Thermodynamic description of the liquid metals at pulsed energy flows impact

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Abstract. Here we suggest semiempirical equations of state defining the behavior of some solid metals at pulsed energy flows impact. A new wide-range two-phase equation of state of metals is proposed. These equations have few free parameters. They are estimated for Na and Cu. Melting curves of metals are defined within both one-phase approximation using Lindeman criterion, and two-phase-approximation. Volume and entropy discontinuities are calculated as a function of pressure at melting curve for Na and Cu. We also compared all the simulations results to the available experimental data for these metals.

1. Introduction
Construction of models for metal at high energy density represents the big interest for research of the physical processes taking place in strongly coupled coulomb systems [1–3], and also for simulation of influences of intensive beams of charged particles or laser irradiation on matter, particularly on construction materials in order to modify their properties [4]. During these types of interaction a strongly coupled, generally non-equilibrium, plasma is formed.

Nowadays available experimental data leads us to the existence of both quasi-crystal close order [5] and to structural phase transitions in liquids at high pressures [6]. At that x-ray scattering in liquid within supercritical range experiments [7] show that the liquid might coexist in two phases, i.e. at both solid- and liquid-state densities. Structure evolution and properties of liquids within wide range of temperatures and pressures are challenging when defined in context of microscopic theoretical models [3, 8, 9] because of long-range order absence.

Hence the objective of the paper is discussion of a quite simple liquid metal phenomenological model, allowing to qualitatively and quantitatively represent the behavior of metals within wide range of temperatures and pressures.

2. Model
According to Frenkel [5], who assumed, that melting occurs as a result of a lattice stability loss due to the avalanche-like growth of the Frenkel pairs (“vacancy-interstitial atom”) in the vicinity of the melting temperature ($T_m$). The molten metal in the vicinity of the melting curve can be represented as a mixture of clusters and gas, partly filling intercluster (free) volume. As a first approximation, we can conclude that the density of matter in clusters approaches the density of solid state on the melting curve. The size of the short-range order ($R_{\text{max}}$) can be determined by x-ray scattering near the melting curve. We used the experimental data from [10] for radial
Table 1. The size of the short-range order in the clusters.

|      | Cu | Fe | Hg | Na | Pb |
|------|----|----|----|----|----|
| $R_{\text{max}}$, nm | $\approx 1.0$ | $\approx 1.0$ | $\approx 1.5$ | $\approx 1.6$ | $\approx 1.25$ |

distribution functions of atoms in liquid to achieve constant values. Obtained values for some metals are shown in table 1.

Thus, the diameter of the short-range spherical order—the cluster is $\leq 2$ nm. Cluster fluctuation “disappears” (is destroyed) at sizes less than some critical one [11]. The symmetry defining clusters oscillatory spectrum differs from the symmetry of a crystal lattice near the melting curve and can be described within the Debye model, or the Einstein model, or even as a superposition of spectra of these models.

Briefly we will consider the thermodynamic description of solid [12] and liquid [13] metal. Free energy of solid metal $F_s(V, T)$ we will write down in the form of the sum of three terms: the cold compression energy $\varepsilon_\pi(V)$, considering the interaction of nuclei and all electrons, including conductivity electrons; the free energy of lattice thermal excitations $F_{\text{sl}}(V, T)$ and free energy of electronic thermal excitation $F_{\text{se}}(V, T)$:

$$F_s(V, T) = \varepsilon_\pi(V) + F_{\text{sl}}(V, T) + F_{\text{se}}(V, T).$$

(1)

The basis of our model for the description of thermodynamic functions of metals at $T = 0$ is valid for most metals, including transition ones; binding energy expression, according to the works [12, 14] and citing papers there, can be determined as:

$$\varepsilon_\pi(x) = \Lambda \left(1 - \frac{1}{\alpha - 1} \left[\alpha \exp \left(\frac{\eta}{\sqrt{a}} \left(1 - x^{1/3}\right)\right) - \exp \left(\eta \sqrt{a} \left(1 - x^{1/3}\right)\right)\right]\right) \times$$

$$\times \frac{1 + ax^{-1/3} + bx^{-2/3}}{1 + a + b},$$

(2)

where $x = V/V_0$ is specific volume at $T = 0$, $\Lambda$ is the binding energy of metal at $V = V_0$ and $T = 0$. Free parameters $a, b, \alpha, \eta$ are defined from the requirement of agreement to the curve of cold compression calculated on Tomas–Fermi’s model with quantum and exchange corrections (TFC) [15]. The values of free parameters for Cu and Na are given in table 2. Using the Debye model of a solid body taking into account an anharmonicity, addend in (1) can be written as [12]:

$$F_{\text{sl}}(V, T) = \frac{9k_B T_D}{8MA} + \frac{k_B T}{MA} \left[3 \ln \left(1 - \exp \left(-\frac{T_D}{T}\right)\right) - D \left(\frac{T_D}{T}\right)\right] -$$

$$- \frac{3k_B \chi_s T_D^3}{4MA T_D^2} \left(\text{cth}^2 \left(\frac{T_D}{2T}\right) - 1\right),$$

(3)

$$F_{\text{se}}(V, T) = -\frac{\beta_0}{2} \left(\frac{\bar{z}_c}{\bar{z}_{c0}}\right)^{1/3} \left(\frac{V}{V_0}\right)^{1/3} \left(\frac{V}{V_0}\right) \left(\frac{V}{V_0}\right) T^2.$$

(4)

In equations (3) and (4) $T_D = h \omega_D/k_B$ is the Debye temperature; $\omega_D(V)$ is the Debye frequency; $T_D^0$ is the Debye temperature at $T = 0$ K; $M = 1.66 \times 10^{24}$ g/cm$^3$, $A$, atomic mass unit and atomic weight of the element correspondingly; $\beta_0$ is the proportionality factor of the electronic
heat capacity at $V = V_0$; $\tilde{z}_c$ is the free electron number per atom at $T = 0$; $\chi_s$ is a constant, defined by the lattice heat capacity value at the melting temperature; variables with subscript “0” correspond to $V = V_0$.

Free energy of the melt equals to the sum of free energies of clusters $F_{cl}$, which in a first approximation equals to the free energy of solid state with the formed lattice defects $\Delta F_{Def}$, ideal gas $F_g$ and electron gas $F_{Le}$ with variable number of particles. Thus, the liquid metal free energy can be determined as:

$$F_L(V,T) = c_{cl} F_{cl}(V,T) + (1 - c_{cl}) F_g(V,T) + F_{Le}(V,T),$$

(5)

where $c_{cl} = V_{cl}/V$—the relative concentration of areas with quasicrystalline order, $V_{cl}$—specific volume of clusters in the melt, which approaches to the specific volume of solid state at the melting curve at $T = T_m$, $T$—temperature of matter; the free energy of clusters:

$$F_{cl}(V,T) = \varepsilon(V) + \frac{9k_BT_{cl}}{8MA} + \frac{k_BT}{MA} \left[ 3\ln \left( 1 - \exp \left( -\frac{T_{cl}}{T} \right) \right) - D \left( \frac{T_{cl}}{T} \right) \right] -$$

$$- \frac{3k_B\chi_{cl}}{4MA} \frac{T_{cl}^2}{T_{cl}^0} \left( \text{cth}^2 \left( \frac{T_{cl}}{2T} \right) - 1 \right) + \Delta F_{Def},$$

(6)

where $T_{cl}$ is the Debye temperature of cluster phase of liquid metal.

Contribution of lattice defects to the free energy of the melt is described by a modified theory of Eyring characteristic functions [16]. The essence of the modifications is in the use of the Debye model for the description of the vibrational spectrum of the cluster, not the Einstein model (according to Eyring). Contribution of lattice defects:

$$\Delta F_{Def} = -\frac{k_BT}{MA} \ln \left( 1 + \varphi_1(c_{cl}) \exp \left( -\varphi_2(c_{cl}) MA \right) \right),$$

(7)

where $\varphi_1(c_{cl}) = \xi(1 - c_{cl})/c_{cl}$ and $\varphi_2(c_{cl}) = \zeta c_{cl} \Lambda / (1 - c_{cl})$ (according to Eyring [17]) or $\varphi_2(c_{cl}) = \zeta \Lambda$ (used in our calculations); it is interesting to note that the function $\varphi_2(c_{cl})$, suggested by Eyring, can not describe the pressure dependence of experimental data of the melting curve of metal according to our calculations. The form of the functions $\varphi_1(c_{cl})$ and $\varphi_2(c_{cl})$ is the subject of further work. $\xi, \zeta, \chi_{cl}$—the phenomenological parameters of the model. They are defined under equality requirement of the theoretical and experimental values of the discontinuous jumps of volume ($\Delta V_m$) and entropy ($\Delta S_m$) and equality of the Gibbs potentials in the vicinity of the melting curve at $P_0 = 1.01325$ bar, see table 2 and following equations:

$$\begin{align*}
F_s(V_{sm},T_m) + P_0V_{sm} &= F_L(V_{Lm},T_m) + P_0V_{Lm}, \\
\Delta S_m(P_0) &= S_{Lm}(V_{Lm},T_m) - S_{sm}(V_{sm},T_m), \\
P_s(V_{sm},T_m) &= P_L(V_{Lm},T_m) = P_0.
\end{align*}$$

(8)

Table 2. Free parameters of our model for Na and Cu.

|   | $\alpha$ | $\eta$ | $a$  | $b$  | $\chi_s, 10^{-3}$ | $\chi_{cl}, 10^{-3}$ | $\xi$ | $\zeta$ |
|---|---------|-------|------|------|-------------------|---------------------|-------|--------|
| Na| 2.95    | 3.70  | -0.50| 0.25 | -6.0              | 7.0                  | 9025  | 0.25   |
| Cu| 2.95    | 5.20  | 0.18 | 0.11 | -1.3              | -5.0                 | 218   | 0.15   |
To verify the above-presented model the comparison of theoretical and experimental melting curves has been performed. Melting curve was found as the boundary between phases with the corresponding equations of state. Figures 1 and 2 show the theoretical and experimental melting curves for Cu and Na correspondingly. 

To obtain the values $V_s, T_m, \Delta V_m, \Delta S_m$ near the melting curve at $P \neq P_0$ the following algorithm was used. First, we evaluate the melting temperature $T_{\text{Lind}}$ using Lindeman criterion at given pressure $P$. Afterwards we find specific volumes $V_s$ and $V_L$ of the solid and liquid phases near melting curve from equations (9) and (10) and check the equality of the Gibbs potentials of both solid and liquid phases. If the Gibbs potentials are not equal—we change initial $T_{\text{Lind}}$ and then repeat the volumes calculations and checking procedures until the potentials equality is satisfied with given accuracy. In addition, in the case of Gibbs potentials being equal, we

\begin{align}
    \text{Pressure of solid } P_s \text{ and liquid } P_L \text{ metal can be represented as: } & \quad P_s(V_s, T) = P(\text{V}_s) + \frac{\gamma_s(V_s) k_B}{M \text{AV}_s} \left( \frac{9}{8} T_TH + 3T_D \left( \frac{T_D}{T} \right) \right) + \frac{3X_s T^3_{\beta_0}}{4 T^2} \times \\
    & \times \left( \cosh^2 \left( \frac{T_D}{2T} \right) - 1 \right) \left( \frac{T_D}{T} \cosh \left( \frac{T_D}{2T} \right) + 2 \right) + \frac{1}{4} \beta_0 \left( \frac{\tilde{V}(V_s)}{\tilde{\rho}(0)} \right)^{1/3} T^2 \left( \frac{\tilde{V}(V_s)}{V_0 V_s} \right)^{1/2}, \quad (9) \\
    \text{Pressure of liquid } P_L(V_L, T) = & \quad c_d \left( P(\text{V}_L) + \frac{\gamma(V_L) k_B}{M \text{AV}_L} \left( \frac{9}{8} T_dT + 3T_d \left( \frac{T_d}{T} \right) \right) + \frac{3X_d T^3_{\beta_0}}{4 T^2} \left( \cosh^2 \left( \frac{T_d}{2T} \right) - 1 \right) \times \\
    & \times \left( \frac{T_d}{T} \cosh \left( \frac{T_d}{2T} \right) + 2 \right) \right) + \left( 1 - c_d \right) \frac{k_B T}{MAV_L} + \frac{1}{3} \beta_0 \left( \frac{\tilde{V}(V_L)}{\tilde{\rho}(0)} \right)^{1/3} T^2 \left( \frac{\tilde{V}(V_L)}{V_0^{2/3} V_L^{1/3}} \right). \quad (10) 
\end{align}
calculate the entropy jump and move on to the next point of pressure near the melting curve. Thus, we calculated the equilibrium melting curve.

Fluctuation of the volume discontinuity and entropy jump along the melting curve demonstrated in figure 3 for sodium and copper. The change of the volume discontinuity is reduced quite significantly at low pressure. This phenomenon is explained by the fact that the compressibility of liquids is much larger than the compressibility of a solid at low pressures. The value of liquids compressibility \( \Delta V_m/V_s \) goes down at pressures range \( P = 0.1-0.2 \text{ Mbar} \) and tends to a finite limit when pressure rises. Sodium experimental melting curve shows the structural phase transitions existence and volume negative jumps within the pressures range from 0.3 to 1.2 Mbar. Fluctuation of the volume discontinuity and entropy jump evaluation along the melting curve are challenging and estimated data for Cu is the result of theoretical shock adiabat analysis within equation of state suggested in [21].

In our opinion, in order to adequately describe the experimental melting curves of metals at \( P \geq P_0 \) it is necessary to take into account the free energy of both solid and clusters dependence of local symmetry at a given pressure. It is supposed to be the subject of further investigation.

4. Conclusion

A new wide-range equation of state for liquid metals is suggested. Free parametrs of Gibbs potential for liquid Na and Cu at \( P = P_0 \) are estimated. Melting curves of metals are defined within both one-phase approximation using Lindemann criterion, and two-phase-approximation. Volume and entropy discontinuities are calculated as functions of pressure at melting curve for Na and Cu. We also compared all the simulations results to the available experimental data for these metals.

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