

Quantum Molecular Dynamics of Partially Ionized Plasmas

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Abstract

We study a partially ionized hydrogen plasma by means of quantum molecular dynamics, which is based on wave packets. We introduce a new model which distinguishes between free and bound electrons. The free electrons are modelled as Gaussian wave packets with fixed width. For the bound states the 1s-wave function of the hydrogen atom is assumed. In our simulations we obtain thermodynamic properties in the equilibrium such as the internal energy and the degree of ionization. The degree of ionization is in good agreement with theoretical predictions. The thermodynamic functions agree well with results from quantum statistics for $10000\text{K} \lesssim T \lesssim 40000\text{K}$.

Key words:

quantum molecular dynamics, wave packet simulation, dense plasma, thermodynamic properties of plasmas, degree of ionization, ionization and recombination processes

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1 Introduction

An understanding of dense plasmas is important to many areas of physics such as astrophysics or solid state physics. Because a complete analytic theory has not yet been advanced, several simulation techniques have been developed [1, 2, 3, 4, 5] in order to determine properties of plasmas. In such systems, however, the fermionic character and the long-range Coulomb forces cause many difficulties.

Quantum molecular dynamics (QMD) has been used to solve these problems [6, 7]. This method has been developed as an extension of classical molecular dynamics [8]. In QMD, wave packets are used as an approximation of the wave function of particles. Their dynamics can be derived from a time-dependent variational principle [6, 9]. It is possible to consider bound states, exchange effects and correlations in this method.

The traditional QMD technique is based on Gaussian wave packets. The first simulations of this kind were carried out by Heller [10]. This technique was further developed in nuclear physics to study scattering processes of nuclei [6, 7] and recently has been successfully applied to plasma physics by Klakow et al. [5, 11]. Both equilibrium and non-equilibrium properties of dense plasmas can be studied.

In this paper we describe a new QMD model for partially ionized plasmas, which extends the previous work by incorporating free and bound states and transitions of the electrons. In plasmas, such transitions can be caused by radiation and by collisions. Only the latter transitions are important in the range of temperature and density that we are considering. The description of such processes is very complicated, especially because the microscopic treatment of the 3-particle recombination is still an open question.

There have been recent attempts made to introduce transitions in QMD. In these it has been necessary to upgrade to Hamiltonian dynamics by use of additional elements. Ohnishi and Randrup have proposed to allow transitions on the basis of a stochastic dynamics [12]. Tully has developed a branching concept in order to study electronic transitions at surfaces [13]. In his approach the Hamiltonian dynamics was interrupted at certain points and a quantum mechanical transition was carried out.

In our model we start with a similar idea. In order to describe ionization and recombination processes we implement two possible transitions: A free electron can ionize an atom in a collision, and an ion and an electron can recombine in a 3-particle collision of two free electrons and an ion. We use the well-known cross section for the ionization process [14, 15]. In order to model the rather complicated recombination process we have developed a preliminary model. We study the partially ionized, weakly degenerate ($n_e \Lambda^3 < 0.15$) hydrogen plasma at a density of $1.35 \times 10^{22} \text{cm}^{-3}$ in the temperature range from 10000K to 200000K (see fig. 1). This is a much lower density than those studied by Pierleoni et al. [16] and Klakow et al. [11]. Simulations based on this model converge into an equilibrium of ionization and recombination with the degree of ionization in good agreement with theoretical predictions.

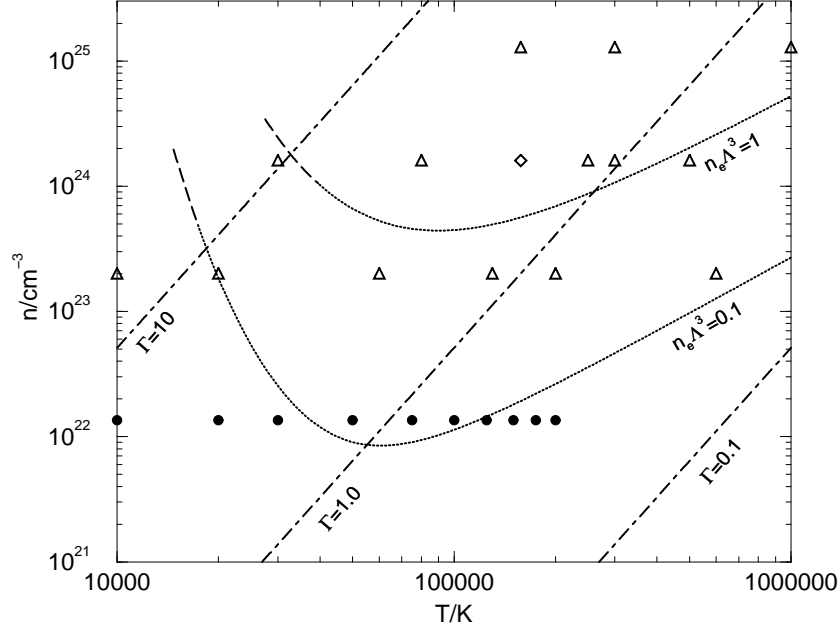


Figure 1: Characteristic lines of the hydrogen plasma in the temperature-density plane and data points of different investigations: • indicate our calculations, Δ are those of [16] and \diamond are those of [11].

2 Basic assumptions

2.1 Quantum molecular dynamics

Quantum molecular dynamics is a computational technique to study quantum many body systems. It is based on an approximation for the single particle wave function. Such a trial state $\Psi_{q_\nu(t)}$ contains the essential degrees of freedom and the parameters $q_\nu(t)$ represent the coordinates in a generalized phase space. The time evolution of the trial wave function is specified by the dynamics of the time-dependent parameters $q_\nu(t)$. For a chosen parameterization of the trial state, the equations of motion for the parameters can be derived from a time-dependent variational principle [6]:

$$\delta \int_{t_1}^{t_2} dt \left\langle \Psi_{q_\nu(t)} \left| i \frac{d}{dt} - \hat{H} \right| \Psi_{q_\nu(t)} \right\rangle = 0 \quad . \quad (1)$$

The equations of motion can be written in the general form [6],

$$\dot{q}_\mu = \sum_\nu A_{\mu\nu}^{-1} \frac{\partial H}{\partial q_\nu} \quad , \quad (2)$$

in which the Hamilton function H is defined as the expectation value of the Hamiltonian \hat{H} ,

$$H(q_\nu(t)) = \left\langle \Psi_{q_\nu(t)} \left| \hat{H} \right| \Psi_{q_\nu(t)} \right\rangle \quad , \quad (3)$$

and where

$$A_{\nu\mu} = 2 \operatorname{Im} \left\langle \frac{\partial}{\partial q_\mu} \Psi_{q_\mu(t)} \left| \frac{\partial}{\partial q_\nu} \Psi_{q_\nu(t)} \right. \right\rangle \quad (4)$$

is a skew-symmetric matrix [6, 17]. In certain trial wave functions, the parameters can be grouped into pairs of canonical variables and the matrix assumes the canonical form

$$A_{\nu\mu}^{-1} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad (5)$$

which leads to a Hamiltonian dynamics for the parameters. Gaussian wave packets (GWP) obey this type of dynamics.

2.2 Free electrons

GWP have a long tradition in QMD [6, 5, 10, 11, 18, 7]. We use them as trial wave function to describe the free electrons in the plasma:

$$\Psi_{GWP}(\vec{x}) = \left(\frac{2}{\gamma^2 \pi} \right)^{3/4} \exp \left\{ -\frac{(\vec{x} - \vec{r})^2}{\gamma^2} + i\vec{p}(\vec{x} - \vec{r}) \right\} \quad (6)$$

The position \vec{r} and the momentum \vec{p} stand for the expectation values of the relevant quantum mechanical operators. The parameter γ determines the width of the wave packet. Klakow et al. [5] made the first plasma simulation with GWP. In their model γ is a complex parameter of the dynamics and an additional degree of freedom of the trial wave function. We have shown that this ansatz leads at high temperatures to a heat capacity per electron greater than $\frac{3}{2}k_B$ [17].

Because of this principle problem we fixed the width of the GWP in our simulations. A condition for γ can be derived from the Kelbg potential [19]:

$$V^{Kelbg}(r) = \frac{e^2}{r} \left[1 - e^{-r^2/\lambda^2} + \frac{\sqrt{\pi}r}{\lambda} \left(1 - \operatorname{erf} \left\{ \frac{r}{\lambda} \right\} \right) \right] \quad (7)$$

$$\lambda = \frac{\hbar}{\sqrt{mk_B T}} \quad \text{valid for} \quad \xi = \frac{e^2}{\hbar} \sqrt{\frac{2m}{k_B T}} \ll 1,$$

which should approximately coincide with the interaction potential of two GWP [11]

$$V_{ee,GWP-GWP}(r) = \frac{e^2}{r} \operatorname{erf} \left\{ \frac{r}{\gamma} \right\} \quad (8)$$

Assuming $V_{ee,GWP-GWP}|_{r=0} = V^{Kelbg}|_{r=0}$ we fitted

$$\gamma = \frac{2}{\pi} \lambda \quad (9)$$

This ansatz leads to canonical equations of motion for the parameters \vec{r} and \vec{p} .

2.3 Bound electrons

In our simulation we consider the 1s-ground state of hydrogen explicitly. The best approximation for the ground state with GWP leads to an energy of 11.5 eV instead of 13.6 eV [11]. GWP with a dynamics derived from (1) have a continuous spectrum of excitation and a gap is missing. This results into unphysical excitations in many particle simulations and strongly influences the thermodynamic properties of the system [17]. That is why we introduce a 1s wave function (1sWF) to describe bound states,

$$\Psi_{1sWF}(\vec{x}) = \frac{1}{\sqrt{\pi a_0^3}} \exp \left\{ -\frac{1}{a_0} |\vec{x} - \vec{r}_I| \right\} \quad (10)$$

where \vec{r}_I is the position of the core. This wave function is an eigenstate of the Schrödinger equation.

2.4 Simulation of Hydrogen Plasma

The hydrogen plasma consists of ions with positive charge and electrons with negative charge. In order to incorporate quantum mechanical effects, the electrons in our model are treated as wave packets. The ions, which have much greater mass, are considered to be classical particles. We distinguish between free and bound states of the electrons by representing free electrons by GWP (6) and bound electrons by 1sWF (10). Our method is based on the Hamilton function H , which consists of the several parts,

$$H = T_i + T_e + V_{ii} + V_{ee} + V_{ei} \quad . \quad (11)$$

The classical ions contribute kinetic and potential energy,

$$T_i = \sum_k \frac{\vec{p}_k^2}{2M_k} \quad , \quad (12)$$

$$V_{ii} = \sum_{k < l} \frac{e^2}{|\vec{r}_k - \vec{r}_l|} + \Phi_{Ewald}(|\vec{r}_k - \vec{r}_l|) \quad , \quad (13)$$

where the Ewald potential is used for periodic boundary conditions [1, 8]. The following terms depend on the trial wave functions of the electrons,

$$T_e = \sum_k T_{e,k} \quad , \quad (14)$$

$$V_{ee} = \sum_{k < l} V_{ee,k,l} + \Phi_{Ewald}(|\vec{r}_k - \vec{r}_l|) \quad , \quad (15)$$

$$V_{ei} = \sum_{k,l} V_{ei,k,l} - \Phi_{Ewald}(|\vec{r}_k - \vec{r}_l|) \quad , \quad (16)$$

$$T_{e,k} = \left\langle \Psi_k \left| \frac{\vec{p}_k^2}{2m} \right| \Psi_k \right\rangle \quad , \quad (17)$$

$$V_{ee,k,l} = \left\langle \Psi_k(\vec{x}) \Psi_l(\vec{y}) \left| \frac{\mathbf{e}^2}{|\vec{x} - \vec{y}|} \right| \Psi_l(\vec{y}) \Psi_k(\vec{x}) \right\rangle , \quad (18)$$

$$V_{ei,k,l} = \left\langle \Psi_k(\vec{x}) \left| \frac{-\mathbf{e}^2}{|\vec{x} - \vec{r}_l|} \right| \Psi_k(\vec{x}) \right\rangle . \quad (19)$$

For GWP and 1sWF, this leads to

$$T_{e,GWP} = \frac{1}{2m} \left(\frac{3}{\gamma^2} + \vec{p}^2 \right) , \quad (20)$$

$$T_{e,1sWF} = \frac{1}{2m} \left(\frac{1}{a_0^2} + \vec{p}^2 \right) , \quad (21)$$

$$V_{ei,GWP} = -\frac{\mathbf{e}^2}{r} \operatorname{erf} \left\{ \frac{\sqrt{2}r}{\gamma} \right\} , \quad (22)$$

$$V_{ei,1sWF} = -\frac{\mathbf{e}^2}{r} \left[1 - e^{-2r/a_0} \left(\frac{r}{a_0} + 1 \right) \right] , \quad (23)$$

where r is the distance between the particles. Different wave functions lead to different potentials for the electron-electron interaction. The interaction of two GWP is given by (8). The interaction of a 1sWF with either a GWP or a second 1sWF is given by

$$V_{ee,GWP-1sWF} = \frac{\mathbf{e}^2}{r} \operatorname{erf} \{r/d\} - \mathbf{e}^2 \frac{e^{-r^2/d^2}}{2r} \left[f \left(\frac{d}{a_0} + \frac{r}{d} \right) - f \left(\frac{d}{a_0} - \frac{r}{d} \right) \right] , \quad (24)$$

$$f(x) = e^{x^2} \operatorname{erfc}\{x\} \left(x \frac{d}{a_0} - 1 \right) , \quad d = \frac{\gamma}{\sqrt{2}} ,$$

$$V_{ee,1sWF-1sWF} = \frac{\mathbf{e}^2}{a_0 \rho} e^{-2\rho} \left[1 + \frac{5}{8}\rho - \frac{3}{4}\rho^2 - \frac{1}{6}\rho^3 \right] , \quad \rho = \frac{r}{a_0} . \quad (25)$$

An atom in the simulation consists of a proton and an electron in the 1s-ground state. The interaction potentials of atoms are obtained by adding the contributions from both parts.

The ansatz (6) reveals the extra term $3/(2m\gamma^2)$ in the kinetic energy of a GWP (20), which has its origin in the shape of the GWP. Since $T_{e,GWP}$ is not consistent with the classical limit of free particles for high temperatures $\vec{p}^2/2m$ we omit this term.

3 Thermodynamic Model

In this paragraph it will be shown how the QMD can be used to determine the degree of ionization \bar{z} (the average charge number) of the plasma. In the usual approach one derives the degree of ionization from the free energy F , which is minimal at

constant volume and temperature. Alternatively it can be determined by using the condition that the internal energy U is minimal at constant entropy and volume.

$$\left(\frac{\partial F}{\partial \bar{z}}\right)_{T,V,n} = 0 \quad , \quad \left(\frac{\partial U}{\partial \bar{z}}\right)_{S,V,n} = 0 \quad . \quad (26)$$

The free energy is not available in QMD simulations. That is why the second condition is used to find the equilibrium-degree of ionization. In order to find the minimum of the internal energy U a number of separate simulations with different degrees of ionization were carried out without including transitions between free and bound states.

The entropy must be the same in all of these simulations. This requires a different temperature in every simulation. It can be obtained from entropy function S , which has to be known in our method. We use the entropy of the ideal hydrogen plasma,

$$S(N_e, N_i, N_0) = \sum_k N_k k_B \left[\frac{5}{2} - \log \left(\frac{\Lambda_k^3 N_k}{g_k V} \right) \right] \quad , \quad \Lambda_k = \frac{h}{(2\pi m_k k_B T)^{1/2}} \quad . \quad (27)$$

N_k is the number of particle in the volume V and g_k is the degeneracy parameter due to the spin, where the index k runs over all particle types. If one describes a hydrogen plasma in the chemical picture [20] one has to consider atoms ($g_0=2$), ions ($g_i=1$) and free electrons ($g_e=2$). The degree of ionization is defined by $\bar{z} = N_e/N$, where $N_e=N_i$ and $N = N_0 + N_i$.

Under the condition of fixed entropy the appropriate temperature can be derived by equation (27) for any degree of ionization. In the simulations we use a velocity-scaling procedure [8], which forces the system towards the desired temperature. Then the internal energy is obtained by averaging over many phase space configurations of the system. In this way the internal energy can be determined point by point on an adiabatic and its minimum can be found. The exact value for the minimum is obtained by quadratic approximation (fig. 2). The temperature belonging to this minimum has to be calculated from (27) since the temperature in all simulations is different.

Results

We study a partially ionized hydrogen plasma at a density of $1.35 \times 10^{22} \text{cm}^{-3}$ in the temperature range from 10000K to 200000K. The plasma is weakly degenerate: $n_e \Lambda^3 < 0.15$, where n_e is the density of the free electrons derived from the ideal Saha equation [20]. We consider 32 electrons and 32 ions in our simulations.

In figure 3, the degree of ionization from the simulation in the thermodynamical model is compared with results from the Padé approximation in the chemical picture (PACH) [21] and from the ideal Saha equation. The PACH approach is based on Padé formulae for the thermodynamic functions [22] and on the non-ideal Saha equation [20]. All methods show no ionization below 20000K, then the degree of ionization increases sharply. The values from our simulation and from the PACH

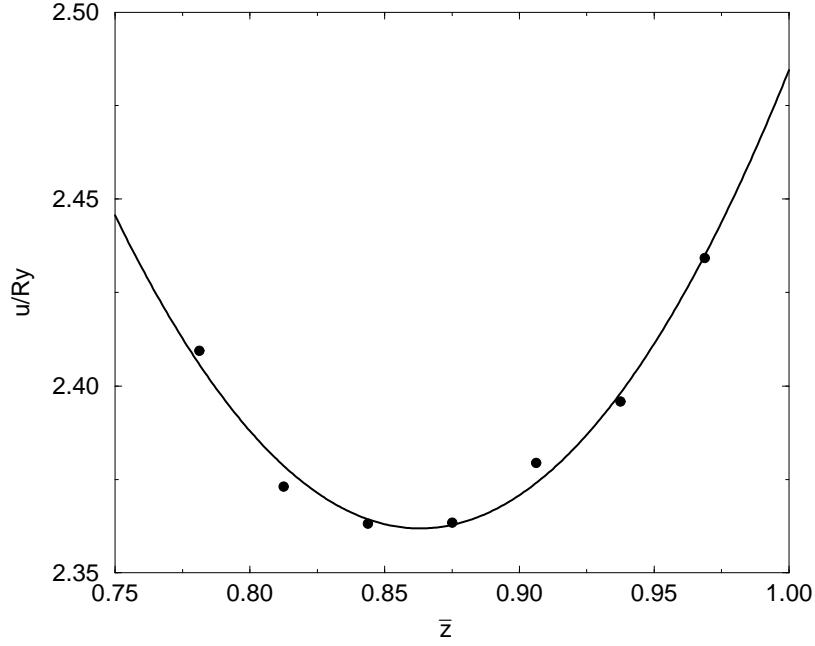


Figure 2: Internal energy u as function of the degree of ionization at constant entropy.

are higher than that of the ideal plasma because the Coulomb interaction leads to a reduction of the effective ionization energy. At higher temperatures, the Coulomb interaction is less important, therefore the difference between the results from our simulation and the ideal Saha equation becomes smaller. The values from the PACH are still 6% higher because the Planck-Larkin partition function, which takes into account excited states is used in these formulas [20].

The internal energy per particle from the simulation in the thermodynamic model u_{th} , from the PACH u_{PACH} and from the ideal plasma u_{id} are shown in figure 4 and 5. Under 20000K hydrogen behaves like an atomic gas, so u increases like $3/2 k_B T$. All three theories coincide in this region. With increasing temperature u_{th} and u_{PACH} rise more quickly than u_{id} because of the higher degree of ionization, which leads to additional contributions to the kinetic energy. At high temperatures, negative contributions from the Coulomb interaction determine the corrections to u_{id} . So u_{th} and u_{PACH} intersect with u_{id} at an intermediate temperature.

The agreement between the u_{th} and u_{PACH} is fairly good in the region $10000K \lesssim T \lesssim 50000K$. For higher temperatures, deviations start to occur. Above 75000K, u_{th} and u_{PACH} show the same behavior but differ by a constant. The PACH predicts a smaller energy although the degree of ionization is higher. One possible explanation is that there are no interactions of charged and neutral particles taken into account in these formulas. Further we have to mention that our approach neglects excited states, which are taken into account in the PACH approach [21].

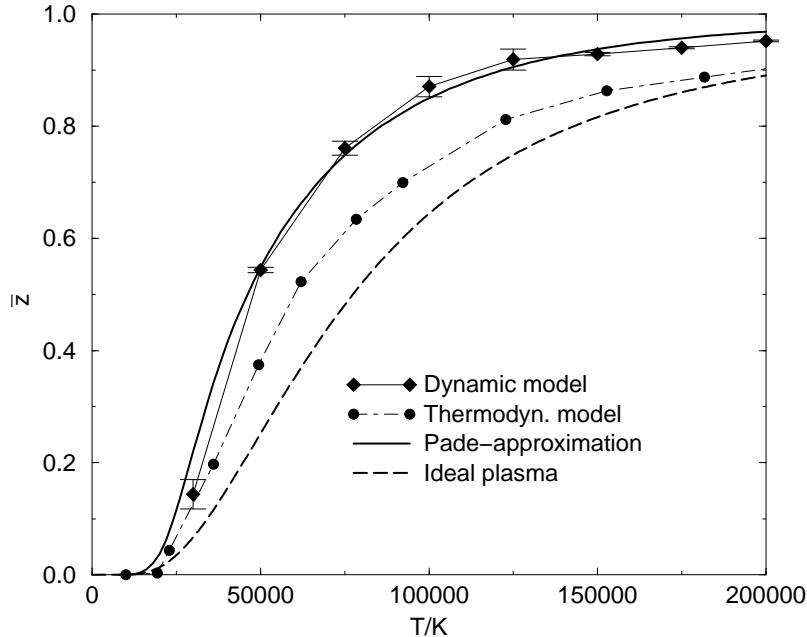


Figure 3: Degree of ionization versus temperature

4 Dynamic Equilibrium of Ionization and Recombination

There have been several attempts to model reactions by QMD. Tully developed a branching concept for transitions between different electronic states [13]. In this approach, the transition probabilities were derived from a Greens function technique. Hamiltonian dynamics is still used most of the simulation. Only in the case of a transition, dynamics are interrupted, new initial conditions for the particles are formulated and then the dynamics are continued.

In our simulation we must deal with ionization and recombination processes. If an electron with an impact energy greater than 1 Ry collides with an atom, ionization can take place. In order to include such transitions in QMD, knowledge of the microscopic dynamics of such a process is necessary. The ionization of one hydrogen atom in a plasma was studied in [23]. Here we investigate the much more complicated case where many atoms are present and include ionization as well as recombination. The ionization cross section for hydrogen is known various theoretical and experimental predictions [15, 14]. We use the semi-empirical formula [15, 23]:

$$\sigma(E) = c \frac{\ln\left(\frac{E}{I}\right)}{EI} \left[1 - \exp\left(1 - \frac{E}{I}\right)\right] \quad \text{if } E > I, \quad I = 1 \text{ Ry}, \quad c = 7.7 \text{ Ry}^2 a_0^2. \quad (28)$$

Adapting the cross section to the wave packet model we imagine a sphere of radius $\sqrt{\sigma_I(E)/\pi}$ around every atom. If a free electron enters this sphere with an impact energy E greater the 1 Ry the ionization of the atom occurs. The electron

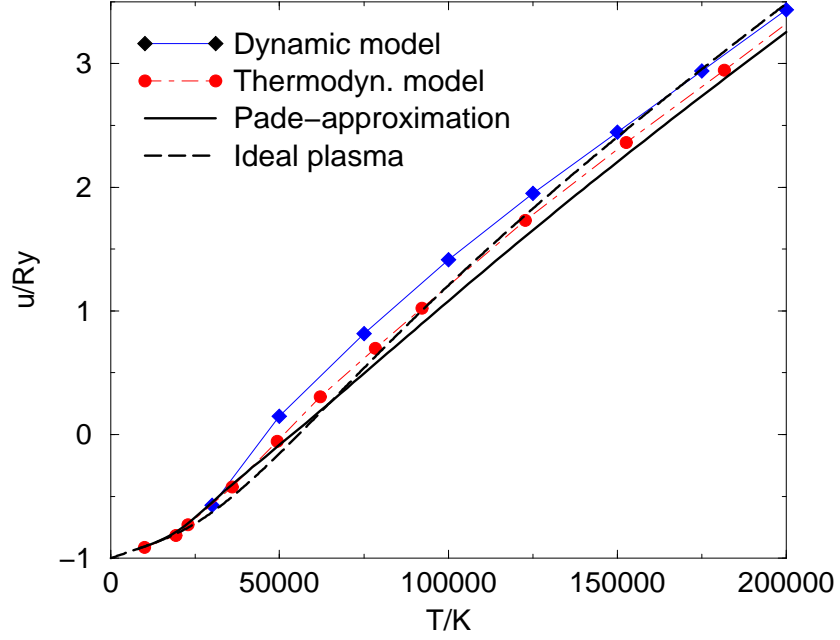


Figure 4: Internal energy u versus temperature

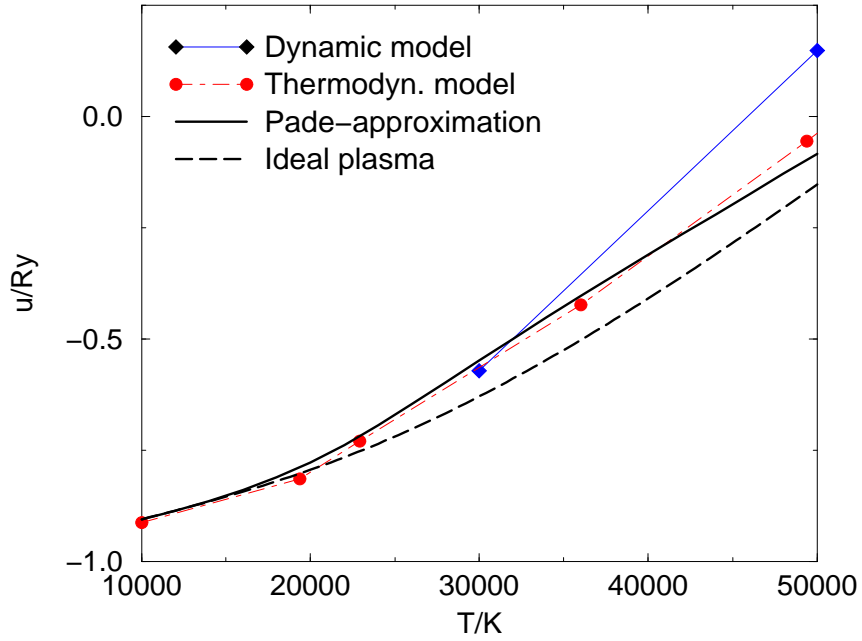


Figure 5: Internal energy u versus temperature

in the 1s ground state is replaced by free GWP, which is placed at the opposite point on the sphere. The momenta are chosen arbitrarily under conservation of energy.

A microscopic description of the recombination process is more difficult. However special information on recombination is available from various investigations. Besides the cross sections in different approximations which were derived from scattering theory, also the global recombination rate β is known from the theory of the rate coefficients [14, 24]. A microscopic description of the recombination process in QMD has not been derived yet. As a preliminary model we propose the following mechanism: If two electrons are simultaneously in a sphere of radius $\rho_R = 1 a_B$ around an ion the recombination will take place. One electron is moved into the ground state and the other changes its momentum so that the total energy is conserved.

Results

We carried out simulations at the same density from 30000K (128 ions and 128 electrons) to 200000K (32 ions and 32 electrons). The system converges into a dynamic equilibrium of ionization and recombination. The degree of ionization we get from this simple model is surprisingly good (fig.3). It agrees well with the PACH approach in the considered temperature range. We do not claim that we give with our simple microscopic model a rigorous description of the recombination process but, rather, we deduce that our mechanism leads to a correct global rate β in the temperature range studied here. Correct in context means that the average number of recombination processes per time unit is in agreement with the number ionization processes so that the detailed balance is satisfied.

In our model, we have found a dependence of β on ρ_R and a setting of $\rho_R = 1 a_0$ turned out to be a good estimate.

The internal energy u derived from these simulations leads to qualitatively correct results (fig.4) but quantitatively the results only agree well up to temperature of 40000K (fig.5). Beyond of that our results are systematically high in comparison to the PACH, which may be caused by an insufficient description of the electron-ion interaction. Because our results were generally too high in comparison to the PACH model. Evidently simulations above 40000K require a more precise description of the interaction between free electrons and ions than that given in our QMD model.

5 Conclusion

We expect that the model presented in this paper will prove to be a promising approach for the description of plasmas in the partially ionized region. We have substantially extended the traditional QMD model with the consideration of free and bound states. We have shown how thermodynamical functions can be derived from a model with free and bound states but still without transitions. Furthermore we presented a preliminary model for the dynamic description of ionization and recombination in plasmas. As a first test we calculated the degree of ionization and the

internal energy of the hydrogen plasma.

The model can be improved in several ways. First of all a detailed quantum mechanical description of the 3-body recombination process would be useful in future studies. Furthermore it would be interesting to study the formation of molecules [17]. One must also take into account the fermionic character of the electron wave function [7, 11]. Our results offer hope that it soon will be possible to describe hydrogen in the whole temperature range from the molecular gas to the completely ionized plasma.

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