An equation of state for expanded metals

W Schirmacher\textsuperscript{1,*}, W-C Pilgrim\textsuperscript{2} and F Hensel\textsuperscript{2}

\textsuperscript{1} Institut für Physik, Johannes-Gutenberg-Universität Mainz, Staudinger Weg 9, D-55099 Mainz, Germany

\textsuperscript{2} Fachbereich 15, Chemie, Physikalische Chemie, Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4 D-35032 Marburg, Germany

E-mail: walter.schirmacher@uni-mainz.de

Received 29 June 2020, revised 2 September 2020
Accepted for publication 9 September 2020
Published 12 October 2020

Abstract

We present a model equation of states for expanded metals, which contains a pressure term due to a screened-Coulomb potential with a screening parameter reflecting the Mott–Anderson metal-to-nonmetal transition. As anticipated almost 80 years ago by Zel’dovich and Landau, this term gives rise to a second coexistence line in the phase diagram, indicating a phase separation between a metallic and a nonmetallic liquid.

Keywords: expanded metals, metal–nonmetal transition, equation of state

(Some figures may appear in colour only in the online journal)

1. Introduction

For almost 80 years the relation of the metal-nonmetal and liquid–vapour transition of expanded metals is not understood [1–5], despite several efforts in the last decades [4, 6].

In their original paper [1] Zel’dovich and Landau (ZL) present arguments that in expanded metals, in particular mercury, in addition to the usual liquid vapour coexistence line, a second coexistence line (with a second critical point) exists in the \((p,T)\) (pressure–temperature) phase diagram, which involves a phase separation between a metallic and nonmetallic liquid.

Experiments in expanded mercury [4, 5, 7–9] and, more recently in expanded rubidium [10] revealed a density regime, in which there is evidence for an emulsion of a metallic and a nonmetallic phase, thus confirming the ideas of ZL.

The arguments of ZL had been based on the assumption that at zero temperature a discontinuous metal–nonmetal transition takes place, which continues to be present at elevated temperatures.

At these times the only known mechanism for a crossover from a metal to a dielectric was the de-overlapping of bands. ZL argued that a continuous band-de-overlapping transition cannot take place, because in the insulating state an excited electron across the gap interacts via the Coulomb interaction with the hole left behind and thus enhances the gap, when, in the absence of the interaction it would go continuously towards zero.

The role of the electronic Coulomb and exchange interaction on the metal–nonmetal transition has been addressed extensively by Mott (Mott transition) [11–14]. He realized that these combined interactions produce two separate bands of electrons with opposite spins, giving rise to antiferromagnetic ordering in the insulating state. This scenario, which can be described by the Hubbard model [15], was called Mott transition. Mott believed that the metal–nonmetal transition was discontinuous and postulated the existence of a minimal metallic conductivity. These ideas have been quantified by Yonezawa and Ogawa [2] for calculations of the thermodynamic properties of expanded metals based on the Hubbard model and the coherent-potential approximation. In these calculations an unstable density regime due to the metal–nonmetal transition was identified.

Anderson [16] showed that disorder can be another reason for a metal–nonmetal transition. This was first demonstrated for non-interacting electrons (Anderson transition). It was then shown [17] that the Anderson transition is an interference phenomenon and could be identified as a second-order (i.e. continuous) phase transition with a non-thermal control parameter, namely the amount of spatial potential fluctuations, seen by an electron. The Anderson scenario, i.e. an electron in a random potential, could be mapped onto the nonlinear sigma model of planar ferromagnets [18–20], which obeys the same scaling as the Anderson transition. In this field theory the density of states at the Fermi level \(\mu\) was identified as the order parameter, but the critical exponent \(\beta\) turned out to be zero, so that in the ‘non-ordered state’, the nonmetallic, \(\mu\) remained finite.
That the Anderson transition is continuous was confirmed by experiments on doped semiconductors [21].

The nonlinear-sigma-model description was generalized to include the electronic Coulomb interaction (Mott–Anderson transition) [22–24]. In the presence of the interaction the critical order-parameter exponent $\beta$ became non-zero, so that $\mu$ acquired its usual order-parameter role. A severe drawback of the nonlinear-sigma-model approach is that it is based on treating the variance of the potential fluctuations as small parameter, so the theory is restricted to the weak-disorder limit.

A quite different approach, which does not suffer from this shortcoming, is the dynamical mean-field theory (DMFT) based on the Hubbard model [25–27] and turned out to be a reliable means for treating correlated electronic systems and the Mott transition.

By including disorder into the Hubbard model it proved possible to treat the Mott–Anderson transition by means of the DFMT [28–31]. These developments showed that the local single-site density of states $\mu_i$ of the disordered interacting electron system exhibits a very broad distribution. As a consequence the arithmetic mean $\langle \mu \rangle$ and the geometric one $\langle \mu \rangle^g$ was shown to become very different in the limit of strong disorder. It was shown, that, in fact $\langle \mu \rangle^g$ is critical at the Anderson–Mott transition, even in the Anderson case, whereas $\langle \mu \rangle$ is not [28–31].

In the present contribution we shall show that such a continuous Mott–Anderson transition of the electrons produces in an expanded metal an instability in the density regime near the transition, and thus a second phase-separation line between a metallic and nonmetallic liquid phase, as anticipated by ZL.

We argue that in expanded metals the transition scenario for the electrons is a qualitatively different one from that for the metallic atoms/ions. For the electrons the transition is one with increasing spatial disorder in the presence of the electron–electron interaction. This means that for the electrons the disorder is of quenched type. This is so because of the adiabatic principle: on their time scale the electrons experience a snapshot of the atomic arrangements. These arrangements produce increasing spatial potential fluctuations with decreasing density, so that at a critical density the Anderson–Mott transition takes place.

On the other hand, for the atoms/ions the transition scenario is not governed by quenched disorder but by equilibrium thermodynamics. The electronic degrees of freedom provide a density dependent interaction. Using the standard expression for the equation of states for a simple liquid with a potential, which includes a density-dependent screened Coulomb term, we demonstrate that an unstable density interval appears, which, in turn, produces the metal–nonmetal separation in the liquid state. This mechanism of phase separation into a metal-rich and metal-depleted liquid is very similar to that suggested some time ago [32–34] for solutions of metals in molten salts [35, 36].

In section 2 we introduce our model and present the resulting equation of state. In section 3 we show isotherm calculations, which are used to calculate a phase diagram. We conclude with discussing achievements and shortcomings of our approach.

## 2. Model

### 2.1. General formalism

We start with the expression for the pressure equation of states [34, 37]

$$P(V, T) = \frac{k_B T}{V} \left( 1 - \frac{1}{6} \frac{1}{V k_B T} \int d^3 r r^2 g(r) \right)$$

(1)

where $g(r)$ is the radial distribution function, $T$ the temperature, $k_B$ Boltzmann’s constant, $V = M/\rho_M$ the atomic volume, $\rho_M$ the mass density, and $M$ the atomic mass.

We now assume that the interatomic potential is composed of three contributions:

(a) A hard-sphere contribution $\phi_{hs}$;
(b) An attractive contribution $\phi_{att}$;
(c) A screened-Coulomb contribution $\phi_{sc}$.

We now lump the free-gas contribution to the pressure and the hard-sphere potential together to a hard-sphere pressure $P_{hs}$ and write

$$P(V, T) = P_{hs}(V, T) - \frac{1}{6 V^2} \int d^3 r r^2 [\phi_{att}(r) + \phi_{sc}(r)] g(r)$$

$$= P_{hs}(V, T) + P_{att}(V) + P_{sc}(V).$$

(2)

For the hard-sphere pressure we use the Van-der-Waals repulsion term

$$P_{hs}(V, T) = \frac{k_B T}{V - B}$$

(3)

with $B \approx d^2$, where $d$ is the distance of nearest approach or effective hard-sphere diameter. $B$ is also of the order of the atomic volume at melting.

Because the radial distribution function is strongly peaked near the nearest-neighbour distance $d$, and the potential contributions vanish for $r \gg d$ we may replace $\phi'(r) g(r)$ by a delta function and approximately write

$$\frac{1}{V} \int d^3 r r^2 \phi_{att;sc}'(r) g(r) \approx Z(V) d_{att;sc}'(d)$$

(4)

with the coordination number

$$Z(V) = \frac{1}{V} \int_{|r| \leq r_Z} d^3 r g(r)$$

(5)

where $r_Z$ is taken to be at the first minimum of $g(r)$. It has been found experimentally [38] that in some expanded metals $Z$ increases linearly with density

$$Z(V) = Z_0 / V$$

(6)

with $Z_0 \approx 8 V_{M,mp}$ for both expanded Rb and Cs, where $1/V_{M,mp}$ is the density at the melting point. So we may write

$$\int d^3 r r^2 \phi_{att;sc}'(r) g(r) \approx Z_0 d_{att;sc}'(d).$$

(7)

3 See e.g. reference [34] for the identification of Van der Waals’s $k_B T/(V - A)$ term with the repulsive pressure.
As generally the minimum of the attractive potential contribution is located at $r_{\text{min}} > d$, $\phi_{\text{at}}(d) < 0$ and we get a Van-der-Waals term

$$P_{\text{at}}(V) = -A \frac{1}{V^2},$$

with

$$A = \frac{Z_0}{6} r |\phi_{\text{at}}(d)|.$$  \hspace{1cm} (9)

Without the screening term the equation of states $p_{\text{at}}(V) + p_{\text{el}}(V)$ becomes the Van-der-Waals equation of states, which gives the usual liquid–vapour transition scenario.

### 2.2. Screening length and metal–nonmetal transition

We now turn to the main object of the present exercise, namely the screened Coulomb interaction.

As indicated in the introduction we rely on the adiabatic principle, from which follows that in the situation of an expanded metal the (interacting) electrons experience a strongly spatially fluctuating external potential due to the ion cores. These fluctuations are ‘frozen’ on the time scale of the electrons ($\sim 1$ fs). In contrast to this the system of the metallic atoms/ions experience effective pairwise interaction potentials (see below), which are mediated by the electrons with their Mott–Anderson scenario. If the electrons are in the metallic state, they are able to screen the interionic Coulomb interaction. The resulting effective interatomic interaction is subject to equilibrium thermodynamics. So the electrons experience quenched disorder, the atoms/ions experience annealed disorder. The resulting electronic quenched-disorder Mott–Anderson transition is continuous, the thermodynamic one—as we shall see—is discontinuous below the corresponding critical point.

The effective pairwise interaction potential between the ions/atoms in a simple liquid metal can be written as the sum below the corresponding critical point.

The thermodynamic one—as we shall see—is discontinuous.

So we have

$$\lambda(V) = \lambda_0 f(x(V))$$

with the normalized density $x(V) = \frac{\rho_{\text{MNM}}}{V} - 1$ and

$$f(x) = \theta(x),$$

where $\theta(x)$ is the step function and $V_{\text{MNM}}$ is the critical atomic volume of the metal–nonmetal transition.

So we have

$$\lambda(V) = \lambda_0 f^{1/2}[\chi(V)]$$

with $\lambda_0^2(V) = 4\pi\epsilon^2 \mu_F(V)$. As the density, viz, volume dependence of $\lambda_0$ is considerably weaker than the critical one we set $\lambda_0$ constant, i.e. $\lambda_0(V) = \lambda_0$. Finally we may write

$$p_{\text{el}}(V) = \frac{C}{V^2} [1 + \lambda(V) d] e^{-\lambda V d}$$

with $C = c(R_{\text{c}})Q^2 Z_0/6d$.

Collecting all the terms contributing to the pressure we obtain our central result

$$P(V, T) = \frac{k_B T}{V - B} - \frac{A}{V^2} + \frac{C}{V^2} [1 + \lambda(V) d] e^{-\lambda V d}.$$ \hspace{1cm} (20)

Beyond the Anderson–Mott transition ($V > V_{\text{MNM}}$) we have

$$p_{\text{el}}(V) = \frac{C}{V^2}$$ \hspace{1cm} (21)

so that in this limit we obtain an effective Van-der-Waals equation of states with

$$A_{\text{eff}} = A - C.$$ \hspace{1cm} (22)
It should be noted that the equation of states (20) interpolates [43] between that of a liquid metal (small V) and a free gas (large V).

2.3. Inhomogeneities and smoothing of the metal–nonmetal transition

Relation (18) together with (17) describes (at zero temperature) a rather sharp transition between the metallic and nonmetallic state. Such a transition is predicted by the generalized nonlinear sigma model, which is based on weak disorder [22–24]. At elevated temperature one may expect this transition to be somewhat smoothed.

On the other hand, the alternative theory of the Mott–Anderson transition, tailored for the case of strong correlations and strong disorder [28–31], predicts a very broad distribution of local densities of state $\mu_i$. A sharp transition is found for the geometric average $\langle \mu \rangle_g = \exp \{ \langle \ln \mu \rangle \}$, whereas the arithmetic average $\langle \mu \rangle_A$ is non-critical.

We now phenomenologically introduce a smoothing of the critical law [44]. We replace the function $f(x)$ in equation (16), which is the antiderivative of the step function $\theta(x)$, by the antiderivative $\tilde{f}(x)$ of the complementary Fermi function $[1 + e^{-x/s}]^{-1}$:

$$
\mu(V) = \mu^{(0)}\tilde{f}(x(V)) \quad (23)
$$

with

$$
\tilde{f}(x) = s \ln \left[ 1 + e^{x/s} \right] \quad (24)
$$

where $s$ is the smoothing parameter. For $s \rightarrow 0$ we recover (16).

In figure 1 we show the influence of $s$ on the critical law. As intended by construction the curves become increasingly smoother with increasing $s$.

3. Results

We now use dimensionless units $v = V/B$, $t = k_B T A_{\text{eff}}$ and $p = P B^2 / A_{\text{eff}}$. In these units the equation of states takes the form

$$
p(v, t) = \frac{t}{v - 1} \left[ 1 + \frac{c}{v^2} \right] \exp \left[ \frac{1 + \lambda(v) t}{c} \right] e^{-\lambda(v) t}, \quad (25)
$$

with $c = C/A_{\text{eff}}$.

In these units the critical liquid–vapour quantities are given by

$$
\lambda_c^{LV} = \frac{8}{27} \approx 0.3 \quad v_c^{LV} = 3 \quad p_c^{LV} = \frac{1}{27} \approx 0.037. \quad (26)
$$

In figure 2 we show the isotherms predicted by the equation of states (25) with the parameters indicated in the caption. These isotherms show two unstable regimes: at high atomic volume the usual liquid–vapour one, at low volume the unstable regime due to the density dependence of the screening, caused by the (continuous!) metal–nonmetal transition. As to be expected, the two-liquid instability occurs in the vicinity of the critical Mott–Anderson volume $v^\text{MNM}$.

We have calculated the equilibrium volumes, pressures and temperatures using both the Maxwell construction and the double-tangent method [45]. For the regime above $v^\text{MNM}$ we used Gibbs’ parametric solution of the Van-der-Waals coexistence problem [46]. Below $v^\text{MNM}$ we implemented a graphical double-tangent construction. In the immediate vicinity of the critical point we used a numerical Maxwell construction, i.e. equating the volumes above and below the coexistence pressure. The resulting phase diagrams are shown in figure 2 (dashed lines) and in figure 3.

It is remarkable that the smoothing of the electronic metal–nonmetal transition results in a strong reduction of the critical endpoint of the corresponding atomic transition.

Let us now consider the situation in expanded Hg and Rb. We chose our parameter $v^\text{MNM}$, which is equal to $3 P_c/\rho^\text{MNM}$, to be equal to 1.3, which corresponds to the value of $\rho^\text{MNM}/\rho_c = 2.3$ in expanded Rb [10]. Pilgrim et al [10] have evidence by inelastic neutron scattering that in the density range around

![Figure 1](image1.png)

**Figure 1.** The function $\mu(v)/\mu^{(0)}$ of equations (23) and (24) for smoothing parameters $s = 0.0, 0.01, 0.02, 0.03, 0.04$ from bottom (blue) to top (red).

![Figure 2](image2.png)

**Figure 2.** $p – v$ isotherms according to our equation of states (25) for zero smoothing parameter $s$ (thin lines) and $s = 0.02$ (thick lines) for the temperature range $0.2 \leq T \leq 0.3$. Further parameters used are $v^\text{MNM} = 1.3$ and $A_{\text{eff}} = 8$. The dashed lines are the equilibrium pressures calculated with the Maxwell and double-tangent construction. Inset: $p – t$ phase diagram. The dots indicate the critical points.
2.3ρc a micro-emulsion of two liquids is present. Similar evidence has been presented earlier by Ruland and Hensel [9] for expanded Hg in the range around 1.2ρc by analyzing published small-angle scattering data [7, 8]. This would correspond to υ_{BBM} = 2.5. It has been pointed out in references [9, 10], that the Coulomb interaction between the metallic micro-droplets, surrounded by the second-phase nonmetallic material prevents a complete demixing and establishes the micro emulsion.

4. Discussion

By combining the standard expression for the pressure equation of state of a simple liquid with a hard-core repulsion, a short-range attraction and a screened Coulomb potential reflecting the Mott–Anderson transition via a density-dependent screening length, we have constructed an equation of state of a simple liquid with a hard-core repulsion. In a future publication we shall present a more refined version of our equation of state [20].

We find that the smoothing results in a reduction of the length of the coexistence line. Let us consider again the reasons for such a smoothing to happen. First of all, the electronic transition does not take place at zero temperature but at a temperature approaching the Fermi temperature. Secondly, for T = 0 we assumed the critical exponent of the Mott–Anderson transition to be 1. If it would be larger than one the curve would look like a rounded transition. Thirdly, as mentioned before, the local density of electronic states in the Mott–Anderson scenario as given by the DMFT [28–31] is known to exhibit strong spatial fluctuations, so this as well will effectively lead to a smoothing of the transition. So a more detailed experimental investigation of the liquid–liquid separation line will shed light on the details of the mechanism of the Mott–Anderson transition.

Finally we would like to discuss a point concerning the temperature dependence of our model. Our equation of states (20) has a linear temperature dependence like the Van-der-Waals one. By elementary thermodynamic relations one can show that if the second temperature derivative (at constant volume) of the pressure is zero, such is the first volume derivative of the specific heat (at constant temperature). This implies that the specific heat does not depend on the volume. Of course, in a material, in which the electronic degrees of freedom play a dominant role, the linear-temperature term of the specific heat should be present, which is proportional to the density of states at the Fermi level and, hence, should exhibit the same volume dependence as the screening parameter λ(V)². This is not included in our rather crude model. The model has mainly been introduced in order to demonstrate, how a smooth metal–nonmetal transition can lead to a first-order phase transition in an expanded metal and a second coexistence line, as anticipated by ZL [1]. A more refined version should include a term quadratic in the temperature, which is then related to the specific heat. This term will be a correction of the order of (kT/EF)², where EF is the Fermi energy. In a future publication we shall present a more refined version of our equation of states, in which the delta-function approximation of (4) will not be made, and the T² term, related to the electronic specific heat, will be included.
[12] Mott N F and Davis E A 1971 *Electronic Processes in Non-crystalline Materials* (Oxford: Clarendon)
[13] Mott N F 1982 *Proc. R. Soc. A* **382** 1
[14] Mott N F 1990 *Metal–Insulator Transitions* (London: Taylor and Francis)
[15] Hubbard J 1963 *Proc. R. Soc.** 276** 238
[16] Anderson P W 1958 *Phys. Rev.* **109** 1492
[17] Abrahams E, Anderson P W, Licciardello D C and Ramakrishnan T V 1979 *Phys. Rev. Lett.* **42** 673
[18] Wegner F J 1976 *Z. Phys.* B **25** 327
[19] Schäfer L and Wegner F 1980 *Z. Phys.* B **38** 113
[20] McKane A J and Stone M 1981 *Ann. Phys., NY* **131** 36
[21] Rosenbaum T F, Andres K, Thomas G A and Bhatt R N 1980 *Phys. Rev. Lett.* **45** 1723
[22] Finkel’stein A M 1983 *Sov. Phys - JETP** 57** 97 (Engl. transl.)
Finkel’stein A M 1983 *Zh. Eksp. Teor. Fiz.* **84** 168
[23] Belitz D and Kirkpatrick T R 1994 *Rev. Mod. Phys.* **66** 261
[24] Belitz D and Kirkpatrick T R 1995 *Z. Phys.* B **98** 513
[25] Metzner W and Vollhardt D 1989 *Phys. Rev. Lett.* **62** 324
[26] Jani V 1989 *Phys. Rev.* B **40** 11331
[27] Georges A and Kotliar G 1992 *Phys. Rev.* B **45** 6479
[28] Dobrosavljević V and Kotliar G 1997 *Phys. Rev. Lett.* **78** 3943
[29] Byczuk K, Hofstetter W and Vollhardt D 2005 *Phys. Rev. Lett.* **94** 056404
[30] Dobrosavljević V 2010 *50 Years of Anderson Localization* ed E Abrahams (Singapore: World Scientific) p 473
[31] Byczuk K, Hofstetter W and Vollhardt D 2010 *50 Years of Anderson Localization* ed E Abrahams (Singapore: World Scientific) p 473
[32] Holzhey C and Schirmacher W 1985 *J. Phys. Colloq.* **46** C8
[33] Holzhey C and Schirmacher W 1988 *Z. Phys. Chem.* **156** 163
[34] Schirmacher W 2015 *Theory of Liquids and Other Disordered Media* (Lecture Notes in Physics vol 887) (Berlin: Springer)
[35] Bredig M A 1964 *Molten-salt Chemistry* ed M Blander (New York: Interscience) p 367
[36] Garbade K and Freyland W 1988 *Ber. Bun. Phys. Chem.* **92** 1131
[37] Hansen J-P and McDonald I 1986 *Theory of Simple Liquids* (New York: Academic)
[38] Winter R, Pilgrim C and Hensel F 1991 *J. Phys. Colloq.* **C 5** 45
[39] Evans R and Schirmacher W 1978 *J. Phys. C: Solid State Phys.* **11** 2437
[40] Harrison W A and Wills J M 1982 *Phys. Rev.* B **25** 5007
[41] Ashcroft N W and Mermin N D 1976 *Solid State Physics* (New York: Holt, Rinehart and Winston) p 340
[42] Ashcroft N W 1966 *Phys. Lett.* **23** 48
[43] Landau L D and Lifshitz E M 1980 *Statistical Physics* (Oxford: Pergamon) p 232
[44] Vojta T 2003 *Phys. Rev. Lett.* **90** 107202
[45] Huang K 2001 *Introduction to Statistical Physics* (London: Taylor and Francis)
[46] Lekner J 1982 *Am. J. Phys.* **50** 161