

For Noble Gases, Energy is Positive for the Gas Phase, Negative for the Liquid Phase

ASANUMA Nobu-Hiko*

An independent researcher without any research affiliation

We found from experimental data that for noble gases, energy is positive for the gas phase, and negative for the liquid, at least almost exactly. The line $E = E_c$ in the supercritical region is found to lie close to the Widom line.

Nature of the cited experimental data—As “experimental” data, we rely on NIST Chemistry WebBook data on fluids.¹⁾ In fact it’s not true experimental data, but the output of the program “REFPROP” which computes model equations, of which parameters are fit to the result of experiments done in various conditions, ranging from low to high temperature and pressure, and near and far from the critical point. In addition, models differ from substance to substance. Thus accurate error estimate is not available.²⁾ However, we are sure of our qualitative conclusions.

The lower bound of the temperature at that REFPROP provides data is T_{tp} , the triple point temperature, and for He, the λ -point temperature.

The sign of the energy determines the phase—What distinguishes the gas phase from the liquid phase? For noble gases, we declare that it’s the sign of the energy E :

$$E > 0 \text{ for gases, } E < 0 \text{ for liquids.} \quad (\Xi)$$

It’s because a gas is an unbound state, so it cannot be $E < 0$; otherwise, it would condense. Similarly, if $E > 0$, a liquid could not be a bound state. Of course, this argument is mean field theoretic—at best. Actually it’s too crude, and we cannot justify it logically. However, as we will see from experimental data, it is almost correct, if not exact. This fact somehow seems to have been unnoticed,^{3,4,7)} despite its simplicity and decisive power. If we write $E = K + U$, where K is the kinetic energy and U is the interaction energy, the rule Ξ can be restated as $K \geq |U|$. Laxer explanations like “ $K \gg |U|$ for gases, $K \ll |U|$ for solids, and $K \approx |U|$ for liquids” are on the other hand common.

We now define the zero of the energy. For noble gases, we safely ignore internal states, i.e. thermal excitation of electrons.⁸⁾ Then the natural definition is to take $E = 3/2Nk_B T$ at dilute limit, and we use this in this letter. For molecules, the internal degrees of freedom, namely ro-vibrational modes, exist. Intermolecular interactions depend on the internal states, or in other words, it is not possible to define the quantity U separate from internal states.

If Ξ is correct on the saturation curve (gas-liquid coexistence curve), it is clear that it extends to the almost entire (T, p) range, where p is pressure, except the supercritical region, where gas and liquid are no longer distinct. It’s because specific heat is positive, and on the isotherm $\partial E / \partial p < 0$ if the pressure is not too high (but in that case probably the system crystallizes), since the more dilute a fluid is, atoms feel the less attractive force. We are not sure for the region $T < T_{tp}$

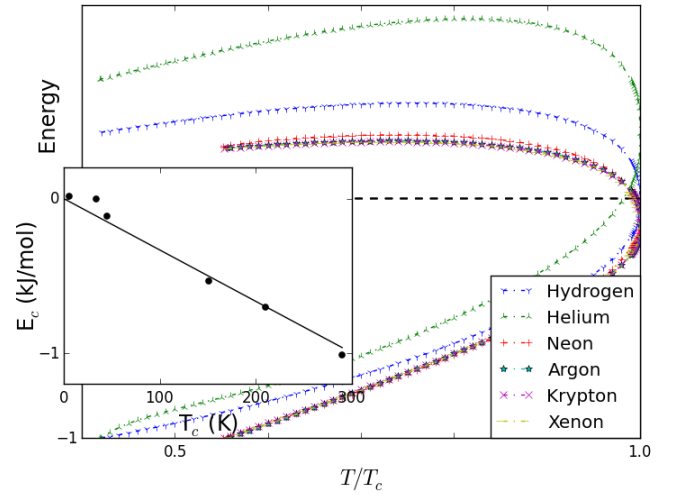


Fig. 1. (Color online) The energy of 5 noble gases and H₂ on the saturation curve. The upper curve is of the gas phase, and the lower of the liquid. Horizontal dashed line is for $E = 0$. Inset shows the E_c and T_c for these 6 fluids, and the line is for $E = -0.4Nk_B T$.

for which REFPROP doesn’t provide the data.

In Fig. 1 we show the experimental data of the energy of gas and liquid on the saturation curve for 5 noble gases. We calibrated the zeros of energy from the data at $p = 0$ MPa,⁹⁾ $T = T_c$, the critical temperature. At these points, $|C_v/(3/2Nk_B) - 1| < 10^{-3}$ for all available substances, where C_v is the constant-volume specific heat, so this extrapolation is acceptable. The energy in the plot is so scaled that the energy of liquid at the triple point is -1 .¹⁰⁾ As it can be seen, Ξ is satisfied except the vicinity of the critical point. Helium is the worst case, where it only holds for $T/T_c < 0.98$, and for the rest, as far as $T/T_c < 0.994$. Considering the inherent uncertainty of REFPROP data and experimental difficulty, this agreement is remarkable.

In this figure, the curve for H₂ is included, because for $T \leq T_c$ internal excitations are almost frozen.¹¹⁾ From the WebBook it’s not clear if it is true equilibrium hydrogen, or “normal hydrogen”, i.e. the 3:1 mixture of orthohydrogen and parahydrogen. Even if it is normal hydrogen, our claim remains valid. In that case, an orthohydrogen molecule should be considered as stable, not an excited state of parahydrogen, so still the zero of the energy is determined as $E = 3/2Nk_B T$ at $T = T_c, p = 0$. The claim Ξ applies not only to pure substances, but also to mixtures.

Helium is to some extent a quantum fluid on the saturation

*phys.anh@z2.skr.jp

curve, since $\lambda^3\rho = 0.57 \sim 1$ at the critical point, where λ is the thermal de Broglie wavelength and ρ is the number density. But it's common to both classical and quantum mechanics that boundness is determined by the sign of the energy, so it is not necessary to modify Ξ for this case.

If Ξ is exact, it means E_c , the energy at the critical point, is equal to 0. In any case, the situation is that $E > E_c$ for gas, and $E < E_c$ for liquid for all available REFPROP data.

In the inset of Fig. 1 we plot E_c and T_c of the same 6 fluids, together with the line $E = -0.4Nk_B T$, which is “fit by eye.” We're tempted to say that this fit is satisfactory, so indeed $E_c \neq 0$, but we avoid to draw any conclusion. For example in dilute limit experiments the contribution from the atom's interaction with the container wall becomes more significant.

The line $E = E_c$ in the supercritical region and Widom line—For this dozen years or so, the notion of the “Widom line”¹²⁾ has been discussed. It's defined as the line of sharp maximum of C_p , the constant pressure specific heat, in the supercritical region, starting from the critical point. More precisely, the C_p divergence at the critical point does not form a round peak, but on each isothermal and isobaric line near the critical point, a sharp C_p maximum exists, and by connecting those maxima, a “ridge” is formed, and it is the Widom line. It is also characterized as the collection of maxima of various thermodynamic response functions. Even though the validity of the Widom line notion is questioned,¹³⁾ there is no problem as long as we consider an area close enough to the critical point.

We can not tell if E_c is exactly = 0, but the question if the line $E = E_c$ is still meaningful in the supercritical region is natural, possibly representing a crossover, dividing liquid-like and gas-like behavior.¹⁴⁾ As shown in Fig. 2, we found that the line $E = E_c$ lies near the Widom line, in the region of low enough temperature where the Widom line can be recognized without ambiguity. This fact does not seem to be known before. We plotted also the line of C_v maximum. When the system moves far away from the critical point, C_v maximum disappears, and the Widom line may not be well-defined there. In that region, the line $E = E_c$ departs from the C_p maximum line. We give the plots of xenon and neon in Fig. 2, but our result applies to hydrogen, argon and krypton, too. We cannot assert anything on Helium: Data close enough to the critical point are not provided by REFPROP; for the region with data, the line $E = E_c$ and C_p maximum do not agree well, and C_v maximum cannot be observed.

Discussion and outlook—The rule Ξ , which we judge almost correct, raises many questions. First of all, is it exact? Experimental verification will be difficult, so computer simulation should prove it—rather, a disproof will be easier than a proof. If correct, it must be so for any short-ranged interactions, independent of dimensionality.¹⁵⁾ Then it can be used for precision check in simulation, and for calibration in experimental data analysis.

If the claim Ξ is exact, then $K = |U|$ at the critical point. This indicates symmetry. Even if not exact, we can say there is approximate symmetry. What symmetry is it precisely? Are there any system for which exactly $E_c = 0$? If $E_c \neq 0$, how can it be calculated theoretically? (In that case, $E_c = 0$ can be used as the mean-field, zeroth-order value.) The property Ξ implies $\partial E / \partial N \rightarrow 0$ in thermodynamic limit at the critical point. Intuitively E being = 0 is the edge of boundness, and

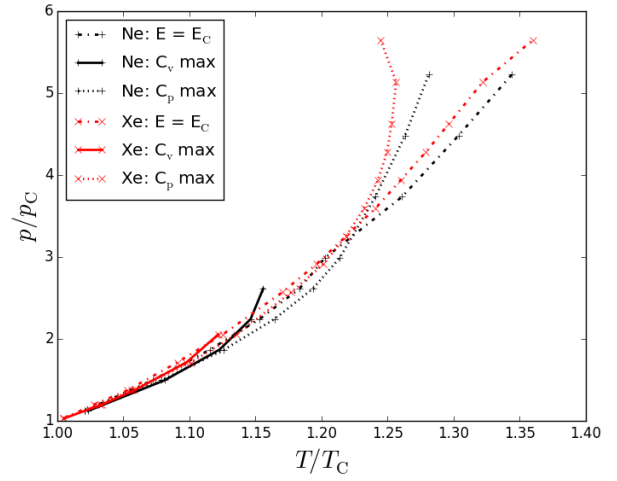


Fig. 2. (Color online) The lines of C_v and C_p maximum and $E = E_c$ in the supercritical region for neon and xenon.

is also the point where a dimensionful constant vanishes, so it seems to be related to the scale invariance of the critical point. However the condition of $E = 0$ is not sufficient, since the line of states $E = 0$ do exist in the supercritical region too.

As we cautioned, the statement Ξ is very rough. It also treats the energy from the viewpoint of mechanics, but the energy of a fluid is a thermodynamic quantity, the (canonical) ensemble average, which is not conserved. Definition of boundness is very involved, if ever possible, for a many-body case. At the same time, treatment in microcanonical, or dynamical system theory may be possible.

Yet, Ξ 's incisive simpleness allows a clear understanding, or new definitions of gas and liquid. For example, consider the solution of solute A and solvent B. Then A is gaseous inside the solution, and B is liquid. Let us write the Hamiltonian H schematically as:

$$H = K_A + K_B + U_{AA} + U_{BB} + U_{AB},$$

where K_A is the kinematic energy of A particles, U_{AB} is the potential between A and B particles, and so on. Now integrate out B's variables. Then we obtain the effective Hamiltonian H_{eff} which looks like:

$$H_{\text{eff}} = K_{\text{Aeff}} + \sum_i U_i,$$

where U_i is the i -body effective potential, which is = 0 when all particles are infinitely apart from each other. Then A is gaseous means $\langle K_{\text{Aeff}} \rangle + \sum_{i \geq 2} \langle U_i \rangle > 0$, where the bracket is the thermal average. But since the whole system is still liquid, $\sum_{i \geq 0} \langle U_i \rangle < -\langle K_{\text{Aeff}} \rangle < 0$. (So, $-\langle U_0 \rangle$ is similar to the work function of metals, although in the current case the temperature is finite.) If A and B demixes so that the A-rich phase and the B-rich phase coexist, then A is gaseous in B-rich phase and liquid in A-rich one, and so on. It seems almost obvious, in reality a mere heuristic though, that the critical point of binary fluid consolution belongs to the same universality class as the gas-liquid's one.

A still easier example is the theory of dilute solutions, found in every textbook of thermodynamics. When the author was a student, he felt the appearance of the gas constant R was sudden and absurd. “Interaction is strong, the ideal gas

has nothing to do here, no?” It is the consequence of thermal average,¹⁶⁾ but we have an alternative view. In fact, solute is a gas trapped in the solvent, and in dilute limit, it becomes an ideal gas, because the interaction between solute molecules can be neglected. The mean free path of the bare solute molecule does not matter.

The rule Ξ imposes a limit on the spinodal curve, too. The spinodal curve is difficult to define theoretically. In textbooks, it is often explained mean-field theoretically as “the” inflection point of (the metastable branch of) free energy.¹⁷⁾ More careful definition is as the occurrence of negative compressibility for *all* wavelengths,¹⁸⁾ but it still suffers from that it may not be well defined due to metastability. We know however that the supercooling of gas and superheating of liquid cannot exceed the line $E = 0$. It is only a necessary condition, but the energy of the system is always defined. At the very least it explains that the two spinodal curves do exist for gas-liquid transition.

In molecular fluids, ro-vibrational degrees of freedom mix with intermolecular interactions. In Ξ translational degrees of freedom are concerned, so to extend Ξ to molecular fluids, we have to extract and separate them from internal degrees of freedom. It must be possible, since critical points exist also for molecular fluids, but we don’t know how to do it.

The assertion Ξ also hints something on the notion of cluster and percolation, which is easiest to describe from the standpoint of Monte Carlo simulation.¹⁹⁾ “Cluster algorithms” in general update all variables in a group, called cluster, but we call it “updating cluster” (UC). There is another cluster, which percolates at the critical point, which we call PC. PC is used to locate the critical point in “invaded cluster algorithm”. In Ising model, PC is the set of parallel spins which are connected. It is also generalized for example to Widom-Rowlinson model, but not for general fluids. UC is a subset of PC, and it has to satisfy detailed-balance. It is usually chosen to make the algorithm most efficient, but it is not necessary. Because percolation is deeply connected to criticality, the current situation where PC is lacking for general systems is unsatisfactory. Our questions are, how to define PC for general systems, and does UC have a physical meaning beyond a mere computational utility? By answering that, it may be possible to obtain more insight on opaque relations between the lattice-gas model and fluids.

In physics, models, even toy models, have served to make various advances, and we inevitably pose this question: Is there any one-particle, central force system, classical or quantum, which has a phase transition at $T = T_c$, and for $T \geq T_c$, $E \geq 0$? For classical cases, natural order parameters are $\langle 1/r \rangle$ and $\langle U \rangle$.

The fact Ξ also suggests the energy may be an order parameter. What we have discovered recently is that the energy difference ΔE on the saturation curve is universal, by being $\propto (T_c - T)^a$, where the exponent a is independent of substances, including molecular fluids.²⁰⁾ We pointed out that E is a quantity that can be defined purely in mechanics, without thermodynamics. But not only ΔE , but also $\Delta 1/V$, the density difference, is an order parameter along the saturation curve, as known very well, and V is a pure mechanical quantity, too. Some mysterious symmetry may be hidden.

- 1) E. W. Lemmon, M. O. McLinden and D. G. Friend, “Thermophysical Properties of Fluid Systems” in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, (retrieved Jan - Mar, 2016). This is the citation style the authors require, as if it is a part of a book, but it really is provided as a website at: <http://webbook.nist.gov/chemistry/fluid/>.
- 2) E. Lemon, *Answers to Frequently Asked Questions*, URL: http://www.boulder.nist.gov/div838/theory/refprop/Frequently_asked_questions.htm (2016). This page is the faq of REFPROP 9. To be precise, the data of Ref. 1 we use was the output of REFPROP 7.
- 3) V. V. Brazhkin, and K. Trachenko, *Phys. Today* **65**, 68 (2012). The very title of this article is: “What separates a liquid from a gas?”
- 4) We couldn’t find any mention to the statement Ξ in statistical physics textbooks⁵⁾ nor in liquid theory textbooks.⁶⁾
- 5) For example R. K. Pathria, P. D. Beale, *Statistical Mechanics* (Butterworth-Heinemann, Oxford, 2011) 3rd ed.; M. Kardar, *Statistical Physics of Particles* (Cambridge University Press, Cambridge, 2007); J. P. Sethna *Statistical Mechanics: Entropy, Order Parameters, and Complexity* (Oxford University Press, Oxford, 2006); P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, 1995); N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Addison-Wesley, Reading, 1992).
- 6) For recent textbooks, see for example W. Schirmacher, *Theory of Liquids and Other Disordered Media* (Springer, Cham, 2014); J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Elsevier, London, 2006) 3rd ed.
- 7) The sole exception seems to be A. Elsner, *Physica B* **407**, 1055 (2012), but the arguments of this article do not make sense. In Sect. 2, they “prove” that the zero of the internal energy in thermodynamics is not arbitrary. This is of course absurd. What’s really proven is that it’s not possible to assign arbitrary zeros to each of subsystems of one entire system. In spite of this assertion, they do not define the zero of the energy, nor does it mention molecule’s internal excitations. Then in Sect. 4, they assume that the sign of energy cannot change within one phase, and concludes $E > 0$ for a gas, $E = 0$ at the critical point, etc.
- 8) The first excitation energy of, for example, He is about 20eV, and that of Xe is 8.3eV. Thermal excitations are not to be confused with *virtual* electron states which give rise to the interatomic interaction U .
- 9) REFPROP does provide (extrapolated?) data down to 0MPa.
- 10) With this rescaling, for curious readers we confirm that the curves of Ne, Ar, Kr and Xe are almost identical.
- 11) According to REFPROP, $|C_v/(3/2Nk_B) - 1| \approx 10^{-4}$ at $T = T_c$, $P = 0$ MPa. It’s because hydrogen is an exceptional molecule by having a large moment of inertia. This is not true even for D₂, deuterium.
- 12) Limei Xu, Pradeep Kumar, S. V. Buldyrev, S.-H. Chen, P. H. Poole, F. Sciortino, and H. E. Stanley, *Proc. Natl. Acad. Sci. USA* **102**, 16558 (2005).
- 13) V. V. Brazhkin, Yu. D. Fomin, V. N. Ryzhov, E. E. Tareyeva, and E. N. Tsiok, *Phys. Rev. E* **89**, 042136 (2014).
- 14) A line of such crossover is already reported, dubbed “Frenkel line.” See V. V. Brazhkin, Yu. D. Fomin, A. G. Lyapin, V. N. Ryzhov and K. Trachenko, *Phys. Rev. E* **85**, 031203 (2012). In fact, we feel that this article is more convincing than those on the Widom line,¹²⁾ but we choose to compare $E = E_c$ line with the Widom line because of the data availability.
- 15) Even though the physics of noble gases is well described by Lennard-Jones potential, the contribution of the three-body forces has to be taken into account to reproduce the third virial coefficient of real noble gases. See N. E. Cusack, *The Physics of Structurally Disordered Matter: an Introduction* (Adam Hilger, Bristol, 1987) Sect. 5.1.
- 16) Thermodynamics of dilute solution can be derived within pure thermodynamics, without the need of statistical mechanics. See for example E. Fermi *Thermodynamics* (Prentice-Hall, New York, 1937; Reprint: Dover Publications, New York, 1956), Chap 7.
- 17) See for example Chaikin and Lubensky in Ref. 5, Sect 8.7.3, or G. R. Strobl *Condensed Matter Physics: Crystals, Liquids, Liquid Crystals, and Polymers* (Springer, Berlin, 2004; Translated from German) Sect. 3.4.3.

- 18) See A. Parola and L. Reatto, Mol. Phys. **110**, 2859 (2012), Sec. III C.
19) See for example D. P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics* (Cambridge University Press, Cambridge, 2015) 4th ed., Sect 5.1.
20) Asanuma N.-H., submitted to J. Phys. Soc. Jpn.