

Orbital-free molecular dynamics simulations of a warm dense mixture: Examination of the excess-pressure matching rule

J-F. Danel, L. Kazandjian,* and G. Zérah

Centre DAM Ile-de-France, CEA, Bruyères-le-Châtel, 91297 Arpajon Cedex, France

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A form of the linear mixing rule involving the equality of excess pressures is tested with various mole fractions and various types of orbital-free molecular dynamics simulations. For all the cases considered, this mixing rule yields, within statistical error, the pressure of a mixture of helium and iron obtained by a direct simulation. In an attempt to interpret the robustness of the mixing rule, we show that it can be derived from thermodynamic stability if the system is regarded as a mixture of independent effective average atoms. The success of the mixing rule applied with equations of state including various degrees of approximation leads us to suggest its use in the thermodynamic domain where quantum molecular dynamics can be implemented.

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I. INTRODUCTION

In various cases of practical interest, it is important to know the equation of state of mixtures in the warm dense matter (WDM) regime characterized by strong coupling and a high electronic degeneracy. This is the case for instance when one wants to calculate the speed of sound in giant planets interiors or in mixtures resulting from the implosion of pellets in inertial confinement fusion. The WDM regime is difficult to describe because, even for a pure phase, the system consists of a variety of particles (electrons, ions, atoms, and clusters) that continuously interact and evolve. The equations of state (EOS) generally applied to such systems are computationally expensive and, when used in hydrocodes, must be tabulated. When mixtures are considered, there is in fact one EOS for each possible distribution of mole fractions; the use of a mixing rule, which provides prescriptions for determining the EOS of a mixture from the EOS of the pure phases, is therefore necessary. The aim of this study is to propose such a mixing rule and to test it with various EOS based on both density-functional theory and molecular dynamics.

In view of the complexity of the WDM regime, the system is generally regarded as a mixture of electrons and nuclei; the adiabatic approximation, which postulates that electrons instantaneously respond to the displacement of nuclei, is assumed and allows to treat electrons and nuclei separately. In the one-component (OCP) model, the ions are regarded as point charges and the electrons are assumed to form a uniform and rigid continuum [1]. This model was generalized to mixtures by Hansen *et al.* [2] who found that the linear mixing rule (LMR, stating that the excess free energy at constant temperature and charge density is a linear interpolation between the excess free energies of the respective pure phases) is accurate for strong coupling and moderate nuclei-charge ratios; DeWitt *et al.* [3] confirmed this result for larger nuclei-charge ratios when the nuclei are treated with hypernetted-chain (HNC) calculations. Chabrier and Ashcroft [4] assume that a binary mixture can be viewed as a

superposition of a uniform electronic background and a screened binary ionic fluid characterized by an effective ionic Hamiltonian depending on the dielectric function; with a HNC treatment of the nuclei, they also find that the linear mixing rule gives good results. Rosenfeld [5] proposes a nonlinear mixing rule for mixtures of charged particles interacting through the Yukawa repulsive potential and, within the HNC approximation, finds it very accurate for a wide range of charge ratios and coupling parameters.

The above approaches involve assumptions about the electronic density or the interactions among nuclei. No such assumption is necessary if the EOS is addressed with first-principles calculations that treat the system as a mixture of electrons and nuclei interacting through Coulombic interactions. In such calculations, the adiabatic approximation is still assumed so that the EOS can be calculated by classical molecular-dynamics simulations of nuclei interacting through forces that can be computed, for each nuclear configuration, from electronic density. It is then possible to consistently combine density-functional theory applied to the calculation of electronic density [6,7] and classical molecular dynamics applied to nuclei. Various density-functional methods can be implemented according to the approximation chosen for the electronic free energy and for the exchange-correlation functional. The Kohn-Sham method [6,7], in which electrons receive a full quantum treatment, gives rise to quantum molecular dynamics (QMD); if the exchange-correlation functional is assumed to be known, QMD yields first-principles calculations of transport coefficients and thermodynamic properties [8–11]. In the framework of QMD, Horner *et al.* [12] recently compared two mixing rules applied to lithium hydride and found that the mixing rule based on total-pressure matching gives superior results for the calculation of pressure; the excess pressure obtained can nevertheless differ from the exact one by 20%. In practice, QMD cannot be implemented at high temperature and/or high density where it gets too computationally expensive. For sufficiently high density and/or temperature, it is possible to calculate the electronic density with the Thomas-Fermi-Dirac (TFD) method in which electrons are no longer described by orbitals but by a free-energy functional depending only on the local electronic density; there is then no need to compute

*Corresponding author; luc.kazandjian@cea.fr

one-electron quantum states and this method is said to be orbital-free. The TFD method has been used, in combination with molecular dynamics, to determine properties of warm dense plasmas [13–17]; a practical advantage of TFD molecular dynamics (TFDMD) is that it is sufficiently computationally cheap that it can be used at high temperature and/or high density where QMD cannot in general be implemented. The Thomas-Fermi-Dirac-Weizsäcker (TFDW) method, another orbital-free approach, extends the domain of validity of the TFD method by taking into account the second term of the gradient expansion of the electronic free energy (the gradient correction) [18,19]; Thomas-Fermi-Dirac-Weizsäcker molecular dynamics (TFDWMD) has been implemented in Refs. [20–22]. TFDMD can be implemented with no exchange-correlation functional; in this case, the method is designated here by TFMD (for Thomas-Fermi molecular dynamics). We therefore find ourselves with three orbital-free approaches of the EOS, namely, TFMD, TFDMD, and TFDWMD, each including more physics (exchange-correlation functional and gradient correction) and having a larger thermodynamic domain of validity than the preceding. In the framework of TFDMD, a form of the linear mixing rule based on excess-pressure matching, that we call here excess-pressure matching rule (EPMR), has been tested mainly on an equimolar mixture of helium and iron and found to be very accurate for the calculation of pressure and internal energy in various thermodynamic conditions of the WDM regime [23].

In this paper, the EPMR is further explored by considering various mole fractions and EOS. In Sec. II, the EPMR is tested with TFDMD on a mixture with various mole fractions of ^4He (atomic mass=4.0026 g.mol $^{-1}$) and ^{56}Fe (atomic mass=55.395 g.mol $^{-1}$). In Sec. III, the EPMR is tested on an equimolar mixture of helium and iron with TFMD, TFDMD, and TFDWMD. In Sec. IV, the success of the EPMR is interpreted, in terms of an average atom model, as a consequence of thermodynamic stability. Suggestions for further use of the EPMR are discussed in the conclusion. The simulations by TFMD, TFDMD, and TFDWMD are performed with the electronic structure package ABINIT [24–26].

II. VARIATION IN THE MOLE FRACTIONS

A. Molecular dynamics simulations

We first apply TFDMD to a mixture of helium and iron with various mole fractions x_{He} and x_{Fe} and we use the pressures obtained for the full mixture as a benchmark against which to assess the EPMR. The system is constructed by replication of a finite sample of N atoms in a basic cubic reference cell. The dynamics of the nuclei is driven by the nuclear Coulomb interactions and by an effective potential equal to the electronic free energy; for given positions of the nuclei and thermodynamic conditions, the electronic free energy is a functional of the electronic density whose value at equilibrium is obtained by minimization with respect to the electronic density under the constraint of charge neutrality. Electronic density is expressed as an expansion on a periodic plane-wave basis; the number of terms in this expansion is chosen with the cutoff energy. The Coulombic electron-

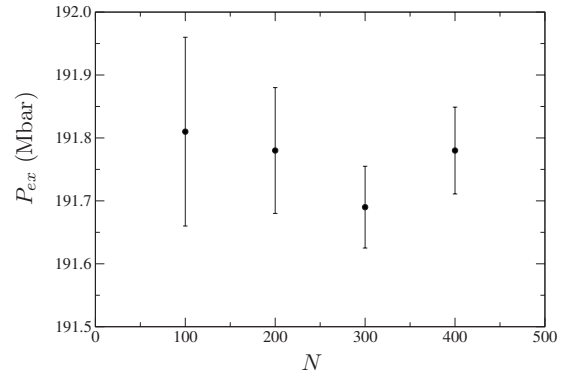


FIG. 1. TFDMD applied to a binary mixture of helium and iron at density $\rho=10$ g/cm 3 and temperature $T=50$ eV. The mole fractions are $x_{\text{Fe}}=0.01$ and $x_{\text{He}}=0.99$. Numerical convergence of excess-pressure P_{ex} with respect to the number N of atoms in the basic reference cell. Vertical bars represent standard deviations.

nucleus interactions are replaced by regularized potentials that are no longer Coulombic below a cutoff radius (one for each type of nucleus); the results found with such regularized potentials are exact if they are obtained as a limit as the cutoff radii are lowered. Nuclei are moved in the isokinetic ensemble so that temperature is exactly known. The exchange-correlation functional is chosen to be the local-density approximation of Perdew and Zunger [27]. Other details about the formalism can be found in Refs. [17,22,23].

Besides the cutoff energy and the cutoff radii, the main numerical parameters intervening in the computation of pressure are the convergence parameter for the calculation of electronic density, the time step Δt used to displace the nuclei, the number N_{time} of time steps used to compute averages over time, and the number N of nuclei in the basic reference cell. All parameters are in principle determined by a systematic search for numerical convergence of pressure within statistical error. But convenient rules of thumb for the choice of the cutoff radii, the cutoff energy, and the time step, given in Refs. [17,23], can be used. All computations have been carried out with $N_{\text{time}}=2000$.

We now describe how the statistical error, i.e., the standard deviation of pressure, is calculated. A relaxation-time τ_R for pressure, beyond which serial correlations are disrupted, is estimated from the correlation coefficient for pressure (see chapter 2 of Ref. [28]). In order to avoid serial correlations, the computed trajectory is divided into m segments, of length τ_R , of consecutive time steps. For each segment, a pressure is calculated as the average of the pressures obtained at each time step. The final result P is the average of these m pressures regarded as uncorrelated; the standard deviation σ_P of pressure is therefore taken equal to [28]

$$\sigma_P = \frac{1}{m^{1/2}} \left[\frac{1}{m-1} \sum_{\ell=1}^m (P - P_\ell)^2 \right]^{1/2}, \quad (1)$$

where P_ℓ is the average pressure obtained for segment ℓ .

In Fig. 1, we illustrate the convergence of pressure with respect to N for $x_{\text{Fe}}=0.01$; it appears that numerical convergence (within statistical error) of excess pressure is obtained

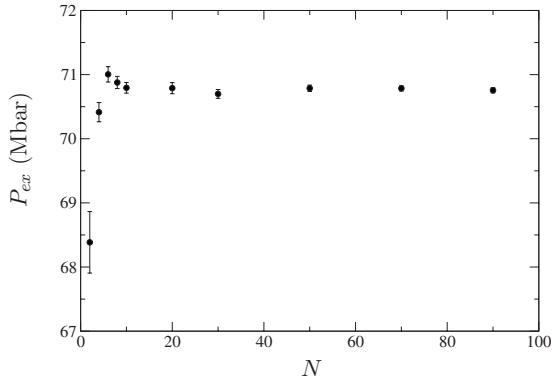


FIG. 2. TFDMD applied to an equimolar mixture of helium and iron at density $\rho=10$ g/cm³ and temperature $T=50$ eV. Numerical convergence of excess-pressure P_{ex} with respect to the number N of atoms in the basic reference cell. Vertical bars represent standard deviations.

with only one atom of iron in the reference cell. This may seem surprising but one should keep in mind that the basic reference cell is infinitely replicated so that an infinite number of atoms is in fact considered. The result obtained is nevertheless influenced by the artificial periodicity, depending on N , introduced in the description of the system. In the case $x_{\text{Fe}}=0.01$, as shown in Fig. 1, this periodicity effect cannot be distinguished from statistical uncertainty even with a single atom of Fe in the reference cell. For $x_{\text{Fe}}=0.5$, the convergence of pressure with respect to N is illustrated in Fig. 2 where it appears that $N=30$ is a suitable choice. More generally in the present work, the values of N retained for computation are such that the periodicity effect cannot be distinguished from statistical uncertainty.

B. Results

We define the excess pressure of a system by

$$P_{\text{ex}} = P - nkT, \quad (2)$$

where P is the total pressure, k is the Boltzmann constant, and n is the number of nuclei per unit volume.

With TFDMD, we calculate the excess pressure of a mixture of helium and iron at density $\rho=10$ g/cm³ and temperature $T=50$ eV for various mole fractions; the results obtained are given in Fig. 3 and in Table I. It is worthy of note that changing x_{Fe} from 0 to 0.02 lowers the excess pressure by 17%. This variation can be interpreted with the EPMR in assuming that the excess pressure of the pure phases behaves as the electronic pressure in the average atom model [29] (treated with the TFD method in the present case). With the EPMR [23] applied to a mixture of helium and iron, the partial atomic volumes v_{He} and v_{Fe} are defined by

$$x_{\text{He}}v_{\text{He}} + x_{\text{Fe}}v_{\text{Fe}} = \frac{1}{\rho}(x_{\text{He}}A_{\text{He}} + x_{\text{Fe}}A_{\text{Fe}}), \quad (3)$$

$$P_{\text{ex,He}}(v_{\text{He}}, T) = P_{\text{ex,Fe}}(v_{\text{Fe}}, T), \quad (4)$$

where A_{He} and A_{Fe} are the atomic masses of helium and iron, and $P_{\text{ex},\alpha}(v, T)$ is the excess pressure of a pure phase of α

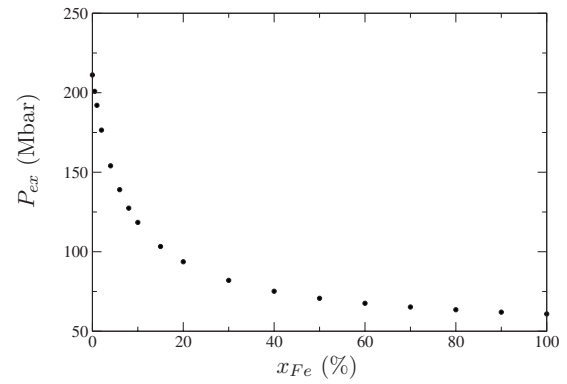


FIG. 3. TFDMD applied to a binary mixture of helium and iron at density $\rho=10$ g/cm³ and temperature $T=50$ eV. Excess-pressure P_{ex} vs the mole fraction of iron x_{Fe} . Standard deviations are too small to be visible.

with an atomic volume v at temperature T . The excess pressure of the mixture is then the common value of $P_{\text{ex,He}}$ and $P_{\text{ex,Fe}}$ in Eq. (4). It is assumed that there is a one-to-one relationship between atomic volume and pressure in Eq. (4) so that v_{He} and v_{Fe} are uniquely defined.

We first interpret the variation in excess pressure with mole fractions. The additivity of partial atomic volumes expressed by Eq. (3) can be rewritten

TABLE I. Excess pressure of a binary mixture of helium and iron, at density $\rho=10$ g/cm³ and temperature $T=50$ eV, vs the mole fractions. P_{ex} is the excess pressure calculated by a TFDMD simulation of the full mixture. $P_{\text{ex}}^{\text{EPMR}}$ is the excess pressure calculated from the pure phases with TFDMD and the EPMR.

x_{He} (%)	x_{Fe} (%)	P_{ex} (Mbar)	$P_{\text{ex}}^{\text{EPMR}}$ (Mbar)
100.0	0 0	211.17 (2.1×10^{-1})	
99.5	0.5	200.87 (1.0×10^{-1})	200.54 (1.9×10^{-1})
99.0	1.0	192.08 (1.4×10^{-1})	191.49 (1.5×10^{-1})
98.0	2.0	176.49 (2.0×10^{-1})	176.04 (1.8×10^{-1})
96.0	4.0	154.02 (1.4×10^{-1})	153.63 (1.2×10^{-1})
94.0	6.0	139.02 (1.2×10^{-1})	138.22 (1.2×10^{-1})
92.0	8.0	127.41 (1.7×10^{-1})	126.76 (1.0×10^{-1})
90.0	10.0	118.43 (1.1×10^{-1})	117.91 (1.3×10^{-1})
85.0	15.0	103.29 (1.1×10^{-1})	102.72 (1.0×10^{-1})
80.0	20.0	93.686 (9.5×10^{-2})	93.081 (8.8×10^{-2})
70.0	30.0	81.965 (9.1×10^{-2})	81.507 (5.5×10^{-2})
60.0	40.0	75.141 (6.1×10^{-2})	74.864 (7.0×10^{-2})
50.0	50.0	70.699 (6.9×10^{-2})	70.496 (4.0×10^{-2})
40.0	60.0	67.574 (5.2×10^{-2})	67.437 (4.6×10^{-2})
30.0	70.0	65.230 (4.0×10^{-2})	65.149 (4.4×10^{-2})
20.0	80.0	63.505 (4.3×10^{-2})	63.367 (5.0×10^{-2})
10.0	90.0	62.007 (2.7×10^{-2})	61.992 (5.2×10^{-2})
0.0	100.0	60.851 (3.0×10^{-2})	

$$v_{\text{He}} - \frac{A_{\text{He}}}{\rho} = \frac{x_{\text{Fe}}}{1 - x_{\text{Fe}}} \left(\frac{A_{\text{Fe}}}{\rho} - v_{\text{Fe}} \right). \quad (5)$$

Equation (5) shows that either $A_{\text{Fe}}/v_{\text{Fe}} > \rho > A_{\text{He}}/v_{\text{He}}$ or $A_{\text{Fe}}/v_{\text{Fe}} < \rho < A_{\text{He}}/v_{\text{He}}$. Since $P_{\text{ex},\alpha}$ is assumed to behave as the electronic pressure in the average atom model (treated in the TFD approach), it is determined by the superficial electronic density. In the limit of very high densities, electronic density is essentially homogeneous so that Eq. (4) implies $Z_{\text{He}}/v_{\text{He}} = Z_{\text{Fe}}/v_{\text{Fe}}$, where Z_{He} and Z_{Fe} are the atomic numbers of helium and iron. In general, with $Z_{\text{Fe}} \gg Z_{\text{He}}$, it is more difficult to ionize iron than helium so that the equality of electronic pressures, equivalent (in the average atom model) to the equality of superficial electronic densities, implies a larger average electronic density for iron, that is $Z_{\text{He}}/v_{\text{He}} < Z_{\text{Fe}}/v_{\text{Fe}}$. As the atomic numbers and atomic masses are nearly proportional, this condition implies $A_{\text{He}}/v_{\text{He}} < A_{\text{Fe}}/v_{\text{Fe}}$; we therefore find ourselves in the situation where $A_{\text{Fe}}/v_{\text{Fe}} > \rho > A_{\text{He}}/v_{\text{He}}$. As, in pure helium, v_{He} is obviously equal to A_{He}/ρ , adding iron into pure helium results in an increase of v_{He} and therefore in a decrease in the superficial electronic density and in the electronic pressure determined by Eq. (4). A similar interpretation allows to explain why adding helium into pure iron results in an increase in excess pressure.

We still have to interpret the rate of variation in excess pressure with respect to mole fractions. When iron is added into pure helium, Eq. (5) shows that the atomic volume A_{He}/ρ of pure helium differs from v_{He} by the product of a factor close to x_{Fe} (say, if $x_{\text{Fe}} \ll 1$) and of a factor on the order of A_{Fe}/ρ ; as $A_{\text{Fe}}/\rho \gg A_{\text{He}}/\rho$, the rate of variation of v_{He} , and therefore of excess pressure, with respect to x_{Fe} is large. Conversely, when helium is added into pure iron, this rate is small. It must be noted, however, that the rate of variation in excess pressure with respect to mole fractions depends on the thermodynamic conditions; indeed, in the limit of high densities where the equality of excess pressures implies $Z_{\text{He}}/v_{\text{He}} = Z_{\text{Fe}}/v_{\text{Fe}}$, Eq. (5) shows that, as $A_{\text{Fe}}/A_{\text{He}} \approx Z_{\text{Fe}}/Z_{\text{He}}$, v_{He} , and v_{Fe} remain close to A_{He}/ρ and A_{Fe}/ρ so that excess pressure varies little with mole fractions.

The excess pressures obtained by a direct simulation of the full mixture of helium and iron are the benchmark against which the excess pressures given by the EPMD are tested. The results are indicated in Table I and a graphic comparison is given in Fig. 4 (the error bars in this figure are obtained by standard differentiation with all terms positive). In all cases, the results obtained with the EPMD agree with the benchmark within statistical error.

III. USE OF VARIOUS EQUATIONS OF STATE

After testing the EPMD for a given EOS (TFDMD) and various mole fractions in Sec. II, we now test it for an equimolar mixture of helium and iron and three EOS resulting from an orbital-free approach, namely, TFMD, TFDMD, and TFDWMD. The density is $\rho = 10 \text{ g/cm}^3$ and the temperatures are $T = 2, 5, 10, 20, 50, 100, 200,$ and 500 eV . As shown in Fig. 5, this range of temperature allows us to explore gradual relative differences among the three EOS.

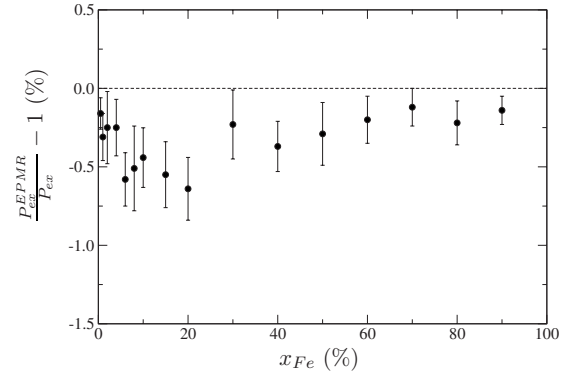


FIG. 4. TFDMD applied to a binary mixture of helium and iron with various mole fractions at density $\rho = 10 \text{ g/cm}^3$ and temperature $T = 50 \text{ eV}$. Comparison of the excess pressures calculated by the excess-pressure matching rule ($P_{\text{ex}}^{\text{EPMR}}$) with the excess pressures calculated by a direct simulation of the full mixture (P_{ex}). Vertical bars represent standard deviations.

These relative differences continuously decrease when T increases; this is because, when T gets larger at given density, the kinetic energy of electrons increases and progressively prevails over both exchange-correlation and the gradient correction.

A. Computational details

The formalism used and the choice of the numerical parameters are already presented in Sec. II A. We only address specific points here. The same exchange-correlation functional is used for TFDMD and for TFDWMD (by construction, there is none for TFMD). In the TFDWMD approach, the gradient correction of the electronic free energy is calculated according to the prescriptions of Perrot [29]. For TFDWMD, we have noted that a computation does not necessarily converge for any choice of cutoff radii; when it does, however, it converges to the excess pressure sought. We therefore choose, for TFDWMD, the largest cutoff radii that allow convergence of the excess pressure. For the three EOS, all calculations are carried out with $N_{\text{time}} = 2000$, $N = 30$ for

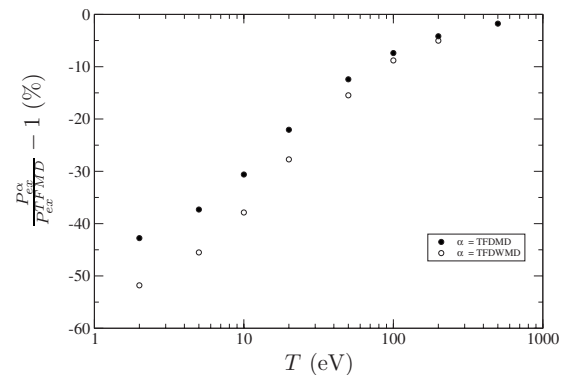


FIG. 5. Comparison of the excess-pressures P_{ex}^{α} calculated with $\alpha = \text{TFMD}$, TFDMD, and TFDWMD for an equimolar mixture of helium and iron at density $\rho = 10 \text{ g/cm}^3$ and various temperatures. Standard deviations are too small to be visible.

TABLE II. Excess pressure, P_{ex} , of an equimolar mixture of helium and iron, at density $\rho=10$ g/cm³, vs temperature T . P_{ex} is calculated by TFMD, TFDMD, or TFDWMD. “exact” indicates a simulation of the full mixture and “EPMR” indicates a simulation with the EPMR.

T (eV)	P_{ex} (Mbar)					
	TFMD		TFDMD		TFDWMD	
	exact	EPMR	exact	EPMR	exact	EPMR
2	11.97 (1×10^{-2})	11.96 (1×10^{-2})	6.85 (1×10^{-2})	6.82 (2×10^{-2})	5.77 (1×10^{-2})	5.76 (1×10^{-2})
5	14.13 (2×10^{-2})	14.09 (2×10^{-2})	8.86 (2×10^{-2})	8.83 (2×10^{-2})	7.70 (2×10^{-2})	7.65 (2×10^{-2})
10	18.88 (3×10^{-2})	18.82 (4×10^{-2})	13.11 (3×10^{-2})	13.07 (3×10^{-2})	11.73 (3×10^{-2})	11.66 (3×10^{-2})
20	31.06 (4×10^{-2})	30.86 (4×10^{-2})	24.21 (4×10^{-2})	24.00 (4×10^{-2})	22.45 (4×10^{-2})	22.24 (4×10^{-2})
50	80.72 (5×10^{-2})	80.61 (6×10^{-2})	70.70 (7×10^{-2})	70.49 (6×10^{-2})	68.23 (6×10^{-2})	67.98 (6×10^{-2})
100	192.76 (7×10^{-2})	192.48 (8×10^{-2})	178.51 (6×10^{-2})	178.21 (8×10^{-2})	175.79 (7×10^{-2})	175.64 (8×10^{-2})
200	486.94 (1×10^{-1})	486.32 (1×10^{-1})	466.56 (9×10^{-2})	465.93 (2×10^{-1})	463.65 (2×10^{-1})	462.96 (3×10^{-1})
500	1640.7 (3×10^{-1})	1639.8 (5×10^{-1})	1611.6 (3×10^{-1})	1611.1 (5×10^{-1})		

mixtures (15 atoms of helium and 15 atoms of iron) or $N=32$ for pure phases. Again, for these values of N and beyond, the effect of periodic boundary conditions cannot be distinguished from statistical uncertainty (in the thermodynamic conditions considered).

B. Results

For each EOS, we examine the validity of the EPMR in the thermodynamic conditions indicated above; again, the benchmark against which to assess a result is the excess pressure calculated by a direct simulation of the full mixture. We present the excess pressures computed in Table II and on Fig. 6 (the error bars in this figure are obtained by standard differentiation with all terms positive). TFDWMD includes more physics than TFDMD that includes more physics than TFMD; these EOS may yield significantly different excess pressures, at low temperature for instance. Whether this is the case or not, it can be seen on Fig. 6 that, for each EOS considered, all the excess pressures given by the EPMR agree within statistical error with those given by a direct simulation of the full mixture.

IV. DISCUSSION OF THE EXCESS-PRESSURE MATCHING RULE

The EPMR turns out to yield excess pressures in remarkable agreement with those obtained by direct simulation. We now consider, at given mass density and temperature, a binary mixture of elements 1 and 2, with mole fractions x_1 and x_2 , and show that the EPMR is a consequence of thermodynamic stability if it is assumed that the excess free energy can be calculated as if the system was a mixture of independent and identical (for a given type of nucleus) effective average atoms occupying the mixture volume. Then, for given mass density and temperature, there exist atomic volumes v_1 and v_2 such that

$$x_1 v_1 + x_2 v_2 = v, \quad (6)$$

$$f_{\text{ex}} = x_1 f_1(v_1, T) + x_2 f_2(v_2, T), \quad (7)$$

where v and f_{ex} are the volume and excess free energy (free energy minus ideal contribution of the nuclei) per atom of the mixture, and $f_i(v_i, T)$ is a function of v_i and T whose only parameters are the atomic number Z_i and the atomic mass A_i ($i=1$, or 2). $f_i(v_i, T)$ can be regarded as the electronic free energy in an effective average atom characterized by Z_i and A_i .

Thermodynamic stability implies that, at given v and T , v_1 and v_2 must be such that the free energy per atom, and therefore f_{ex} (the ideal contribution of the nuclei is independent of v_1 and v_2), is minimal. Minimizing f_{ex} expressed by Eq. (7) under the constraint (6) yields

$$-\left(\frac{\partial f_1}{\partial v_1}\right)_T = -\left(\frac{\partial f_2}{\partial v_2}\right)_T, \quad (8)$$

so that v_1 and v_2 are determined by Eqs. (6) and (8).

With our assumptions, $f_1(v_1, T)$ and $f_2(v_2, T)$ are the excess free energies of the pure phases 1 and 2 with atomic volumes v_1 and v_2 . Equation (8) therefore expresses the equality of the excess pressures of the pure elements. Finally, v_1 and v_2 are determined by the prescriptions of the EPMR. Once v_1 and v_2 are determined, the excess free energy is calculated with Eq. (7) and the excess-pressure P_{ex} is equal to

$$P_{\text{ex}} = -\left(\frac{\partial f_{\text{ex}}}{\partial v}\right)_{T, x_1, x_2}, \quad (9)$$

that is, with Eqs. (7) and (8),

$$P_{\text{ex}} = -\left(\frac{\partial f_1}{\partial v_1}\right)_T \left[x_1 \left(\frac{\partial v_1}{\partial v}\right)_{T, x_1, x_2} + x_2 \left(\frac{\partial v_2}{\partial v}\right)_{T, x_1, x_2} \right], \quad (10)$$

or, since v_1 and v_2 verify Eq. (6),

$$P_{\text{ex}} = -\left(\frac{\partial f_1}{\partial v_1}\right)_T. \quad (11)$$

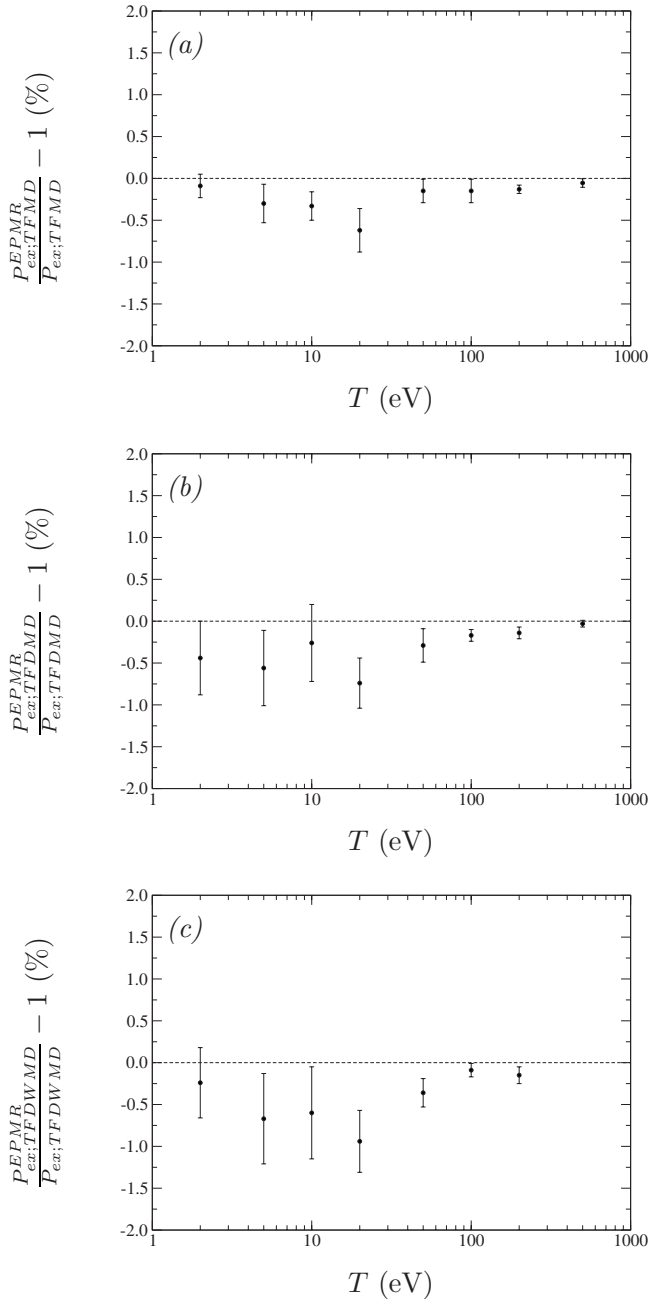


FIG. 6. Equimolar mixture of helium and iron at density $\rho = 10 \text{ g/cm}^3$ and various temperatures. The equation of state is obtained with (a) $\alpha = \text{TFMD}$, (b) $\alpha = \text{TFDMD}$, and (c) $\alpha = \text{TFDWMD}$. Comparison of the excess-pressures $P_{ex,\alpha}^{\text{EPMR}}$ calculated by the excess-pressure matching rule with the excess-pressures $P_{ex,\alpha}$ calculated by a direct simulation of the full mixture. Vertical bars represent standard deviations.

P_{ex} is the common value of the excess pressures of the pure phases in Eq. (8) with v_1 and v_2 determined by Eqs. (6) and (8). Therefore, for a binary mixture of independent and identical effective average atoms, the EPMD yields the exact

pressure. The above derivation can be easily extended to a mixture with more than two components. More [30] proposes the EPMD for a mixture of average atoms treated with the TF method; the above derivation indicates that the EPMD can also be applied if the average atoms are treated with any other method (like TFD or TFDW for instance).

The success of the EPMD can therefore be explained if, for its thermodynamic properties, the system considered behaves as a mixture of independent and identical effective average atoms. One is tempted to conjecture that this is the case when the excess pressures of the pure phases are close to the electronic pressures obtained with the average atom model treated with the TF, TFD, or TFDW approach [29]. But the EPMD is also successful when this is not so; we can then only note that the system behaves as a mixture of independent effective average atoms having the EOS of the pure phases.

Finally, it can be noted that the law of volume additivity, Eq. (6), combined with the equality of the average electronic densities for pure elements 1 and 2, gives the same partial densities as those of the mixing rule of Hansen *et al.* [2]. Thus, when the equality of excess pressures is equivalent to the equality of average electronic densities, the EPMD becomes equivalent to that mixing rule; this occurs at very high densities, for instance. The EPMD can therefore be regarded as an extension of the mixing rule of Hansen *et al.*

V. CONCLUSION

We have applied three types of orbital-free molecular dynamics simulations, namely, TFMD, TFDMD, and TFDWMD, to the calculation of pressure in a mixture of helium and iron. We have tested a mixing rule based on excess-pressure matching, called EPMD, on this mixture for various mole fractions and for the three approaches. For all the cases considered, this mixing rule yields, within statistical error, the pressure obtained by a direct simulation of the full mixture. This study, performed on an asymmetric mixture ($Z_{\text{Fe}} \gg Z_{\text{He}}$), complements that in Ref. [23], where only a variation in the thermodynamic conditions is explored, and confirms the remarkable robustness of the EPMD.

In relation to TFMD, TFDMD includes exchange-correlation (assumed to be known) and TFDWMD includes both exchange-correlation and the gradient correction of the electronic free energy. The success of the EPMD in thermodynamic conditions where these three approaches, with various physical contents, give significantly different pressures, leads us to suggest the use of the EPMD with QMD (in which the electronic free energy is calculated with a full quantum treatment).

It is possible to find a physical basis for the EPMD. We have shown that it is a consequence of thermodynamic stability if the system is assumed to behave thermodynamically as a mixture of independent and identical effective average atoms whose EOS is that of the pure element.

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