Universality of Energy Difference and Latent Heat in Gas-Liquid Phase Transition

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We found universality in energy difference ΔE and latent heat $T\Delta S$ on the gas-liquid phase coexistence curve, expressed as power laws which are valid down to triple points, with exponents which are independent of fluids.

A well-known feature of the gas-liquid phase coexistence curve, a.k.a. the saturation curve (SC), is that

$$\Delta\rho \propto t^{\beta}, \tag{1}$$

where the exponent β is a constant independent of fluids. Our definition of symbols is given in Table I. In this formula subleading terms, known as "correction-to-scaling",[1] are ignored. But what is striking is that Eq. (1) is correct not only in the asymptotic region, namely the $t \to 0$ limit, but also on the entire saturation curve, down to the triple point, as shown in Fig. 1.

We recently reported[2] that for noble gases and H_2 it almost exactly holds that E is always > 0 for the gas phase, and < 0 for liquid, with a natural definition of the zero of E. This motivates us to seek the possibility that E is an order parameter. If $\Delta E \propto t^a$ for some a on SC, similar relation(s) have to be satisfied for $T\Delta S$ and/or $p\Delta V$ $(= -\Delta F)$ in order to cancel the ΔE's singularity as $t \to 0$, because on SC,

$$\Delta G = 0 = \Delta E - T\Delta S + p\Delta V, \tag{2}$$

In fact in 1984 Torquato et al. reported[3] that $T\Delta S$, the latent heat, shows a remarkable property that the curves $T\Delta S/(T\Delta S)_{\rm tp}$ of 20 fluids plotted against $\tau := (T_c - T)/(T_c - T_{\rm tp})$ are well approximated by a single curve on the entire SC. (See Fig. 1 for $T\Delta S/(T\Delta S)_{\rm tp}$ of 74 fluids given in Ref. 4.) Their result is known to some extent from engineering interest, but seems to be virtually unknown in the communities of liquid and field theories.

We noticed that they missed a crucial point; the normalization is done with τ, not with the reduced temperature $t = 1 - T/T_c$, but their result applied well for example to water, n-nonane, and argon, of which solid structures are not the same, meaning that the triple point is not universal. So $T\Delta S$ should be $\propto t^b$ for a universal constant b, that is, it can be expressed by a single power of t, in order for various $T\Delta S/(T\Delta S)_{\rm tp}$ curves to collapse into one. This argument is indeed correct, as shown in Fig. 1.

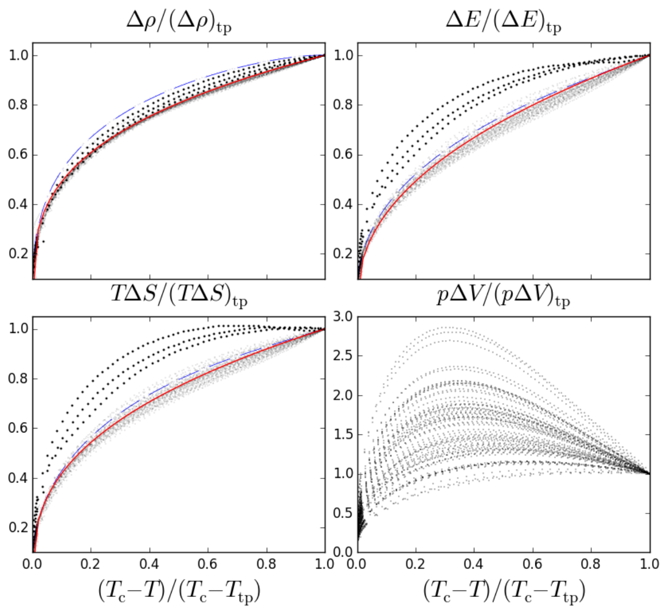

Fig. 1. (Color online) Plots of $\Delta\rho, \Delta E, T\Delta S$ and $p\Delta V$ of 74 fluids,[4] normalized to 1 at the triple point. The solid lines mean $\Delta\rho \propto t^{0.31}, \Delta E \propto t^{0.44}$, and $T\Delta S \propto t^{0.38}$. Except the plot of $p\Delta V$, the data of He, H_2, and D_2 are represented by specially thick dots, and those of water by a dashed line; all other fluids are by dots. In the $\Delta\rho$ curves all substances except these 4 are almost indistinguishable. We omit the plot of parahydrogen, which is similar to that of hydrogen. Notice these exponents are *not* critical exponents. See the text for the details.

Table I. Definition of symbols.

p, T	Pressure and temperature.
V, E, S, F, G	Volume, energy, entropy, Helmholtz energy and Gibbs energy per particle.
ρ	Particle density.
t	$(T_c - T)/T_c$, the reduced temperature.
τ	$(T_c - T)/(T_c - T_{\rm tp})$.
$X_{\rm liquid}, X_{\rm gas}$	Quantity X of the liquid and gas phases on the saturation curve.
$X_c, X_{\rm tp}$	Quantity X at the critical point and the triple point.
$\Delta X(t)$	$X_{\rm gas}(t) - X_{\rm liquid}(t)$. The symbol t is often suppressed.

We now comment on the nature of the "experimental" data of fluids cited in this letter. We rely on NIST Chemistry WebBook data on fluids.[4] Actually they are 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, near and far from the critical point. In addition, models differ from substance to substance. As a result, accurate error estimate is not available,[5] so we don't try to draw quantitative conclusions. However, we are sure of our qualitative results. The lower bound of the temperature at that REFPROP provides data is $T_{\rm tp}$, and for He, the λ-point temperature. They provide data of 75 fluids. In Fig. 2, points of 8 fluids for t down to 1×10^{-3} are shown,

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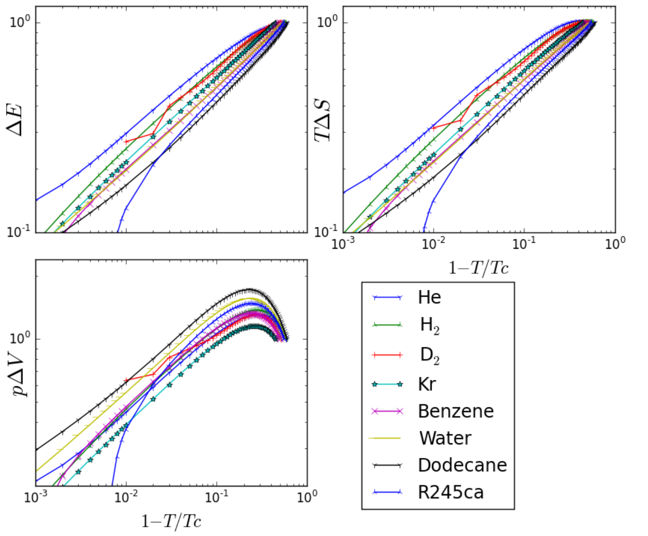

Fig. 2. (Color online) Log-log plots of $\Delta E, T\Delta S$ and $p\Delta V$ of several fluids.

but that precision is not available for every fluid.[6] It can be seen the behavior of some fluids appear heretic for $t \ll 1$. They are probably not experimental facts, but a reflection of REFPROP's limitation.

In Fig. 1 ΔE and $p\Delta V$ are also plotted. We can see the following points: (i) Matches of curves of various fluids to a single curve is very good for ΔE and $T\Delta S$, and extremely good for $\Delta\rho$, (ii) but not at all possible for $p\Delta V$. (iii) Then this non-universality of $p\Delta V$ has to be canceled by ΔE and $T\Delta S$, reducing their substance independence to some extent. (iv) ΔE and $T\Delta S$ curves are well approximated in the form t^x on the "entire SC" (see below) down to the triple point, where x is independent of substances. (v) The ΔE and $T\Delta S$ curves of He, H_2, and D_2 (deuterium) differ very much from the rest.[7]

We use the term "the entire SC" to mean the entire SC *except the critical region* for convenience. The exponents of the curves t^x in Fig. 1 are chosen to fit on the entire SC, but as we will see soon, their values differ from the critical exponents.

The above mentioned non-universal characters (ii) and (v) are nonetheless partial. As can be seen in Fig. 2, the log-log plots of these quantities are almost parallel in the range $10^{-2} \lesssim t \lesssim 10^{-1}$, including He etc. Thus we attempted fit of power law t^x to $\Delta\rho, \Delta E, T\Delta S$, and $p\Delta V$ in log-log form by least square method, in two ranges of t, for $0.01 \le t < 0.1$ and $0.1 \le t \le t_{tp}$.[8] We excluded the latter range from $p\Delta V$, and for He, H_2, D_2, also from ΔE and $T\Delta S$, because of the lack of universality. The result is shown in Table II. We also fitted $p_c - p$ to a power law, which we will use later.

As we have said, we should be careful about the quantitative reliability of these values. Even so, we draw these conclusions: (i) The value $\beta = 0.36(3)$ for $0.01 \le t < 0.1$ agrees with the widely accepted critical exponent. Its standard deviation is comparable to those of a and b. For $0.1 \le t$, the standard deviations are smaller. There *does* exist universality for ΔE and $T\Delta S$, too. (ii) As we said a should be $= b$ as $t \to 0$, and the result of the range $t < 0.1$ does not contradict, being $a, b \approx 0.4$. (iii) Exponents differ considerably between the two t regions. It may be due to crossover, but we do not exclude other technical reasons like experimental difficulty or model artifact of REFPROP. (iv) So the exponents for $t < 0.1$ can be said as critical exponents, and there're also other universal exponents for the entire SC. (v) We are not sure of $p\Delta V$. As $t \to 0$, $c = \beta$ should be satisfied since $-p\Delta V = pV_{\text{liquid}}V_{\text{gas}}\Delta\rho$ and $0 < pV_{\text{liquid}}V_{\text{gas}} < \infty$, but c looks closer to a and b than to β. We do not pursue this issue in this letter.

Table II. (Critical) exponents, definitions, means and standard deviations of 74 fluids, fitted in two ranges of t.

Exp.	of ...	$0.01 \le t < 0.1$		$0.1 \le t \le t_{\text{tp}}$	
		mean	st. dev.	mean	st. dev
β	$\Delta\rho$	0.355	0.028	0.312	0.013
a	ΔE	0.400	0.028	0.436	0.023
b	$T\Delta S$	0.398	0.029	0.381	0.022
c	$p\Delta V$	0.384	0.034	-	
d	$p_c - p$	0.897	0.033	-	

Discussion—If our result $T\Delta S \propto t^b$ as $t \to 0$ is correct, it predicts one point, but first we give a brief survey of prominent theories. (i) Within field theory, ϵ-expansion to the order ϵ^3 has been done[9] to work out the corrections to scaling[1] that is specific to fluids and is lacking in Ising model. But their validity is unclear, because of its poor convergence and of experimental difficulty.[10] In addition, the relation of the model to real fluids cannot be explained within pure field theory. (ii) Hierarchical reference theory[11] (HRT) is a successful theory, by unifying liquid theory and non-perturbative renormalization group. It enables various numerical calculations, near and far from the critical point. (iii) Scaling theory on gas-liquid criticality is, although hypothetical, practical phenomenology, which can supplement other theories, and is still advancing. "Complete scaling",[12,13] an improved theory over conventional "revised scaling",[14] has been studied since around 2000.

We now compare what is said about the asymptotic pressure on SC, of which common understanding is lacking. (i) From our result $T\Delta S \propto t^b$, with $b \approx 0.40 > \beta$, it follows that $\Delta S \propto t^b$ as $t \to 0$. By the Clausius-Clapeyron formula, $p_c - p \propto t^{1+b-\beta}$. (ii) NIST WebBook[4] cites Refs. 15 and 16 for model equations of R125 and N_2 respectively, and therein the leading term of $p_c - p$ is taken to be $\propto t$ without stating the reason. (iii) However NIST WebBook does not clarify which equations in cited literature they really utilize, and probably the model equations we have just mentioned are not used. We found $p_c - p \propto t^d$ where $d = 0.90(3)$ for REFPROP's fluids. (iv) In complete scaling papers[17] it is asserted that $p_c - p \propto t^{2-\alpha}$, where the critical exponent $\alpha \approx 0.11$ is defined as $C_v \propto t^{-\alpha}$, C_v being the constant volume specific heat. However, this conclusion can be wrong. Their derivation is as follows: From the Yang-Yang relation,[18] $\rho C_v/T = \left(d^2p/dT^2\right)_{\text{SC}} - \rho\left(d^2\mu/dT^2\right)_{\text{SC}}$. Complete scaling predicts the singularities of p and μ have to be common. Then they assumed that their leading singularity is $\propto t^{2-\alpha}$. But it is possible that p and μ have stronger singularities, like $t^{1+b-\beta}$ we saw, if they are canceled in the Yang-Yang relation. The last condition requires yet another special relation, and the singularities of p and μ are one of their main results, so this point deserves attention.

We note that the universality of ΔE and $T\Delta S$ is surprising and uncanny because molecules have the energy of internal states, i.e. ro-vibrational energy, and there are a variety of them. Compare for example dodecane, water and noble gases.

At the same time, internal states mix with intermolecular interactions. This complicates, but it clearly must be taken into account.

Not only the universality of the exponents, but also the applicability of power law form t^x to the entire SC is also puzzling, including the well known case of $\Delta\rho$. Scaling relations normally appear, as first envisioned by Widom,[19] near the critical point. The point we saw is of different nature. It is also interesting to compare it with scaling theories. Conventional "revised scaling" of gas-liquid criticality assigns a special role to the pressure p over T and μ (more precisely $p_c - p$ etc); complete scaling on the other hand treats these three variables on equal footing. (But we found t is a good parameter, or better than previously thought, on SC.) In both, and in renormalization group in general, scaling variables and their conjugate scaling operators are distinguished. But if ΔE and $T\Delta S$ scales as t^x—both asymptotically and on the whole SC—such distinction may not be valid.

Simultaneous power law behavior of these variables together with $\Delta\rho$ seems to suggest that something like symmetry or other ruling structure is hidden. This should be contrasted to ordinary first order phase transitions which are a mere coincidence of the free energy; both phases are "unaware" of each other, so to say.

Our starting point was that E may be an order parameter.[2] First we naturally investigated the spatial energy *density*, but we could not discover anything conclusive.

Gas-liquid transition was the first class of phase transitions where the universality was experimentally suggested. Guggenheim showed in 1945 that the curves of T/T_c vs ρ/ρ_c of 8 fluids along SC almost overlap each other.[20] (In hindsight, it was fortuitous. The true universality exhibits itself as $\Delta\rho \propto t^\beta$.) Despite the deepness of theoretical achievements in gas-liquid transition, the wideness of the range that the relation (1) holds remains to be a mystery. Even HRT cannot give a qualitative, simple explanation. Under such circumstances, more qualitative input should be welcome. We hope that our results encourage more advances in this field.

In summary, we found that ΔE and $T\Delta S$ on the saturation curve show universal behavior, in the sense that both are expressed by power laws t^x and the same exponents are shared by many fluids, which applies to a wide range of t down to the triple point. These exponents differ from the critical exponents, which are also independent of fluids for ΔE and $T\Delta S$.

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2) Asanuma N.-H., submitted to J. Phys. Soc. Jpn.
3) S. Torquato and P. Smith, J. Heat Transfer **106**, 252 (1984). Their main claim is $\Theta := T\Delta S/(T\Delta S)_{\mathrm{tp}}$ can be well expressed by polynomials of τ. However they are not *qualitatively* reliable and the success is only numerical, perhaps with overfitting. They wrote $\Theta = \sum_{1\le j\le 6} a_j \tau^{b_j}$, where $b_j = \{\beta, \beta+\Delta, 1-\alpha+\beta, 1, 2, 3\}$ and "β" $= 1/3$, "α" $= 1/8$, "Δ" $= 0.789 - \beta$, and the substance dependent coefficients a_j were chosen to fit to experimental data.

By definition, Θ should be $= 1$ at $\tau = 1$, i.e. the triple point, but for seven substances, the values significantly deviate from 1. For example, propane's curve of Θ coincides well with the other 13 fluids for $\tau \lesssim 0.7$, but in the rest interval it grows upward steeply. It's probably because they fitted the polynomials only in the region where experimental data are available. They say "less than half" fluids experimental data are not available at the triple point. They give the table of $T\Delta S$ at $\tau = 1$ but therein experimental data and values extrapolated by their polynomials are mixed, without clarifying which are which.
4) 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/`.
5) 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. 4 we use was the output of REFPROP 7.
6) The lower bounds of t except $t = 0$ are $> 1\times10^{-3}$ for these 5 substances: decafluorobutane, deuterium, parahydrogen, R115, and R245ca.
7) This may be due to quantum effect. For He, H_2, and D_2, $\lambda^3\rho$ at the triple point, where λ is the thermal wavelength, are 4.5, 0.8 and 0.2, respectively, much bigger than that of other substances.
8) For a practical reason about Ref. 4 web interface, evenly spaced 10 (at maximum) points of t, not τ, are used for each interval.
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15) See Sec 4.2 of E. W. Lemmon and R. T. Jacobsen, J. Phys. Chem. Ref. Data **34**, 69 (2005).
16) See Sec 2.6 of R. Span, E. W. Lemmon, R. T. Jacobsen, W. Wagner and A. Yokozeki, J. Phys. Chem. Ref. Data **29**, 1361 (2000).
17) See Eq. (35) in Ref. 13.
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19) B. Widom, J. Chem. Phys. **43**, 3898 (1965).
20) E. A. Guggenheim, J. Chem. Phys. **13**, 253 (1945).