cornu F and Martin Ph A 2003 Screened cluster expansions for partially ionized gases *J. Stat. Phys.* **113** 455–503
- [11] Alastuey A, Ballenegger V, Cornu F and Martin Ph A 2008 Exact results for thermodynamics of the hydrogen plasma: low-temperature expansions beyond Saha theory *J. Stat. Phys.* **130** 1119–76
- [12] Alastuey A, Ballenegger V and Cornu F Numerical data for hydrogen in the Saha regime from asymptotic expansions *Phys. Rev. E* submitted
- [13] Militzer B and Ceperley D M 2001 Path integral Monte Carlo simulation of the low-density hydrogen plasma *Phys. Rev. E* **63** 066404
- [14] Däppen W 2006 The equation of state for the solar interior *J. Phys. A: Math. Gen.* **39** 4441
- [15] Lieb E H and Lebowitz J 1972 The constitution of matter: existence of thermodynamics for systems composed of electrons and nuclei *Adv. Math.* **9** 316–98
- [16] Macris N and Martin Ph A 1990 Ionization equilibrium in the proton-electron gas *J. Stat. Phys.* **60** 619–37
- [17] Fefferman C 1985 The atomic and molecular nature of matter *Rev. Math. Iberoamericana* **1** 1–44
- [18] Rogers F J 1974 Statistical mechanics of Coulomb gases of arbitrary charge *Phys. Rev. A* **10** 2441
- [19] Ginibre J 1971 Some applications of functional integration in statistical mechanics *Statistical Mechanics and Quantum Field Theory* ed C DeWitt and R Stora, Les Houches (London: Gordon-Breach)
- Cornu F 1996 Correlation in quantum plasmas : Resummations in Mayer-like diagrammatics *Phys. Rev. E* **53** 4562
- Martin P A 2003 Quantum Mayer graphs: applications to Bose and Coulomb gases *Acta Phys. Pol. B* **34** 3629
- [20] Ballenegger V, Martin Ph A and Alastuey A 2002 Quantum Mayer graphs for Coulomb systems and the analog of the Debye potential *J. Stat. Phys.* **108** 169–211
- [21] Kremp D, Kraeft W D and Lambert A J M D 1984 Equation of state and ionization equilibrium for non-ideal plasmas *Physica A* **127** 72–86
- [22] Iosilevski I L and Gryaznov V K 1981 Comparative accuracy of thermodynamic description of properties of a gas plasma in the Thomas-fermi and Saha approximations *High Temp.* **19** 799
- [23] Kaklyugin A S and Norman G E 2000 Thermodynamic functions (analytic expressions) for partially ionized strongly coupled plasmas. Bound and free states contributions *J. Physique IV* **10** 153
- [24] Starostin A N and Roerich V C 2006 Bound states in non-ideal plasmas : formulation of the partition function and application to the solar interior *Plasma Sources Sci. Technol.* **15** 410–5
- Starostin A N and Roerich V C 2006 Equation of state of weakly non-ideal plasmas and electroneutrality condition *J. Phys. A: Math. Gen.* **39** 4431–9