Physics Letters A 395 (2021) 127207

Contents lists available at ScienceDirect

Physics Letters A

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Concentration discontinuity of alkalies at high pressures

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ARTICLE INFO

Article history:
Received 13 January 2021
Received in revised form 4 February 2021
Accepted 5 February 2021
Available online 8 February 2021
Communicated by A. Eisfeld

Keywords:
Equation of state
Dense matter
Thomas-Fermi theory

ABSTRACT

An equation of state of a gas of electrons of dense matter at high pressure is proposed with basis on the Thomas-Fermi theory by taking into account a modification of an adiabatic relation. The formulation is applied to describe the behavior of the concentrations of alkali metals subjected to pressure excesses up to 100,000 kgf/cm^2. The outcomes suggest a mechanism to explain the observed concentration discontinuity of Cesium. Also predicted are the values of the pressure excesses at which the concentrations of the remaining alkalies shall exhibit the same behavior as that of Cesium. The results may be of interest in the search for exoplanets, development of new materials, geologic metamorphism, among other related lines of investigation.

1. Introduction

The equation of state of a given substance is generally expressed in terms of its pressure, volume, and temperature. Information on the total energy (kinetic plus potential energies) of electrons provides the description of a set of microscopic states of the atom. Those microscopic states determine the macroscopic state of the system as a whole. In most cases, the high computational complexity of the self-consistent field theory of Hartree-Fock makes it hard to apply in the investigation of atomic behavior [1]. In order to circumvent those difficulties, one often makes use of the much simpler semi-classical Thomas-Fermi model, which introduces a statistical potential that depends only on the atomic number and distance from the central nucleus [2]. As a result, information on alteration of the atomic boundary may be obtained by modifying the external conditions. This means that the Thomas-Fermi method can be used to find the atomic behavior under high pressure.

An important development was achieved by the numerical treatment of Feynman, Metropolis, and Teller [3]: exchange effects were included in the Thomas-Fermi framework. Later on, Salpeter extended the formulation to investigate the behavior of dense matter in nuclear astrophysics [4]. However, it was soon realized that the numerically computed zero-pressure densities were smaller than the empirical ones [5]. Such a finding suggested that long-range interactions between electrons should be included in the numerical analysis in order to obtain a better agreement with experimental data. Since then, that conjecture has deeply influenced the numerical investigation of the equation of state of dense matter in plasma physics [6], astrophysics [7], geophysics [8], condensed matter physics [9], high pressure physics [10], among other related lines of research.

However, the more general problem of determining a statistical model of matter, suitable for electron-nuclear systems (atoms, solids, plasmas etc.), remains an open issue. As noted by Kirzhnits, Lozovik, and Shpatakovskaya [11], difficulties arise due to shell effects in the thermodynamics of highly-compressed matter that lead to the occurrence of first-order phase transitions associated with the "squeezing-out" of discrete shells into the continuous spectrum. As a consequence, the behavior of the Thomas-Fermi equation of state in the limits of hot and cold matter would heavily rely on the degree of ionization of the substance, with and without the exchange correction [12]. Recent numerical models, including ab initio cold curve under compression, isotherm, Hugoniot, off-Hugoniot, and sound velocity data illustrate the huge difficulty in validating the Thomas-Fermi equation of state in high temperature and pressure limits [13]. The situation only gets worse if explicit effects due to density-dependent magnetic fields are included to find out relativistic stable configurations in astrophysics [14].

Bridgman was the first to develop an apparatus that was able to generate pressure excesses up to 100,000 kgf/cm^2 (10 GPa or 100,000 atm) [15]. With that device, he obtained the volumes of the five alkali metals, Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), and Cesium (Cs), as functions of the pressure excesses. A discontinuity in the volume of Cs was reported at a critical high pressure excess. The result attracted immediate attention

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https://doi.org/10.1016/j.physleta.2021.127207
0375-9601/

[16–18] and remains influential up to date [19–22]. In this work, we propose an equation of state of a gas of electrons of dense matter at high pressure with basis on the Thomas-Fermi theory by taking into account a modification of an adiabatic relation. Our formulation, not only, explains the aforementioned Bridgman's observation for Cs, as well as predicts the occurrence of the same behavior for the remaining alkalies.

2. Alkalies at high pressures

Since the beginning of quantum mechanics, alkali metals have been viewed as the prototype of a nearly free electron system [23, 24]. Actually, the weak interaction between their stiffly screened atomic core and single s valence electron provides a much delocalized conduction band, thereby leading to a high electric conductivity at room pressures [25]. However, at much higher pressures, unexpected behaviors ensue, such as enhanced resistivity in Rb and Cs [26], superconductivity in Li at relatively high temperatures [27], and metal-semiconductor-metal, and metal-insulator transitions in Li, and Na, respectively [28].

In Bridgman's experiment, the pressure excess on the alkali samples may be defined as the surplus of the bulk pressure P over the interface pressure P_∞ (the choice of the index ∞ shall soon be clear). In order to establish an accurate relation between the volume and electronic concentration ν (number of electrons per unit volume) of the samples, one needs a detailed microscopic theory of matter. A thorough model describing the effect of a dense charged environment on a single ion might reflect the lowering of its continuum level [29]. The resulting energy shift should modify the ionization balance in the system, which determines its equation of state [30]. However, in spite of some recent progress, experimental validation of models for continuum lowering and ionization potential depression often meets huge difficulties in both creating well defined dense systems [31] and devising reliable diagnostics [32]. In this work we do not attempt to rely on any microscopic theory of matter, but merely assume that the electronic concentration ν may be univocally determined by the reciprocal volume of the samples in Bridgman's experiment. As we will show, such a simple hypothesis will be fully justified by our outcomes.

A discontinuity in the concentration of Cs was observed by Bridgman at the pressure excess $P - P_\infty \sim (40 - 50)\, P_0$, where $P_0 = 1{,}000\ \mathrm{kgf/cm^2}$ [15]. In the next section, we derive an equation of state which both explains such a concentration discontinuity for Cs, as well as predicts the same behavior for the remaining alkali metals.

3. Equation of state

Let us consider a material medium composed of particles with mass μ, charge q, and concentration ν. In the absence of a magnetic field, the time evolution of the flow $\vec{u}$ of the particles is determined by the gradients of the electrostatic potential Φ and isotropic pressure P in the medium through the equation of motion (Euler equation in dense ideal inviscid matter follows from a variational extreme condition on the free energy of the system [33–35])

$$\mu\left[\frac{\partial \vec{u}}{\partial t} + \left(\vec{u}\cdot\nabla\right)\vec{u}\right] = -q\nabla\Phi - \frac{\nabla P}{\nu}. \tag{1}$$

On the assumption of an adiabatic equation of state, the pressure gradient is described in terms of the concentration gradient by

$$\nabla P = \gamma k_\mathrm{B}\Theta\nabla\nu, \tag{2}$$

where γ is the adiabatic index (the ratio of specific heats at constant pressure to volume), k_B is the Boltzmann constant and Θ is the constant temperature. It is a well known fact, especially in plasma physics, that, for $\gamma = 1$ (typically, an isothermal electron gas), the stationary state of equilibrium of the system (the left hand side of eq. (1) vanishes) recovers the Boltzmann relation [36]

$$\nu = \nu_\infty \exp\left(-\frac{q\Phi}{k_\mathrm{B}\Theta}\right), \tag{3}$$

where ν_∞ is the concentration of particles at infinity (the magnitude of the electrostatic potential falls off very rapidly with the distance from the charges in a plasma). Inspired by that remark, in this work, we develop an argument along the following lines.

First, we recall that, in condensed matter physics, plasmons (the quanta of plasma oscillations) are frequently described by assuming that an electron gas satisfies the Thomas-Fermi relation [37]

$$\nu = \nu_\infty\left(1 - \frac{q\Phi}{\mathcal{E}_\mathrm{F}}\right)^{3/2}, \tag{4}$$

where $\mathcal{E}_\mathrm{F}$ is the Fermi energy of the system,

$$\mathcal{E}_\mathrm{F} = \frac{\hbar^2\kappa_\mathrm{F}^2}{2\mu}, \tag{5}$$

with $\hbar$ denoting the normalized Planck constant (defined as $\hbar = h/(2\pi)$ in terms of the Planck constant h) and κ_F denoting the Fermi wave number,

$$\kappa_\mathrm{F} = \left(3\pi^2\frac{\mathcal{N}}{\mathcal{V}}\right)^{1/3}, \tag{6}$$

where $\mathcal{N}$ is the total number of particles occupying the volume $\mathcal{V}$.

Second, our main hypothesis: we assume that the adiabatic equation of state does not hold any longer and that the pressure gradient is now determined by

$$\nabla P = k_\mathrm{B}\Theta\nabla\left(\gamma\,\nu\right), \tag{7}$$

where $\gamma = \gamma\left(\nu\right)$ is a function of the concentration of particles in the medium, no longer the adiabatic index.

Third, for a stationary state of equilibrium of the system, we substitute eq. (7) in eq. (1), with account of eq. (4), to get

$$\nabla\left(\frac{\gamma}{\gamma_\infty}\frac{\nu}{\nu_\infty}\right) = \left(\frac{\nu}{\nu_\infty}\right)^{2/3}\nabla\left(\frac{\nu}{\nu_\infty}\right), \tag{8}$$

where we have defined the quantity

$$\gamma_\infty = \frac{2}{3}\frac{\mathcal{E}_\mathrm{F}}{k_\mathrm{B}\Theta}. \tag{9}$$

Integration of eq. (8) yields

$$\frac{\gamma}{\gamma_\infty} = \frac{2}{5}\frac{\nu_\infty}{\nu} + \frac{3}{5}\left(\frac{\nu}{\nu_\infty}\right)^{2/3}. \tag{10}$$

As one may easily check, γ_∞ is the minimum value of γ. Of course, γ_∞ shall be greater than unity. Actually, if $\gamma_\infty = 1$, the system is a Boltzmann gas, not a Thomas-Fermi gas.

Fourth, we substitute eq. (10) in eq. (7) and, subsequently, integrate the result to obtain the equation of state of the gas of charged particles,

$$P - P_\infty = \frac{3}{5}\left[\left(\frac{\nu}{\nu_\infty}\right)^{5/3} - 1\right]P_\infty, \tag{11}$$

where we have defined the pressure

$$P_\infty = \frac{2}{3}\mathcal{E}_\mathrm{F}\nu_\infty \tag{12}$$

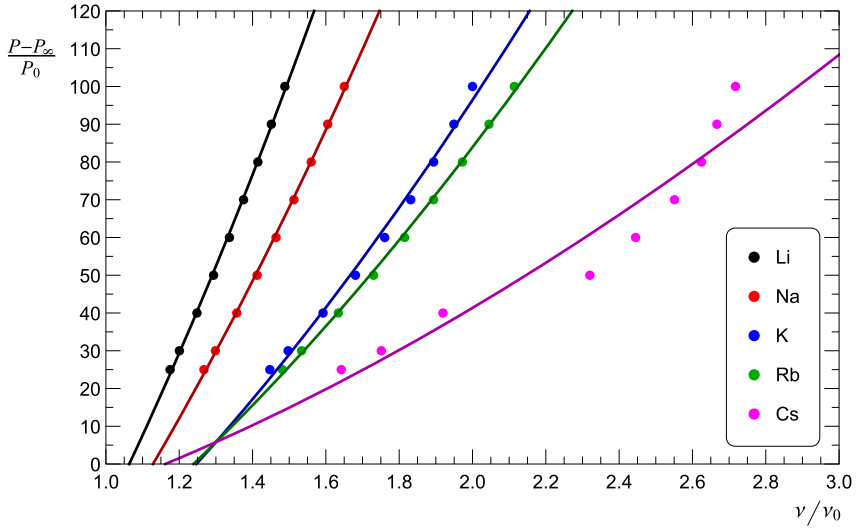

Fig. 1. The curves fitting the distribution of points in Bridgman's experiment [15] as given by expressing the pressure excess in the alkalies by eq. (11) and applying the regression method of least squares. For all metals, the coefficient of determination $r^2 = 0.99$, except for Cs, for which $r^2 = 0.98$.

of the gas at infinity.

As previously observed, the magnitude of the electrostatic potential falls off very rapidly with the distance from the charges in a conducting gas. This means that we may regard the pressure at infinity as being approximately equal to the pressure at the interface of the gas with the outer medium. In the sequel, we apply our theory to explain the aforementioned Bridgman's experimental results on the concentration discontinuity of Cs, as well as to predict the occurrence of the same behavior with the remaining alkali metals.

A brief note on the limitations of our main hypothesis, the replacement of eq. (2) with eq. (7), is in order now. From eq. (10), we may compute the total derivative of γ/γ_∞ with respect to ν/ν_∞,

$$\left(\frac{\gamma}{\gamma_\infty}\right)' = -\frac{2}{5}\left(\frac{\nu_\infty}{\nu}\right)^2 + \frac{2}{5}\left(\frac{\nu_\infty}{\nu}\right)^{1/3}. \tag{13}$$

Multiplying both hand sides of eq. (13) through ν/ν_∞, we get

$$\frac{\nu}{\nu_\infty}\left(\frac{\gamma}{\gamma_\infty}\right)' = -\frac{2}{5}\frac{\nu_\infty}{\nu} + \frac{2}{5}\left(\frac{\nu}{\nu_\infty}\right)^{2/3}. \tag{14}$$

Subtracting eq. (14) from eq. (10), we obtain

$$\frac{\gamma}{\gamma_\infty} - \frac{\nu}{\nu_\infty}\left(\frac{\gamma}{\gamma_\infty}\right)' = \frac{4}{5}\frac{\nu_\infty}{\nu} + \frac{1}{5}\left(\frac{\nu}{\nu_\infty}\right)^{2/3}. \tag{15}$$

Our argument is that eq. (2) shall be replaced with eq. (7) whenever both terms on the left hand side of eq. (15) become of the same order of magnitude. As one may easily check, eq. (15) achieves its minimum value, ~ 0.683, at $\nu \sim 2.93\ \nu_\infty$. It would be interesting if such an estimate could be tested in the laboratory. That could clarify, at least on experimental grounds, the transition from the adiabatic regime, eq. (2), to the non-adiabatic one, eq. (7). However, we realize that a more fundamental justification of our phenomenological hypothesis is beyond the scope of this work.

4. Concentration discontinuity

Let us describe the pressure excess in the alkali samples by eq. (11) and, subsequently, apply the regression method of least squares to determine the best curves that fit the distribution of points in Bridgman's experiment [15]. The results are shown in Fig. 1. As a by-product of the application of the method of least squares, the variables of state P_∞ and ν_∞ in eq. (11) may be also obtained. The values are shown in Table 1.

Table 1
The variables of state P_∞ and ν_∞ in eq. (11), as a by-product of the application of the method of least squares. The numerical values confirm the observed concentration discontinuity of Cs and predict the same phenomenon for the remaining alkalies.

Variables of state	Li	Na	K	Rb	Cs
P_∞/P_0	220	187	134	114	46.8
ν_∞/ν_0	1.06	1.13	1.25	1.24	1.16

To explain concentration discontinuities of alkalies at high pressures, we propose the following mechanism. As the pressure excess $P - P_\infty$, in the sample, increases, the pressure P, in the bulk sample, also increases, in such a way that the pressure P_∞, at the interface of the sample with the outer medium, remains constant. When $P - P_\infty$ achieves the value P_∞, the bulk pressure P ceases to increase, because then the interface pressure remains momentarily constant. However, $P - P_\infty$ continues to increase, which implies a sudden increase in P, in order to prevent a change in P_∞, the interface pressure. This is the above referred steep increase in the bulk pressure P which provokes the concentration discontinuity of the alkalies.

The proposed mechanism is confirmed by the numerical results. In the last column of Table 1, we see that $P_\infty = 46.8\ P_0$, and $\nu_\infty = 1.16\ \nu_0$ for Cesium. Consistently, in Fig. 1, the concentration discontinuity of Cesium occurs at $P - P_\infty \sim 46.8\ P_0$ (which lies in the interval $(40 - 50)\ P_0$, as previously observed by Bridgman [15]), and the corresponding curve crosses the horizontal axis at $\nu \sim 1.16\ \nu_0$. According to Table 1, the value of the interface pressure P_∞ is larger than $100\ P_0$ for the remaining alkalies. This is the reason why no concentration discontinuity can be observed in Fig. 1 for those metals.

One realizes that the data fitting for the pressure excess $P - P_\infty$ on Cesium, in Fig. 1 would work better if it covered two independent groups of points: those (1) below, and (2) above the concentration discontinuity. However, in this case, it should be noted that one would lose the proper information on the critical concentration. Actually, in this situation, the pressure P_∞, and concentration ν_∞, at the interface of the samples with the outer medium, would be different for the above referred independent groups of points.

5. Conclusion

In this work, we have proposed an equation of state of a gas of electrons of dense matter at high pressure with basis on the Thomas-Fermi theory by taking into account a modification of an adiabatic relation. Our formulation has been applied to describe the behavior of the concentrations of alkali metals subjected to pressure excesses up to 100,000 kgf/cm^2. In order to validate our results, use has been made of the regression method of least squares to obtain the best curves that fit the available experimental data. Our outcomes have suggested a mechanism to explain the observed concentration discontinuity of Cesium. We have also predicted the values of the pressure excesses at which the concentrations of the remaining alkalies shall exhibit the same behavior as that of Cesium.

Several structures and properties of alkali metals have been extensively examined at high pressures, both experimentally and theoretically [38–42]. Even so, to the best of our knowledge, a specific study of the behavior of the density of the alkalies at high pressures, as comprehensive as that performed by Bridgman [15], has not been pursued in recent years. Therefore, we strongly encourage the experimentalists to try and test our theory. More generally, our results may be of interest in the search for exoplanets [43,44], development of new materials [45,46], geologic metamorphism [47,48], among other related lines of investigation.

Regarding the limitations of our formulation, we emphasize that we do not claim that the pressure P_∞, at the interface of the alkali samples with the outer medium, remains exactly constant while the inner gas pressure, P, varies. What we argue is that our theory is valid as long as P_∞ changes sufficiently slowly with a change of P, such that eq. (11) be satisfied. As we have remarked at the end of the preceding section, P_∞ and ν_∞ will be actually different for the independent groups of points below and above the critical concentration of Cesium.

Finally, it should be noticed that, by following an approach where the Thomas-Fermi equilibrium is replaced with a Lane-Emden equilibrium, an equation of state has been obtained for alkali metals in the limit of very low pressures [49]. A contrast of that formulation with ours may inspire the achievement of a more satisfactory theory in the future.

CRediT authorship contribution statement

Francisco Eugenio Mendonça da Silveira: Conceptualization, Methodology, Investigation, Writing – Original draft preparation. **Rodrigo Silveira Camargo:** Plots, Tables. **Iberê Luiz Caldas:** Conceptualization, Methodology, Investigation, Writing – Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

FEMS is partially supported by São Paulo Research Foundation (FAPESP), under grants numbers 17/20192-2 and 18/03211-6. ILC is partially supported by National Council for Scientific and Technological Development (CNPq).

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