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GENERATOR STUDIES

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EQUATIONS OF STATE OF ARGON FOR SELF-EXCITED MHD GENERATOR STUDIES*

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ABSTRACT

We have constructed a state-of-the-art equation of state (EOS) for argon covering the temperature density range attainable by currently proposed self-excited MHD generators. The EOS for conditions in the flow channel was obtained primarily by a non-ideal plasma code (ACTEX) that is based on a many body activity expansion. For conditions in the driver chamber the EOS was primarily obtained from a fluid code (HDFP) that calculates the fluid properties from perturbation theory based on the insulator interatomic pair potential but including electronic excitations. The results are in agreement with several sets of experimental data in the 0.6 - 91 GPa pressure range.

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I. INTRODUCTION

Non-ideal plasmas occur in several devices currently being studied and/or developed and a full understanding of this state of matter over a very wide range of physical conditions is important in feasibility and design studies. In the present work we are concerned with the EOS of argon which is one of the prime candidate materials for use as the working fluid in a class of self excited, explosively driven, MHD generators.

A model calculation of the EOS of argon based on the Debye-Huckel theory of weakly coupled (slightly non-ideal) plasmas has already been carried out by D. Mukherjee.¹ The purpose of Mukherjee's work was twofold: 1) to generate on a short time scale a useable EOS data base for design studies; and 2) to delineate regions where simple model calculations are not sufficiently realistic to be trusted in the design studies. The present work compliments the previous study in that it works from a more rigorous physical basis and closely matches experimental data in the very non-ideal range. Thus, a reliable estimate of the errors in the model calculations can be obtained. The present calculations should, of course, be used in future design studies that utilize argon, but, guidelines developed from a comparison of the two studies can be used to rapidly generate EOS data bases to evaluate other candidate materials. The purpose of this report is to present our results for rapid dissemination.

II. THEORETICAL METHOD

To properly treat the temperature, density region considered here, i.e., $\rho \leq 3.16 \text{ g/cm}^3$, $1 \text{ eV} < T < 30 \text{ eV}$, we have used two different physical approaches. In the region where the Debye length,

$$\lambda_D = (kT/4\pi e^2 \sum_i \rho_i Z_i^2)^{1/2}, \quad i = \text{charged species type},$$

and/or the ion sphere radius,

$$a = (3/4\pi \rho_{\text{ions}})^{1/3}, \quad \rho_{\text{ions}} = \text{number density of heavy ions},$$

is several times larger than the ionic radii we have utilized a many body activity expansion. In the low temperature high density region where the ion sphere radius is the same size as the core radius, such that repulsions become dominant, we have utilized a high density fluid perturbation theory approach modified to treat small degrees of ionization, i.e., semi-conducting fluids. In principle the many body activity expansion procedure can treat the circumstance that λ_D is the same size as the ionic radii, i.e., the phenomenon of pressure ionization. However, when this occurs, the electron-ion interaction parameter is large and a careful treatment of these interactions beyond $5/2$ power terms is required. This is not a limitation in the present work, as pressure ionization is only starting to occur below 25 eV for the highest density considered here.

a) Activity Expansion Method (ACTEX Code)

The ACTEX (ACTivity EXpansion) code²⁻⁴ treats ionization equilibrium in the presence of plasma coupling and allows for the fact that the heavy ions may be strongly coupled (liquid-like) while the electrons are only moderately coupled (gas-like). ACTEX theory starts with a many-body perturbation expansion of the grand partition function. Three distinct renormalizations are required to handle the general problem, accounting for (1) formation of electron-nucleus composites; (2) coupling of the composite particles to the plasma; and (3) strong coupling of heavy ions having charge $Z \gg 1$.

To carry out numerical calculations, it is necessary to obtain multi-electron bound and scattering states. This is accomplished through the introduction of effective pair potentials. These potentials are composed of a long-range term, plus exponentially screened Coulomb terms for each shell of core electrons. The parameters in the potential are determined from experimental spectroscopic data, and plasma-screening effects are then added to the long-range tail.

Three parameters arise naturally in the perturbation expansion in the activity. The interactions parameter,

$$\Lambda_{ij} = Z_i Z_j e^2 / kT \lambda_D,$$

the diffractions parameter,

$$\gamma_{ij} = \lambda_{ij} / \lambda_D,$$

and the degeneracy parameter,

$$\theta_e = e^{\alpha_e}$$

where,

$$\lambda_{ij} = \text{thermal deBroglie wavelength} = \hbar / \sqrt{2\mu_{ij}kT}$$

$$\mu_{ij} = \text{reduced mass of partials } ij$$

$$\alpha_e = \mu_e/kT$$

$$\mu_e = \text{electron chemical potential}$$

The perturbation expansion is most useful when these parameters are of order unity or smaller and the ACTEX code, using steps (1) and (2) described above, is accordingly only carried through terms of order 5/2 in the activity. Step three goes beyond the 5/2 power terms for the strongly interacting multi-charged heavy-ions, while retaining restrictions on the electron-ion terms. In the temperature density range considered here for argon the interaction parameter in some cases exceeds 10, but the diffraction and degeneracy parameters are always less than 1 and these effects only make small corrections to the EOS.

b) High Density Fluid Perturbations Theory (HDFP code)

The High Density Fluid Perturbation Theory code was developed to provide an analytic tool for studying liquid shock wave data up into the megabar, several electron volts range. This theory has been applied to argon⁵ and xenon⁶ as well as a number of molecular liquids.⁷ The theory treats the nuclear motion and electronic excitation independently. Electron thermal properties are computed using a semiconductor theory in which the energy necessary to excite electrons thermally from the valence to conduction band (the band gap) is computed

from electron band theory. This is computed as a function of density. The variation of the band gap with the degree of thermal excitation is estimated from experimental data on shifts in the excitation levels of the partially ionized atom. The properties of the fluid (the nuclear motion) are determined from fluid perturbation theory using the core-core intermolecular potential obtained from an analysis of the argon liquid shock data to 0.9 mbars. As the temperature increases, and electrons are excited into the conduction band, it is assumed that the core-core interaction remains unaffected but that the ions interact as in a one component plasma fluid with a free electron background.

III. EOS ASSEMBLY

The EOS was constructed from the data base shown in Fig. 1. Data points lying to the left of the cut were calculated with the ACTEX code and data points lying to the right of the cut were calculated with the HDFF code. Both theories have been stretched to the edge of their validity in the vicinity of the cut, consequently, the results here show a slight mismatch. Following standard practice we have cut back both data sets as shown and filled in the empty locations using a cubic spline interpolation. The final data base in density, energy space is shown in Fig. 2. Points are not plotted in the filled region to display how the two sets of data are matched up along isotherms. The interpolation is smooth indicating that the two sets of data are reasonably compatible. The 1 - 3 eV isotherms match up better than the higher temperature, very non-ideal plasma (see Fig. 1) isotherms. Neither code is particularly applicable in the high density intermediate temperature range and additional theoretical effort is needed.

Figure 3 is a three dimensional plot of selected isochores and isotherms vs PV/N_0kT from the final database. The density dependence of the plateaus separating the L and M shells and the K and L shells is clearly visible along the 28 eV and 255 eV isotherms, respectively. Ar-Ar, Ar^+-Ar , and Ar^+-Ar^+ repulsions are responsible for the increase of PV/N_0kT at low temperature and high density. To show the data in a slightly different perspective, Fig. 4 gives an isothermal plot of PV/N_0kT vs density and Fig. 5 gives an isothermal plot of energy vs density.

As stated earlier the most important plasma parameter for present purposes is the interaction parameter, gamma. For plotting purposes it is useful to define an average gamma,

$$\Lambda = \langle z^2 \rangle e^2 / kT\lambda_D$$

where

$$\langle z^2 \rangle = \sum_i z_i^2 \rho_i / \sum_i \rho_i ,$$

is the average of z^2 for all species. We have included neutrals in Λ to more accurately reflect the importance of non-ideality in the EOS, i.e., errors resulting from use of a low order theory to treat slightly ionized, but very non-ideal plasmas, do not substantially effect the total pressures and energies.

Figures 6 and 7 show gamma contours in density-temperature space and pressure-energy space, respectively. The density-temperature space to the left of the shaded area of Fig. 6 is a region of slight non-ideality. The shaded area is a region of moderate non-ideality and the right most area is a highly non-ideal region. In the vicinity of 1 eV and 1 gm/cm³, due to the small amount of ionization, argon is more nearly a strongly repulsive insulating fluid, such that the interaction parameter is not a relevant measure of non-ideality. From about 2 eV to 20 eV coulomb and core repulsions are both large and coupled so that neither code described here is strictly valid. Above 20 eV the ions are sufficiently highly ionized that core repulsions become a secondary effect. At densities beyond those considered here even the

higher temperature isotherms would turn upward due to pressure ionization. At still higher densities they will turn up even more due to electron degeneracy.

A useful chart for determining the physical condition in a explosively driven MHD generator is a display of enthalpy contours in pressure, energy, space. This is shown in Fig. 8 where the solid lines are enthalpy contours and the dashed lines are isochores. Also plotted in Fig. 8 is the experimental gas-gun data of Ref. 3. This data is very accurate with errors in E , and p of approximately 1% and errors in volume of order 2%. Theoretical enthalpy contours were calculated using fluid perturbation theory for precisely the experimental values, so that, differences will show up as ΔE offsets of the points from the lines. As indicated by Fig. 8 these offsets are very small and similar to the uncertainties in the experiments (see Ref. 5). Figure 9 displays isotherms in pressure-energy space.

Only sparing efforts have been published that compare theory and experiment in the non-ideal plasma region. However several sets of gas-compression shock experiments, with final states in the region, have been carried out for argon.

(1) Shock Tube Experiments^{8,9}

Starting from initial pressures ranging from 0.1 - 5 MPa, slightly ionized dense gas final state ($T \sim 20\,000^\circ\text{K}$) were obtained. Due to the large compression ratios the error bars on these experiments are considerably larger than those obtained in Ref. 3 using liquid Ar as the initial state. Accepting the measured P and H values and assigning all the errors to V , these researchers estimate their volume errors (depending on the compression ratio) to be in the range 7 - 20%. In view

of the low ionization state attained in these experiments, only gross details of the Coulomb interaction can be evaluated. However, the densities are high enough that the effect of core repulsions is evident.

(2) High Explosive Shock Experiments¹⁰

Starting with initial gas pressures of only 0.08 MPa, final states having greater ionization but lower densities than those attained in shock tubes, were generated. The error bars on these experiments are estimated at ± 1 for pressure and $\pm 5\%$ for volume.

The ACTEX code is designed to calculate isochores so that a comparison of pressures for the experimentally measured values of V and H is a convenient way to match theory with experiment. The error bars on pressure at fixed V and H are similar to the error bars on V at fixed P and H . Table 1 gives a comparison between theory and the experimental results of Ref. 8 and Ref. 10. The theoretical data comes from ACTEX (A) except for points at $V = 3.01$ and $2.88 \text{ cm}^3/\text{g}$, which come from the fluid perturbation code (H). Subscripts e and t refer to experiment and theory, respectively. Ratios of P_t/P_e are given in the last column and it is seen that theory and experiment agree to within estimated experimental errors except for a couple of points in atomic gas states. The mean differences are small. Temperatures compare similar to estimated experimental uncertainties (5-10%).

Figure 8 shows that at low pressure dH/dE is slightly positive. At high pressure and low temperatures the slope becomes somewhat more positive due primarily to core repulsions. Fig. 10 gives isotherms in density, H/E space, showing that they move to lower values of H/E with increasing temperature until it reaches the value $H/E = 1.2$ near $T = 10.3 \text{ eV}$. For still higher temperature H/E moves up slowly reaching the maximum value $5/3$.

For hydrocode utilizations we have used the VITUS code¹¹ to obtain a 28 term least squares fit to $P(\rho, E)$ having an RMS error of 2.7%. Also given in Table 1 are theoretical values of $VAP/N_0 kT$ and the molar concentration of electrons N_e/N_0 . For an ideal gas these two numbers are the same so that differences arise from non-ideality. The interesting thing to notice is that these differences are considerably smaller than those given by a Debye model and in fact $VAP/N_0 kT$ exceeds N_e/N_0 in some cases due to core repulsion.

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TABLE 1. COMPARISON OF THEORY AND EXPERIMENT

EXPERIMENT				THEORY Constant H, V					
V cm^3/g	$P \cdot 10^{-2}$ MPa	H MJ/Kg	$T \cdot 10^{-3}$ K	$P \cdot 10^{-2}$ MPa	$T \cdot 10^{-3}$ K	$\frac{V \Delta P}{N_0 K T}$	$\frac{N_e}{H_0}$	Λ	$\frac{P_{\text{theory}}}{P_{\text{exp}}}$
<u>Reference 8</u>									
85.8	0.62	21.6		0.57	19.5	0.214	0.27	0.37	0.92
48.4	0.29	3.70		0.29	6.6	0.012	0.00	0	1.00
28.3	1.71	19.9	18.0	1.70	19.9	0.194	0.23	0.84	0.99
25.5	1.79	13.2	19.7	1.58	17.7	0.089	0.10	0.44	0.88
9.60	1.02	2.79		1.18	5.0	0.086	0.00	0	1.16
6.69	6.59	15.6	18.7	6.76	19.1	0.137	0.13	0.67	1.03
4.83	9.92	14.7	19.0	9.51	18.7	0.181	0.11	0.76	0.96
3.01	4.84	3.83		5.60	6.7	0.208	0	0	1.16
2.88	18.0	13.7	18.5	17.0	19.5	0.203	0.06	0.98	0.94
<u>Reference 10</u>									
166.8	0.154	0.0725		0.158	12.4	0.19	0.017	0.01	1.03
153.7	0.168	0.0808		0.185	13.1	0.027	0.027	0.02	1.10
134.6	0.300	0.1407		0.283	17.1	0.113	0.156	0.19	0.94
116.2	0.314	0.1374		0.320	17.1	0.119	0.149	0.21	1.02
101.8	0.441	0.1915		0.444	18.5	0.167	0.215	0.36	1.01
91.7	0.492	0.2127		0.523	19.1	0.192	0.258	0.47	1.06
80.3	0.813	0.3383		0.793	22.6	0.363	0.465	0.98	0.98
81.8	0.848	0.375		0.843	23.7	0.343	0.490	0.91	0.99

ORIGINAL ARGON DATABASE

FIGURE 1

INTERPOLATED ENERGIES

FIGURE 2

ARGON

FIGURE 3

PV/N₀KT VS. DENSITY

FIGURE 4

ENERGY SURFACE: $T < 30 \text{ EV}$

FIGURE 5

TEMPERATURE VS. DENSITY, CONSTANT GAMMA

FIGURE 6

CONSTANT GAMMA IN ENERGY-PRESSURE SPACE

FIGURE 7

FIGURE 8

FIGURE 5

H/E VS. DENSITY ALONG ISOTHERMS

FIGURE 10