

Predicting the Liquid-Vapor Critical Point from the Crystal Anharmonicity

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A “universal” dependence is predicted of the reduced critical parameters, $\frac{k_B T_c}{E_0}(\gamma)$, $\frac{V_c}{V_0}(\gamma)$, and $P_c V_c / k_B T_c = Z_c(\gamma)$, on the crystal anharmonicity γ (closely related to the Grüneisen parameter Γ_G). It is based on a simplified embedded-atom type approach which enables one to utilize the universal zero-temperature equation of state in a version of fluid perturbation theory. This model’s critical temperature and density agree with the experimental results for both the heavy rare gases ($\gamma \approx 2.85$) and heavy alkali metals ($\gamma \approx 1.35$). Predicted critical parameters for many other liquid metals are consistent with previous estimates, but the model is not applicable when directional bonding is important.

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The equation of state of materials reflects the nature of the interatomic interactions and is of fundamental importance in basic and applied science [1,2]. The parameters of the critical point (temperature T_c , density $\rho_c = 1/V_c$, and pressure P_c) of the liquid-vapor transition of metals are of much interest as an essential part of the equation of state of the liquid [3–8]. However, because of the generally extreme temperatures involved they have been inaccessible to direct measurement except for very few cases, notably alkali metals [9–11] and mercury [12]. On the other hand, a great deal of effort has been invested over the years in order to estimate the critical parameters from available data at lower temperatures, using, e.g., corresponding states arguments for the saturated vapor pressure with a constant heat of vaporization, and the law of rectilinear diameter [4,13,14]. There is a large spread in the estimated values given by different authors, as discussed in general [7] and for the particular case of tungsten [15], and as detailed for the alkali metals and mercury [8]. Theoretical models aimed at providing estimates of the critical parameters across the whole table of the elements were invariably based on the van der Waals picture, with hard-sphere [3] or soft-sphere [5] repulsive interactions. More sophisticated perturbation theories for classical fluids [16], in agreement with computer simulations, could successfully reproduce the experimental T_c and V_c of the rare gases [17] by corresponding states using the Lennard-Jones pair potential [18,19]. However, a comprehensive treatment of liquid metals cannot rely on a pair potential picture. At present, neither first principles calculations, e.g., [20], nor sophisticated models [21,22] are predicting accurately the critical parameters of the alkali metals.

In this Letter I consider an intermediate approach [23,24], close in spirit to the “glue” or “embedded-atom” [25] methods, which from the statistical mechanics point of view is about as accurate as the approximations applied for the rare gases, yet is simple enough to enable application to liquid metals across the whole table of elements. The model free energy of the fluid combines a hard-sphere perturbation theory with an empirical

“universal” expression for the zero-temperature cohesive energy of the corresponding crystal as a function of volume. It predicts a universal dependence of the reduced critical parameters on the crystal anharmonicity (which is closely related to the Grüneisen parameter). This model is apparently the first to predict V_c and T_c in reasonable agreement with the available data for *both* the heavy rare gases and the heavy alkali metals. Like other mean-field approaches it tends to predict rather much too high values for P_c . The predicted critical parameters for many other “normal” liquid metals are generally consistent with previous estimates, but the model is not applicable when directional bonding is important.

The present approach is made of two separate ingredients, both known for a long time, that when put together in the context of the critical point can provide new insights. The first ingredient is a special variant of fluid perturbation theory [23,24]. Consider the potential energy of an atom in the field of neighboring atoms, Φ . For the particular configuration of neighbors of the solid it is given by the cohesive energy E . However, for the fluid Φ must be averaged over many configurations of neighbors that are different from those of the solid. In order to be able to treat also liquid metals, where the assumption of additive pair potentials is very poor, Kerley [23] invoked a physical picture by which the fluid is assumed to be a mixture of solidlike clusters of many different densities, and the energy of an atom in a particular cluster is closely related to what it would have in the solid at the same density. He approximated $\Phi(V)$, for a given fluid configuration, by the zero-Kelvin isotherm of the solid, $E(V_s)$, having the same nearest neighbor distance, R_s , as that of the given fluid configuration, with corrections for vacancies. This approach utilizes $E(V_s)$ and requires the distribution of first nearest neighbor distances $p(R_s)$ in order to calculate the potential energy. In analogy with the case of pairwise additive interactions $\phi(r)$ which require the pair distribution function $g(r)$ in order to calculate the potential energy, Kerley’s method enables one to employ fluid perturbation theory with the hard spheres as a reference system. This

methodology, as analyzed in some detail in [24], represents a simplified embedded-atom type approximation [25]. The second ingredient is the surprising discovery of the early 1980s that the zero-temperature equations of state of covalent and metallic solids, when suitably scaled, fall on a universal family of curves [26–28]. The scaled cohesive energy of crystals, E/E_0 , as a function of the scaled specific volume, V/V_0 , is well approximated by a universal function, $\frac{E}{E_0}(\frac{V}{V_0}, \gamma)$, requiring as input only the equilibrium values of the volume V_0 , energy E_0 , and bulk modulus B_0 . It depends parametrically on $\gamma = (\frac{B_0 V_0}{E_0})^{1/2}$, which is a measure of the crystal anharmonicity, closely related to the Grüneisen parameter Γ_G [1]. Indeed, this enables us to construct a fluid model, without any adjustable parameters, that utilizes the universal function $\frac{E}{E_0}(\frac{V}{V_0}, \gamma)$ as the *only* information about the interaction energy. The resulting model free energy for the fluid includes the contributions from electronic binding, and the thermal atomic motion in the force field created by the electrons. If, for simplicity, we keep the electrons in the ground state, and ignore the contributions from thermal electronic excitations, then (independent of the specific details of how the universal function is utilized) the critical parameters from a model thus constructed must obey a generalized “law of corresponding states” by three universal functions of the anharmonicity parameter γ , i.e., $\frac{k_B T_c}{E_0}(\gamma)$, $\frac{V_c}{V_0}(\gamma)$, and $P_c V_c / k_B T_c = Z_c(\gamma)$. The underlying approximations are expected to hold for both the rare gases and alkali metals, which represent two rather extreme values of the parameter γ . The available experimental values, together with the results of a specific model along these lines described below, can be used in order to construct the predicted three universal functions by interpolation (Fig. 1). These can provide estimates for many liquid metals for which the model is expected to provide a good approximation.

There are in principle different possibilities to approximately incorporate the zero-Kelvin isotherm into a fluid model, and the following model free energy [23,24], which is based on the hard-sphere perturbation theory [16], was used in the present work:

$$F(V, T, \sigma(V, T)) = F_{\text{HS}}(V, T, \sigma) + \langle \Phi \rangle_{\text{HS}}. \quad (1)$$

F_{HS} is the free energy for a fluid of hard spheres of diameter σ , and $\langle \Phi \rangle_{\text{HS}}$ is an average of Φ over all configurations of the hard-sphere fluid. Adopting Kerley’s approximation [23,24] $\Phi(V) \approx \frac{V_s}{V} E(V_s)$, then $\langle \Phi \rangle_{\text{HS}}$ is given by an integral of the form $\int E(V y^3) G(y, \eta) d^3 y$, where $\eta = \frac{\pi \sigma^3}{6V}$ is the packing fraction, and $G(y, \eta)$ is related to the short range part of the hard-sphere radial distribution function, $g(y = r/\sigma, \eta)$. The optimal diameter $\sigma(V, T)$ is defined by a variational principle, $\partial F / \partial \sigma = 0$. This specific model has already been applied successfully to a variety of fluids, and is detailed in [23,24]. In order to further check its accuracy as a statistical theory this model of fluids was applied to various systems with known pair

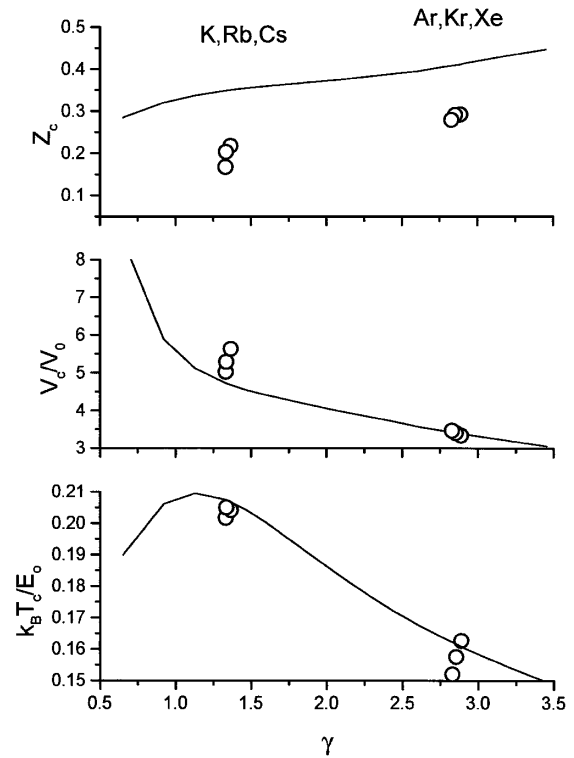


FIG. 1. Reduced critical parameters as functions of the anharmonicity parameter γ . The lines are the predictions of the present theory, and the symbols represent the experimental results for rare gases and alkali metals (see Tables I and II).

potentials $\phi(r)$ from which the inputs $E(V_s)$ were calculated as lattice sums. The results were compared with simulations, and with the corresponding standard hard-sphere perturbation theory which employs directly the same pair potentials. For the Lennard-Jones (LJ) type systems it was found that provided it employs $E(V_s)$ obtained as lattice sum for a close-packed lattice (fcc or hcp), it is of comparable accuracy to the corresponding theory which employs the pair potential as input: For the critical parameters of the LJ (12-6) potential ($k_B T_c/\epsilon$, V_c/σ^3 , $P_c \sigma^3/\epsilon$) it predicts (1.385, 3.21, 0.16) in comparison with the simulations [19] (1.313, 3.23, 0.13) and ordinary perturbation theories [18] (1.32 – 1.36, 2.78 – 3.33, 0.13 – 0.17), respectively.

In combination with the universal zero-Kelvin energy [26–28], this model can now provide a more general outlook. The zero-temperature universal scaled binding energy is well approximated by [28]

$$\frac{E(V)}{E_0} = -(1 + a + 0.05a^3)e^{-a}, \quad (2)$$

where a is a dimensionless scaled length defined by $a = 3\gamma(x - 1)$, with $x = \frac{r_{\text{WS}}}{r_{\text{WSE}}} = (\frac{V}{V_0})^{1/3}$ representing a reduced average interparticle distance, and r_{WS} , r_{WSE} are, respectively, the Wigner-Seitz radius and its value at the equilibrium density. From the zero-temperature equation of state $P = -(\frac{\partial E}{\partial V})$ one finds that the isothermal bulk

TABLE I. Critical parameters of rare gases. Experimental results compared with the present theory.

Element	γ	Method	T_c (K)	ρ_c (g/cm ³)	P_c (bar)	$k_B T_c/E_0$	V_c/V_0	Z_c
Ne	2.794	expt. [17]	44.4	0.48	27.3	0.195	3.12	0.31
		present	36.9	0.44	27.0	0.162	3.42	0.40
Ar	2.889	expt. [17]	150.7	0.53	48.6	0.163	3.33	0.29
		present	149.4	0.52	67.0	0.161	3.38	0.41
Kr	2.856	expt. [17]	209.3	0.91	54.9	0.157	3.40	0.29
		present	215.6	0.91	80.0	0.162	3.41	0.41
Xe	2.829	expt. [17]	289.7	1.09	58.9	0.152	3.46	0.28
		present	308.9	1.11	88.0	0.162	3.40	0.40

modulus $B = -V(\frac{\partial P}{\partial V})_T$ is given at equilibrium by $B_0 = \frac{E_0 \gamma^2}{V_0}$, and its pressure derivative $B' = (\frac{\partial B}{\partial P})_T$ at equilibrium is $B'_0 = 1 + 2.3\gamma$. By comparison, the Dougdale-McDonald expression [1] for the equilibrium Grüneisen parameter $(\Gamma_{G,DM})_0$ is $B'_0 = 1 + 2(\Gamma_{G,DM})_0$. The universal scaling, $\frac{E}{E_0}(\frac{V}{V_0}, \gamma)$, requires only E_0 , B_0 , and V_0 , in order to predict the full zero-temperature equation of state. These input parameters (and thus γ) are readily available (in this work we used the tables in [2]), and for the majority of metals the anharmonicity γ is between 1 and 2. The model free energy thus obtained from Eqs. (1) and (2) predicts a one parameter universal scaled fluid equation of state of the form $\frac{PV_0}{E_0}(V/V_0, k_B T/E_0, \gamma)$. This universal equation of state gives rise to the universal critical parameters $\frac{V_c}{V_0}(\gamma)$, $\frac{k_B T_c}{E_0}(\gamma)$, $P_c V_c/k_B T_c = Z_c(\gamma)$, as presented in Fig. 1 and in Tables I and II.

The results for the critical densities and temperatures of the heavier rare gases agree well with the experimental values, while Z_c has van der Waals-like values (see Table I) as expected from such a mean-field model. These results are in accord with those for the Lennard-Jones system given above. From theoretical cohesive energy calculations it can be expected that alkali metals in a hypothetical fcc or hcp structure also obey the universal scaled form with about the same value of γ as in their physical bcc structure. The present model predicts correctly the available experimental critical densities and temperatures of the alkali metals (Table II), but again with mean-field van der Waals-like values for Z_c (yet smaller than for the rare gases, in agreement with the experimental

trend). It should be emphasized that the predicted larger $\frac{V_c}{V_0}$ of the alkalis automatically accounts for their more asymmetric coexistence region in the $(\frac{T}{T_c}, \frac{\rho}{\rho_c})$ plane. The present approach also accounts well for the experimental critical parameters of heavy molecular gases, and can treat also the lighter rare gases (and also molecular hydrogen) by adding quantum corrections to the model free energy [24]. The predicted universal critical parameters for metals across the whole table of elements are comparable to estimates in the literature based on experimental liquid-vapor coexistence data. In particular, the predicted critical temperatures are comparable to those estimated by [4] and [13] from experimental liquid-vapor coexistence data, while the predicted critical densities are closer to those estimated by [13]. We do not present these many results on Fig. 1 since the large uncertainty of these estimates and the large spread in the estimated values as given by different authors do not allow at present a more meaningful check of the predicted scaling with the anharmonicity γ . The model predicts a maximum value of $\frac{k_B T_c}{E_0}(\gamma) \approx 0.21$ at $\gamma \approx 1.13$, which should eventually be checked experimentally and further investigated.

The present simple model has some obvious shortcomings and, like many before, it leaves much to be desired. It is unable to account for the estimated deviations in the reduced critical parameters between Li and Na [10] and the heavier alkalis. When directional bonding is important, it is expected that the universal equation of state and the Kerley model of fluids [23] may not be accurate. This could be the reason why the universal reduced critical

TABLE II. Critical parameters of alkali metals. Experimental results compared with the present theory.

Element	γ	Method	T_c (K)	ρ_c (g/cm ³)	P_c (kbar)	$k_B T_c/E_0$	V_c/V_0	Z_c
K	1.333	expt. [11]	2180	0.18	0.15	0.202	5.02	0.17
		present	2240	0.19	0.32	0.207	4.71	0.35
Rb	1.367	expt. [9]	2020	0.29	0.12	0.204	5.63	0.22
		present	2040	0.35	0.24	0.207	4.66	0.35
Cs	1.337	expt. [9]	1920	0.38	0.09	0.205	5.28	0.20
		present	1940	0.42	0.18	0.207	4.71	0.35

parameters cannot account for the experimental results (see Table 16.2 in [2]) for As, Se, and Hg, all having particularly small value of $\frac{V_c}{V_0} \approx 2.5$. The model also ignores electronic excitations which can be important when estimating critical temperatures of the order of 1 eV, or for certain special elements, and it does not treat the metal-insulator transition. Nevertheless, it raises the interesting possibility of a rather general approximate universal scaling of the critical parameters with the crystal anharmonicity, and provides concrete insight about major differences between the critical parameters of the rare gases and the alkali metals.

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