Quantum nature of the critical points of chemical elements

To cite this article: S. A. Trigger 2010 *EPL* **91** 66003

View the article online for updates and enhancements.

Quantum nature of the critical points of chemical elements

S. A. Trigger[a]

*Joint Institute for High Temperatures, Russian Academy of Sciences - 13/19, Izhorskaia Str. 13 bild. 2,
Moscow 125412, Russia and*
Eindhoven University of Technology - P.O. Box 513, MB 5600 Eindhoven, The Netherlands, EU

Abstract – Thermodynamics of chemical elements, based on the two-component electron-nuclear plasma model, shows that the critical parameters for the liquid-vapor transition are the quantum values for which the classical limit is absent. The general representations for the critical parameters are found.

For all substances in the vicinity of the critical points of the liquid-vapor transition, the inter-particle interaction is strong. Therefore, theoretical description of critical points seems to be a very complicated problem. Numerical modeling allows approximate calculation of the critical parameters for a known inter-particle interaction potential. However, the use of pair short-range potentials acceptable for the matter of low and moderate density (in gaseous state) cannot be justified for the region of the critical-point parameters. This means that usual numerical calculations of these parameters with the model pair potentials (see, e.g., [1,2]) have empirical nature.

To describe the critical parameters (for concreteness, only the chemical elements are discussed below, although the main statements are universal), we propose to use the pure Coulomb interaction between the electrons and nuclei [3–7]. This basic model, *i.e.*, the two-component homogeneous and isotropic electron-nuclei Coulomb system (CS) has been recently successfully applied to study the properties of dielectric permittivity [7,8]. It was also shown that the critical point of the two-component CS is related to the limiting behavior of the generalized screening length in the electron-nuclear plasma [9].

In this letter, we focus the attention on the fact that in two-component electron-nuclear Coulomb plasma, when the thermodynamic parameters tend to critical, the sole parameter with energy dimension (except the parameters containing the critical ones) is the atomic energy unit (Hartree energy) $me^4/\hbar^2 \simeq 27.21\,\mathrm{eV}$. It should be emphasized that even in a pure Coulomb system for

thermodynamic functions there are other energy scales —temperature T or $e^2 n^{1/3}$. Therefore, restriction of the energy scales is the specific property of critical points. From this reasoning we obtain immediately the exact relation for the critical temperature T_c (in energy units)

$$T_c = \frac{me^4}{\hbar^2}\,\tau\left(z, \frac{m}{M}, \sigma\right). \tag{1}$$

Here m, e are the electron mass and charge, respectively, M and z are the mass and charge number of the element under consideration. The value $\sigma = \pm$ depends on the nucleus spin J (+ for the Fermi statistics, J is a semi-whole number; − for the Bose statistics, J is a whole number). The variables m/M and σ describe the difference of the critical parameters of isotopes. Therefore, the function $\tau(z, \frac{m}{M}, \sigma)$, in general, is the unknown dimensionless function of three dimensionless parameters: z (nuclear charge number), the mass ratio m/M and the variable σ. From physical reasons, we can assume that dependence of the critical temperature on the small parameter m/M (isotopic effect) can be neglected with good accuracy for $z \gg 1$. Then the problem reduces to the determination of only the function $\tau(z, \sigma)$.

At the same time, for $z \gtrsim 1$ the mass dependence in the function τ is important (*e.g.*, for the hydrogen isotopes $T_c(\mathrm{H}) = 33.24\,\mathrm{K}$, $T_c(\mathrm{D}) = 38.35\,\mathrm{K}$ and $T_c(\mathrm{T}) = 43.7\,\mathrm{K}$ [10], see fig. 1).

Since hydrogen (H) and tritium (T) both have $\sigma = +$, these data for the critical temperatures are the evident manifestation of the isotopic effect. At the same time, for hydrogen and deuterium (as well as for He^4 and
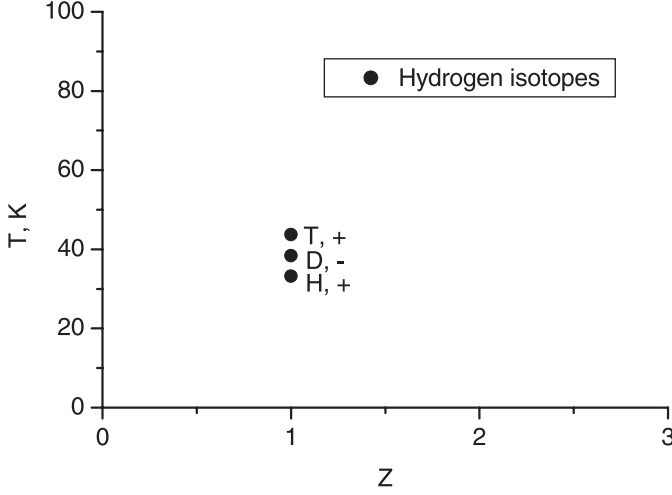
---
[a]E-mail: satron@mail.ru

Fig. 1: Critical temperatures $T_c(z)$ for the isotopes of hydrogen.

Fig. 2: Critical temperatures $T_c(z)$ for alkali metals, noble gases and halogens.

He^3, with the critical temperatures $T_c(\mathrm{He}^4) = 5.20\,\mathrm{K}$ and $T_c(\mathrm{He}^3) = 3.34\,\mathrm{K}$) the temperatures T_c can be different due to distinction of the both values M and σ.

For a large z, when the isotopic mass difference is small, the problem reduces to the determination of only the function $\tau(z, \sigma)$

$$T_c \simeq \frac{me^4}{\hbar^2} \tau(z, \sigma). \tag{2}$$

For the critical pressure, on the same basis as above one can write

$$P_c = \frac{me^4}{a_0^3 \hbar^2} \pi\left(z, \frac{m}{M}, \sigma\right) \simeq \frac{me^4}{a_0^3 \hbar^2} \pi(z, \sigma), \tag{3}$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius. At last, the critical density can be written in the form

$$N_c = \frac{1}{a_0^3} n\left(z, \frac{m}{M}, \sigma\right) \simeq \frac{1}{a_0^3} n(z, \sigma). \tag{4}$$

Usually the critical parameters are measured for chemical elements in normal states for nuclei, when σ is a fixed function of z: $\sigma = \sigma(z)$. The introduced dimensionless functions $\tau(z, \sigma)$, $\pi(z, \sigma)$ and $n(z, \sigma)$ under the condition $z \gg 1$ depend in this case only on the nucleus charge number z.

It is useful to mention, that for practical purposes, and taking into account the isotopic mass dependence of the critical parameters for small z, a more convenient (but also exact, since the functions $\tau(z, \sigma)$, $\pi(z, \sigma)$ and $n(z, \sigma)$ can depend on fundamental constants, e.g., m/m_p) representation of the critical temperatures can be written in the form

$$T_c = \frac{m_p e^4}{\hbar^2} \tilde{\tau}\left(z, \frac{m_p}{M}, \sigma\right), \tag{5}$$

where m_p is the proton mass and we introduced the appropriate energy unit $m_p e^4/\hbar^2 = 5.45 \cdot 10^{-4}$ Hartree $\simeq 172.1\,\mathrm{K}$. This value is more appropriate to the "typical" critical temperatures than the energy unit Hartree since
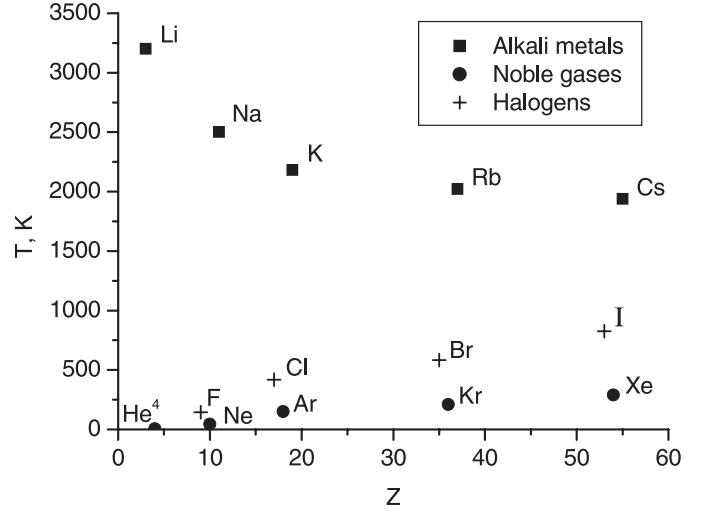
the critical points of elements are distributed in the interval of temperatures $\simeq (1\text{--}2 \cdot 10^4)\,\mathrm{K}$ [10]. The dependence on $m_p/M \sim 1/z$ (rather than m/M) gives the real parameter for influence of the isotopic mass difference on the critical temperatures. The similar "renormalization" can be also applied to the critical parameters P_c and N_c.

Consideration of the experimental data for the critical points for the liquid-vapor transition shows that the function $\tau(z)$ is a rapidly varying function of the variable z (e.g., for Ar ($z = 18$) and K ($z = 19$) the critical temperatures are $150.69\,\mathrm{K}$ and $2.18 \cdot 10^3\,\mathrm{K}$, respectively). These rapid changes are demonstrated in fig. 2, where the critical points for three groups of elements (alkali metals, noble gases and halogens) are drawn.

One can assume that these rapid "irregular" changes in the function $\tau(z)$ have the same physical nature as spasmodic changes in the first ionization potential $I(z)$ and valency $v(z)$ which are conditioned by sequential filling of electron shells in the atomic model of matter. The model, based on these variables has been described in the review paper [11]. The model of quasiatoms with overlapping valent electron shells has been considered and successfully applied to find the approximate effective van-der-Waals–type equation for plasma-like systems. On this basis the critical points of certain metals have been approximately found by use as the fitting parameters the ionization potential I and valency z_0. However, it should be emphasized that the ionization potential and valency are the approximate characteristics for systems with a strong Coulomb interaction. Therefore, the model and assumptions in [11] have a limited and approximate character. Even for alkali metals the scaling rule $T_c \sim I_1$ [11], where $I_1(z)$ is the first ionization potential of the atom in a rarefied gas, is fulfilled with an accuracy of only 20 percent. For other groups of elements, when the model of the overlapping quasiatoms is not applicable, this similarity does not exist even approximately. For example, the

critical temperatures for noble gases and halogens increase with z (fig. 2), although the ionization potentials $I_1(z)$ are the decreasing function of z [10]. The interesting observation is that, according to the experimental data [10], these elements are molecular near the critical points, excepting iodine, which is in the atomic state. Nevertheless, this crucial change of structure has no evident influence on the regular increase of the critical temperatures with increasing nuclear charge z.

As is shown in the present letter, the exact values of critical parameters for all elements should be constructed on the variables me^4/h^2 (or $m_p e^4/h^2$), nuclear charge z and σ.

In one group of the periodic Mendeleev Table of chemical elements, the characteristic functions $\tau(z)$, $\pi(z)$ and $n(z)$ are smooth functions of the variable z. Figure 2 demonstrates the smooth z-dependence of critical temperatures $T_c(z)$ for each of the groups: alkali metals, noble gases and halogens.

The representations (1), (3), (4), (5) are exact, although, in such a general form they cannot provide prediction of the critical points of some elements on the basis of the known critical points of other elements. For such predictions, methods for calculating or physical models of the functions $\tau(z)$, $\pi(z)$ $n(z)$ should be developed.

For more complicated systems (substances), which contain a few species of nuclei, relations for the critical parameters (1), (3) and (4) can be generalized. As is known for, *e.g.*, a two-component system (which has two different types of nuclei with the charges z_1 and z_2) the critical points for the case of two coexisting phases can place on some curve in the space P, T, x, where concentration $x = N_1/(N_1 + N_2)$. Here N_1 and N_2 are the quantities of the nuclei with the charges z_1 and z_2 respectively. For this case the dimensionless functions τ, π contain the additional variable x.

Useful information can be obtained already within the existing model approximations. As an example, let us consider the van der Waals theory. As is known the relation

$$P_c = \frac{3N_c T_c}{8}, \tag{6}$$

follows from this theory.

Although relation (6) is found from the classical and empirical approach, it can be used within the range of its practical applicability to obtain the approximate relation between the functions $\tau(z)$, $\pi(z)$ $n(z)$ for $z \gg 1$. The van der Waals model leads to the relation

$$\pi(z) = \frac{3}{8}\, n(z)\tau(z). \tag{7}$$

Similarly, the modern model theories of the equation of state and critical points of matter (see, *e.g.*, [12] and references therein) can be used to approximate the unknown functions $\tau(z)$, $\pi(z)$ $n(z)$ according to the known experimental data and the periodic Mendeleev table of chemical elements. However, this is not the problem of this letter.

The theory and conclusions of this letter are based on the assumption of gravity-independent critical parameters for CS (influence of an external gravitational field is negligible). This scenario is based on a small value of gravitational force in comparison with the forces of electromagnetic nature. The numerical calculations [13–15] of the state diagram as well as theoretical argumentation [16] confirm, in general, this approach.

As follows from the basic relations (1)–(5) *the parameters of the critical points are the quantum expressions which have not a classical limit or classical analogue.* In this connection, the general question, outside the frameworks of this letter, arises about the classification of the physical characteristics of the Coulomb matter into those having a classical limit and those that do not.

<div align="center">* * *</div>

REFERENCES

[1] Lotfi F., Vrabec J. and Fisher J., *Mol. Phys.*, **76** (1992) 1319.
[2] Charpentier I. and Jakse N. J., *Chem. Phys*, **123** (2005) 204910.
[3] Kraeft W.-D., Kremp D., Ebeling W. and Ropke G., *Quantum Statistics of Charged Particle Systems* (Akademie-Verlag, Berlin) 1986.
[4] Ebeling W., *Ann. Phys. (Leipzig)*, **19** (1967) 104.
[5] Lieb E. H. and Lebowitz J. L., *Adv. Math.*, **9** (1972) 316.
[6] Lebowitz J. L. and Pena R. G., *J. Chem. Phys.*, **59** (1973) 1362.
[7] Bobrov V. B. and Trigger S. A., *Bull. Lebedev Phys. Inst.*, **37**, issue No. 2 (2010) 35.
[8] Bobrov V. B., Trigger S. A., van Heijst G. J. F. and Schram P. P. J. M., *EPL*, **90** (2010) 10003.
[9] Bobrov V. B. and Trigger S. A., *J. Phys. A*, **43** (2010) 365002.
[10] Kikoin I. K. (Editor), *Tables of Physical Values* (Gosatomizdat, Moscow) 1976.
[11] Likalter A. A., *Usp. Fiz. Nauk*, **170** (2000) 831.
[12] Apfelbaum E. M. and Vorob'ev V. B., *J. Phys. Chem. B*, **113** (2009) 3521.
[13] Linkoln R. C., Kolivad K. M. and Ghate P. B., *Phys. Rev.*, **157** (1984) 483.
[14] Daw M. S. and Baskes M. I., *Phys. Rev. B*, **29** (1984) 6443.
[15] Aleksandrov T., Desgranges C. and Delhommelle J., *Fluid Phase Equilib.*, **287** (2010) 79.
[16] Anisimov M. A., *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, Philadelphia) 1991.