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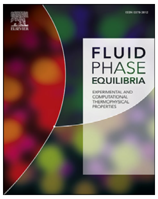

A theoretical analysis on enthalpy of vaporization: Temperature-dependence and singularity at the critical state

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Accurate evaluation of enthalpy of vaporization and its dependence upon temperature is crucial in studying phase transition and liquid fuel combustion. The theoretical calculation of enthalpy of vaporization based on Clapeyron equation involves the vapor-pressure-temperature correlation and the equation of state, and hence an explicit formula is unavailable. The formula for enthalpy of vaporization derived from the corresponding state principle, although in explicit form, is not valid over the entire temperature range. The fitting formulas for enthalpy of vaporization involves various fluid-dependent coefficients and hence are lack of theoretical generality. In this study, the formulas for enthalpy of vaporization are rigorously derived at both the reference and critical states. By appropriate weighing, we propose a composite formula for enthalpy of vaporization that has an elegant and compact form and is free of fitting parameters. Compared to the calculation based on equation of state, the composite formula predicts the evaluation of enthalpy with comparable or improved accuracy. The composite formula implies a unified relationship between normalized enthalpy of vaporization and normalized temperature, which substantiates the appropriateness of the function form of the composite formula.

1. Introduction

In most thermal engineering facilities, liquid fuels are used while chemical reactions occur in the gas phase. Therefore, vaporization of liquid fuel plays a crucial role during its combustion [1–3]. During equilibrium vaporization, a certain amount of energy, defined as enthalpy of vaporization (abbreviated as EoV hereinafter), must be supplied to facilitate the liquid molecules escaping from the restraint caused by intermolecular attractive forces [4]. The EoV shows considerable impact upon the vaporization rate: the lower the EoV, the higher the rate of vaporization [5].

During combustion process, the ambient pressure and temperature undergo noticeable growth. Supplying a proper ignition energy to the combustible reactants, ignition usually occurs at room temperature and atmospheric pressure [6,7]. While, as combustion proceeds, the product temperature and pressure could rise significantly due to the heat release from the exothermic reaction and the confinement of the combustion chamber. Specifically, for droplet combustion at near critical conditions, the exceeding reduction in both surface tension and enthalpy of vaporization, renders the vaporization and the subsequent combustion characteristics quite distinctive in comparison with the physical scenario under normal conditions [2].

Existing literature has shown that the EoV is a function of temperature and pressure [2,8]. In thermodynamics, the EoV appears in the Clapeyron equation, which interprets the phase equilibrium during vaporization, i.e.,

$$\frac{d\ln p_e}{d1/T} = -\frac{L}{R\Delta Z} \tag{1}$$

where p_e is the equilibrium vapor pressure, T the temperature, L the EoV, and ΔZ the compressibility factor ($Z = pV/RT$) difference between the saturated vapor and the saturated liquid. Equation (1) usually serves to interpolate the EoV in terms of vapor pressure data [8–14], which is more readily measurable through experiments. By numerically solving the Clausius-Clapeyron equation in terms of fugacity and appropriately considering the critical singularities, Hsieh et al. [2] calculated the EoV, which agrees well with experimental data over the whole liquid range.

The EoV can also be calculated analytically, and the mainstream approaches can be divided into three categories, i.e.,

(a) the direct calculation of EoV based on equation of state [15–19],

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(b) the formula for EoV based on Corresponding State Principle (CSP) [20–22],
(c) the formula for EoV by fitting with experiments [8,22,23].

With the help of equation of state that could interpret the PVT (pressure-molar volume-temperature) behavior of a fluid system over a wide range of thermodynamic states, covering from liquid regime to gas regime, the EoV can be directly calculated based on its conventional definition, i.e., the molar enthalpy discrepancy between saturated vapor and saturated liquid, yielding

$$L=\int_{V_m^l}^{V_m^v}\left[T\left(\frac{\partial P}{\partial T}\right)_{V_m}-P\right]dV_m+P_e\left(V_m^v-V_m^l\right) \tag{2}$$

where V_m^l and V_m^v denote the molar volumes of liquid and gas phases, respectively. The equilibrium state of vaporization, e.g., V_m's and P_e, can be calculated by simultaneously solving the equation of state respectively at liquid phase and gas phase iteratively according to Maxwell's equal area rule [19], and their temperature dependence shall be determined parametrically. Thus, Eq. (2) should not be regarded as an explicit formula for calculating EoV.

It is suggested that the Soave-Redlich-Kwong EoS [24]and Peng-Robinson EoS [25] are possible candidates because they could predict the densities of a pure substance in both liquid and gas phases with satisfactory accuracy. The method of calculating the EoV based on the EoS is briefly summarized in Appendix A.

The crossover theory takes into account of density fluctuation, which becomes divergently large at the critical state, in the mean-field thermodynamic models and hence is capable to describe the thermodynamic properties of a fluid both close to and far away from the critical state [26]. It is expected that adopting appropriate crossover-theory-modified EoS may result in improved accuracy in the calculation of enthalpy of vaporization in a relatively large neighborhood of the critical state. Nevertheless, the recursive process of using crossover theory tends to be more complicated than the calculation procedure by means of conventional cubic equation of state. Thus, it becomes hopeless to derive an explicit formula for enthalpy of vaporization in concise form based on crossover theory, and hence the corresponding massive calculation is beyond the scope of the present study.

The EoV is found to acceleratingly decay to zero as approaching the critical point, and in particular, the derivative of EoV with respect to temperature becomes infinitely large at the critical state [1,8,23,27]. A credible evaluation of EoV must involve the characteristic of critical state of the fluid and thus be established on the corresponding state principle. Pitzer et al. [20] derived a analytical formula for EoV in terms of reduced temperature and acentric factor ω, which interprets the impact of molecular non-sphericity on the VP-T relation, i.e.,

$$\frac{L}{RT_c}=7.08(1-T_r)^{0.354}+10.95\omega(1-T_r)^{0.456} \tag{3}$$

which is valid for $0.6<T_r<1.0$. Alternatively, Thek and Stiel suggested the Watson relation to predict the EoV [16,21], i.e.,

$$L=L_b\left(\frac{1-T_r}{1-T_{br}}\right)^{n_l} \tag{4}$$

where L_b is the EoV at the boiling temperature and T_{br} the reduced boiling temperature. The factor n_l shall be determined by fitting with experimental results, and a widely adopted value of n_l is around 0.38 [16,21]. The restricted validity range of Eqs. (3) and (4) can be attributed to that the theoretical foundation of CSP is the universality of critical state for various fluids [28–30].

The EoV could be fitted from experimental database alternatively. By comprehensive comparison of a huge experimental database, Majer and Svoboda [22] suggested a fitting formula for EoV in exponential form

$$L=A(1-T_r)^{\beta_f}\exp\left(-\alpha_f T_r\right) \tag{5}$$

where the parameters A, α_f and β_f depends upon the fluid type. Due to its wide application, those fitting parameters have been specified for hundreds of compounds [22] that are commonly used. Besides, a power-law fitting formula of EoV in terms of reduced temperature was proposed by Torquato and Stell [8,23], considering the behaviors of the EoV at both the regular state (remote from the critical point) and the critical state. Those fitting formulas [8,23] are presented in the form of

$$L=a_1\left(\frac{T_c-T}{T_c}\right)^{\beta}+a_2\left(\frac{T_c-T}{T_c}\right)^{\Delta+\beta}+a_4\left(\frac{T_c-T}{T_c}\right)^{1-\alpha+\beta}+\sum_{n=1}^{M}b_n\left(\frac{T_c-T}{T_c}\right)^{n} \tag{6}$$

where α and β are critical exponents describing the singularities associated with the specific heat and density discrepancy, respectively [29,30]. The fitting formulas Eq. (6) gives quite accurate prediction of EoV over the entire liquid range of the substance [8,23]. Due the presence of non-universal parameters, the fitting formulas are incapable of revealing physical insights and somewhat lack of generality.

From the aspect of theoretical study and fast evaluation, it is of high value to derive an analytical formula for EoV, which satisfies: (1) validity over the entire liquid range with acceptable accuracy; (2) concise expression revealing the dependence of EoV on temperature in explicit form; and (3) free of fitting parameters and being available for a variety of fluids.

In Table 1, the primary characteristic of the existing theoretical methods for calculating EoV is summarized. It indicates that the desired theoretical formula satisfying all the preceding requirements is still not in place, which motivates the present study. For physical clarity, we initiate our formulation at molecular level, which avoids the manipulation of the EoS of mathematically complicated form. First, a formulation of EoV at the reference state (which is a particularly defined state for convenience during the formulation and its value of EoV is known) is derived from the principle of energy conservation. Second, an analytical interpretation of the EoV near the critical state is presented in terms of critical exponents, revealing the critical singularity. Finally, a composite formula is constituted by properly weighting the results at the reference and critical states. The performance of the composite formula has been comprehensively assessed through comparison with both experimental data and the theoretical calculation based on equation of state, very good agreement is achieved over the whole temperature range under consideration. Besides, a unified formula for normalized EoV as a function of normalized temperature can be derived from the composite formula. By comparison with experimental results, it is seen that the unified formula, free of adjustable parameters and insensitive to the selection reference state, is capable to evaluate the EoV for various fluids with acceptable accuracy for practical concern.

2. Formulation

2.1. Enthalpy of vaporization at molecular level

The molecular EoV, denoted by l, is given by

Table 1
The characteristic of the existing theoretical approaches in predicting the EoV. The circle indicates that the concerned methods on the upmost row satisfies the specific requirement given in the leftmost column, otherwise, the corresponding box is filled in with a cross.

	Clapeyron equation (based on EoS)	Corresponding state principle	Fitting formula
Valid over entire range	○	×	○
Concise & explicit formula	×	○	○
No fitting coefficients	○	○	×

$$l = \varepsilon_g - \varepsilon_l + p_e(v_g - v_l) \tag{7}$$

where the subscripts l and g denote the liquid- and gas-phase, and ε and v refer to the internal energy and volume per molecule. The internal energy consists of kinetic energy, ε_k, and potential energy ε_p. During vaporization, the fluid temperature is restricted below the its thermodynamic critical point, at which the intramolecular degrees of freedom are seldom activated, and hence the molecules can be approximately considered as being rigid. Therefore, the molecular kinetic energy can be calculated through the heat capacity per molecule, denoted by c_v^{id},

$$\varepsilon_k(T) = \varepsilon_k(T_c) + \int_{T_c}^{T} c_v^{id} dT \tag{8}$$

The pairwise additivity assumption results from the approximate truncation of multi-body interaction among molecules at two-body level and is widely adopted to approximately interpret the intermolecular potential energy in calculating the configuration integrals by means of cluster expansion as well as molecular dynamics simulation. Accordingly, the potential energy of a fluid is simplified as the summation of pairwise intermolecular potential energy, $\Gamma_{ij}(\vec{r}_i, \vec{r}_j)$, where $\vec{r}_i$ refers to the coordinate of the molecule i in phase space. Subsequently, the molecular average potential energy in a fluid system (with N molecules) can be written as

$$\varepsilon_p = \frac{1}{N}\sum_{i<j}\Gamma_{ij}(\vec{r}_i, \vec{r}_j) \tag{9}$$

According to Eyring's significant structure theory [30], the fluid has a lattice-like structure. An individual molecule is surrounded by a number of nearest-neighboring molecules, i.e., the coordination number, denoted by q. As intermolecular potential usually decays rapidly as increasing separating distance between molecules, we can simplify Eq. (9) by considering only the interaction between the molecules and its nearest neighbors, resulting,

$$\varepsilon_p = \frac{1}{2}q_i\Gamma(r), i = l, g \tag{10}$$

where $\Gamma(r)$ without the subscript "ij", refers to the interacting potential energy between adjacent molecules, and the factor 1/ 2 reveals the fact that the pairwise potential energy is equally shared by both participant molecules. Substituting Eqs. (8) and (10) into Eq. (7) yields the EoV per molecule

$$l = \int_{T_c}^{T} (c_{v,g} - c_{v,l}) dT + p(v_g - v_l) + \frac{1}{2}q_g\Gamma(r_g) - \frac{1}{2}q_l\Gamma(r_l) \tag{11}$$

The evaluation of Eq. (11) requires (a) the potential function, $\Gamma(r)$, (b) the molecular heat capacities, $c_{v,g}$ and $c_{v,l}$, (c) the molecular volume, v_g and v_l, and (d) the coordination numbers, q_l and q_g. Since these required quantities are fundamental properties of a fluid, Eq. (11) is generally valid for various fluids at any liquid state.

2.1.1. *Potential function*

For simplicity, we assume that the fluid molecule is non-polar. Then an appropriate mathematical model for Γ is the well-known Lennard-Jones (6–12) potential [31], which can accurately interpret dispersive effect leading to intermolecular attractive force and in the meanwhile appropriately characterize the exceedingly short-ranged intermolecular repulsive force. The mathematical form of Lennard-Jones potential is given by

$$\Gamma(r) = \varepsilon_0\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right] \tag{12}$$

where r_m refers to the molecular distance at which the potential energy is minimum, and ε_0 the depth of the potential well. According to the principles of mechanics, the r_m refers to the intermolecular distance, at which the intermolecular attractive and repulsive forces are balanced with each other, and consequently it represents the equilibrium molecular distance [32]. According to Eq. (12), the intermolecular potential energy between the concerned molecule and its neighbors beyond the first shell, i.e., intermolecular distance being equal to or larger than $2r_m$, decays to 3%, or even much less than the potential well depth, and hence it verifies the simplification of Eq. (9) to Eq. (10).

2.1.2. *Molecular volume*

From the fact that the molecules in liquid are closed packed and the stability of molecular configuration in liquid phase [28,30], we argue that the average molecular volume of liquid can be estimated in terms of equilibrium intermolecular distance, r_m, i.e., $v_l = r_m^3$, which holds approximately at moderate temperature and pressure. However, the low density of gas implies that their average molecular volume tends to be much larger than that of liquid, i.e. $v_g \gg v_l$. For instance, it has $v_g/v_l{\sim}O(10^3)$ at normal conditions [16,29,30], while, as approaching critical state, it becomes $v_{g,c} \cong v_{l,c}$ and the equality holds at the critical state. By means of EoS, the gaseous molecular volume can be correlated to pressure and temperature.

2.1.3. *Molecular heat capacity*

In the gas phase, the degrees of freedom of a rigid molecule are distributed as 3 for translational motion, 3 (or 2 for linear molecule) for rigid rotation. According to the principle of equipartition [4,28], the molecular heat capacity is related to the degrees of freedom of an individual molecule, and consequently we have

$$c_{v,g}^{id} = 3k, c_{v,g}^{id'} = \frac{5}{2}k \tag{13}$$

where k is the Boltzmann constant, and the prime indicates that the molecule has linear structure.

The physical scenario for liquid alters drastically. According to the significant structure theory [30], the liquid molecules undertake two types of motion, i.e. the translational and rotational motion as a whole, corresponding to gas-like mobility, and relative motion between adjacent molecules, corresponding to solid like oscillations. Regarding the considerable intermolecular attractive forces, the liquid molecules are constrained by q_l "springs," in analogy to the bond among solid molecules [28,30,33]. Therefore, molecular heat capacity in liquid phase consists of two parts, relating to the gas-like individual free motion and the solid-like intermolecular oscillation [33]. According to the principle of equipartition, we have

$$c_{v,l}^{id} = 3k + \frac{q_l}{2}k, c_{v,l}^{id'} = \frac{5}{2}k + \frac{q_l}{2}k \tag{14}$$

where the factor 1/2 is introduced for the same reason as in Eq. (10). It is noted that the relations Eq. (13) and Eq. (14) hold at normal conditions. Near the critical state, the molecular heat capacity needs to be reformulated.

2.1.4. Coordinate number

Phenomenologically, the coordination number for fluid consisting of hard-sphere molecules can be calculated in terms of number density, i.e., $q = 4\pi\rho r_{av}^2\sigma$, where r_{av} represents the average distance between two adjacent molecules and σ denotes the thickness of one shell for molecular distribution. For non-ideal fluid, the coordination number shall be calculated by integrating the radial distribution function, which interprets the impact of intermolecular potential upon the distribution of molecules in the fluid, within one shell thickness. The r_{av} is related to the molecular number density, i.e., $\rho\tilde{}r_{av}^{-3}$, and σ can be understood as the physical size of a molecule. Consequently, an estimation of coordination number is given by $q = 4\pi\rho^{1/3}\sigma$. It provides an alternative approach to calculate q_l through a proper correlation to the more readily accessible q_s of the same substance in solid phase in terms of density ratio, giving

$$q = q_s\left(\frac{\rho}{\rho_s}\right)^{1/3} \tag{15}$$

whose results are consistent with physical recognition and experimental observation [34,35]. In the liquid phase, the density ratio is close to unity, implying that q_l is close to q_s, whose representative value results from the closest packing, i.e., $q_{s,R} = 12$, while in the gas phase, the fluid density ratio is of order $O(10^{-3})$, leading to that $q_g \approx 1$.

The coordination number, according to Eq. (15), should be considered as a function of temperature. The reference state is anticipated at the triple point of the concerned substance, where the liquid density deviates from the solid density slightly. The one-third power of the density ratio in Eq. (15) further approaches to unity, i.e., $(\rho_{l,R}/\rho_s)^{1/3} \approx 1$, leading to that $q_{l,R} \approx q_s$.

2.2. Enthalpy of vaporization at the reference state

At moderate temperature and pressure, we have $pv_l \ll pv_g\tilde{}\ kT$, and consequently, the terms containing pv_l/kT and its higher orders could be neglected in the expression of EoV. Substituting Eq. (12)–(14) into Eq. (11), the EoV per molecule becomes

$$l_R = \frac{1}{2}q_{l,R}\varepsilon_0 - \int_{T_c}^{T}\frac{q_l}{2}kdT + kT \tag{16}$$

where we have replaced the term pv_g by kT through the EoS in the gas phase.

Straightforward evaluation of ε_0 requires the solution of the Schrödinger's equation of the molecule including nucleus and electrons [36,37], which is definitely beyond the scope of the present study. Alternatively, we define the reference state where the EoV, denote by l_0, is available from other sources, e.g., experimental data [8–14,38,39] or thermodynamic database [40,41]. Using Eq. (16) to replace ε_0 by l_0, and multiplying the Avogadro's number N_A, we have

$$L_R = L_0 - \int_{T_R}^{T}\frac{q_l}{2}RdT + R(T - T_R) \tag{17}$$

where the capital letters refer to quantities in the molar scale, e.g. $L_0 = N_A l_0$ and $V_l = N_A v_l$, and R is the universal gas constant. Close to the reference state, q_l can be replaced by $q_{l,R}$, and hence L_R can be expanded about T_R, giving

$$L_R = L_0 - \left(\frac{q_{l,R}}{2} - 1\right)R(T - T_R) \tag{18}$$

Eq. (18) indicates that the EoV is a linear function of temperature at the reference state. Conventionally, the reference state is specified at the triple point of the concerned substance, and in general, the selection of the reference state is affected by the availability of the experimental results of EoV [8–14,38,39]. As temperature increasing, Eq. (18) indicates that EoV decays linearly with an identical slope given by

$$\frac{dL_R}{dT} = R\left(1 - \frac{q_{l,R}}{2}\right) \tag{19}$$

Eq. (19) states that the temperature dependence of EoV results from two aspects, corresponding to each term on its right-hand side. The first is the thermal expansion of gas phase fluid under isobaric condition, which leads to a slight increase in the enthalpy of gas molecules and hence an elevation of EoV. The second is that liquid molecules have greater heat capacity because of their strong interactions, which are absent for gas molecules. By unit temperature increment, the liquid molecules can hold additional energy, i.e., being more energetic to escape from the attractive potential imposed by surrounding neighbors, and concomitantly the EoV is reduced. Because of the close packing of liquid molecules, the effect of heat capacity discrepancy always dominates over that of thermal expansion, leading to monotonic decay of EoV with increasing temperature.

In general, Eq. (18), or the more general form Eq. (17) with the knowledge of $q_l = q_l(T)$, interprets the right trend of the variation of EoV with temperature. While substitution of $T = T_c$ into Eq. (18) we have $L_R(T = T_c) \neq 0$, implying that the linear relation given by Eq. (18) is not valid over the entire temperature of liquid. The reason can be understood from two aspects. First, as temperature increasing, the liquid coordination number q_l decreases progressively [34,35]. The overall intermolecular binding in liquid becomes “loose,” and hence according to Eq. (11), the EoV tends to reduce acceleratingly. Second, Eq. (18) has not considered the critical characteristic of the fluid, which considerably affects the behavior of the EoV near the critical state.

2.3. Enthalpy of vaporization near the critical state

At the critical state, the thermodynamic behavior of the fluid is characterized by a number of critical exponents, which correlates various thermodynamic quantities and their discrepancies in terms of temperature deviation from the critical point [29,42,43], i.e. $|T - T_c|$, and beyond, it is known as a λ-like supercritical anomaly [44]. For instance, the density difference and the heat capacity are characterized by temperature deviation, i.e.

$$C_v = f_{c,i}R\left(\frac{T_c - T}{T_c - T_R}\right)^{-\alpha}, \rho_l - \rho_g = f_\rho\rho_c\left(\frac{T_c - T}{T_c - T_R}\right)^{\beta} \tag{20}$$

where ρ_c is the critical density. The universal gas constant is introduced in Eq. (20) for dimensional consideration [29,42]. The factors f_c and f_ρ are nondimensional factors, whose values will be determined subsequently. The parameters α and β are critical exponents, and their values can be approximately calculated through Ising model [29,42]. The more accurate calculation involves the renormalization group theory at the expense of exceedingly involved mathematics and physics [29]. The literature on the critical phenomena [45] suggests that the approximate values of α of β for various fluids are 0.1096 and 0.3265, respectively.

Because of the algebraic dependence on temperature in Eq. (20), the specific values of the factors f_c and f_ρ have no impact upon the singularities of heat capacity and density discrepancy at the critical state. We suppose that the validity of Eq. (20) could be approximately extended to the reference state, where they simultaneously reduce to $C_v = f_{c,i}R$ and $\rho_l - \rho_g = f_\rho \rho_c$. According to Eqs. (13) and (14) and from the fact that $\rho_g/\rho_l \ll 1$ at the reference state, we can evaluate the factors f_ρ and f_c, respectively, giving

$$f_{c,l} - f_{c,g} = \frac{q_{l,R}}{2}, f_\rho = \frac{\rho_{l,R}}{\rho_c} \tag{21}$$

Note that the evaluation of factors f_ρ and f_c does not require the knowledge of specific properties of the concerned fluid, and hence those factors shall not be regarded as fitting parameters.

Substituting Eqs. (20) and (21) into Eq. (11) gives.

$$L = -\frac{q_{l,R}}{2} R \int_{T_c}^{T} \left(\frac{T_c - T}{T_c - T_R}\right)^{-\alpha} dT + \frac{p}{\rho_g} \frac{\rho_{l,R}}{\rho_l} \left(\frac{T_c - T}{T_c - T_R}\right)^{\beta} + \frac{1}{2} N_A q_l \varepsilon_0 \left[2 - \left(\frac{\rho_g}{\rho_{l,R}}\right)^2 - \left(\frac{\rho_l}{\rho_{l,R}}\right)^2\right] \left(\frac{\rho_g}{\rho_{l,R}} + \frac{\rho_l}{\rho_{l,R}}\right) \left(\frac{T_c - T}{T_c - T_R}\right)^{\beta}$$
$$+ \frac{1}{2} N_A \left(q_l - q_g\right) \varepsilon_0 \left(\frac{\rho_g}{\rho_{l,R}}\right)^2 \left[2 - \left(\frac{\rho_g}{\rho_{l,R}}\right)^2\right] \tag{22}$$

The small value of the β in Eq. (20) implies that the density discrepancy remains considerable, i.e. $\rho_g/\rho_{l,R} \ll 1$, in a wide range of thermodynamic state except in the very vicinity of the critical point. In addition, the thermal expansion in liquid tends to be indiscernible than that in the gas phase, thus we approximately have $\rho_l/\rho_{l,R} \approx 1$, which further leads to $q_l \approx q_{l,R}$ according to Eq. (15). Therefore, we can derive the expression for EoV near the critical state

$$L_C = \frac{q_{l,R}}{2(1-\alpha)} (T_c - T) R \left(\frac{T_c - T}{T_c - T_R}\right)^{-\alpha} + \left[L_0 - \frac{1}{2} q_{l,R} R (T_c - T_R)\right.$$
$$\left.\times\right] \left(\frac{T_c - T}{T_c - T_R}\right)^{\beta} \tag{23}$$

where we replaced ε_0 by L_0 as we derive L_R given by Eq. (17).

At the critical state, the EoV calculated by Eq. (23) vanishes identically, and its derivative with respect to temperature, becomes infinitely large as indicated by Eq. (24).

$$\frac{dL_C}{dT} = -\frac{q_{l,R} R}{2} \left(\frac{T_c - T}{T_c - T_R}\right)^{-\alpha} - \left[L_0 - \frac{q_{l,R}}{2} R (T_c - T_R)\right.$$
$$\left.\times\right] \frac{\beta}{T_c - T_R} \left(\frac{T_c - T}{T_c - T_R}\right)^{\beta - 1} \tag{24}$$

This behavior is completely consistent with physical recognition that the EoV vanishes exceedingly rapid as the fluid approaching to its critical state. The singularity of Eq. (24) at the critical state can be understood from two aspects. First, the statistical fluctuation among molecules becomes exceedingly large as at the critical state [4,29], leading to the divergence of heat capacity. Second, the density difference shrinks much more rapidly as temperature changes, which leads to an analogous variation trend for the differential of potential energy. Substituting $T = T_R$ in Eq. (23) results in $L_C(T = T_R) \neq L_0$, implying that L_C cannot be extended to the reference state. This is because the critical expansion Eqs. (20) and (20) do not hold exactly far away from the critical state, which is analogy to the restricted validity range of CSP.

2.4. *Composite formula for enthalpy of vaporization over a broad temperature range*

Equations (18) and (23) are accurate only near the reference and critical states, respectively. A composite formula, denoted by L_I, being valid in the entire temperature range, is appreciated for practical interest. For physical plausibility, the composite formula should satisfy the following requirements:

(I) $\|L_I - L_R\| \to 0$ as approaching the reference state ($T \to T_R$);

(II) $\|L_I - L_C\| \to 0$ as approaching the critical state ($T \to T_c$);Where $\|\cdot\|$ refers to a properly defined norm in the functional space containing the concerned formulas.

In analogy to the mixing rule in interpreting the transport properties of binary mixtures [46], we suggest that the composite formula for EoV could be written as the weighted power average of Eqs. (18) and (23). The weighing exponents should be the normalized temperature, defined by

$$t = \frac{T - T_R}{T_c - T_R} \tag{25}$$

which characterizes the continuous temperature variation from the reference state (with $t = 0$) to the critical state (with $t = 1$). Accordingly, we write the composite EoV formula in the form of

$$\frac{L_I}{L_0} = \left[1 - f_E\left(\frac{q_{l,R}}{2} - 1\right)t\right]^{1-t} \left[f_E \frac{q_{l,R}}{2(1-\alpha)} (1-t)^{1-\alpha}\right.$$
$$\left. + \left(1 - \frac{1}{2} f_E q_{l,R}\right)(1-t)^{\beta}\right]^{t} \tag{26}$$

where we have defined the nondimensional energy factor f_E by

$$f_E = \frac{R(T_c - T_R)}{L_0} \tag{27}$$

whose reciprocal can be understood as the non-dimensional enthalpy of vaporization at the reference state.

At the reference state, Eq. (26) is identical to Eq. (18) and gradually transforms to Eq. (27) at the critical state. Thus, the composite EoV formula given by Eq. (26) satisfies both requirements (I) and (II). Furthermore, the derivative of EoV with respect to temperature by Eq. (26) gives

$$\frac{dL_l}{dT}=(1-t)\frac{dL_R}{dT}L_R^{-t}L_C^{t}+t\frac{dL_C}{dT}L_R^{1-t}L_C^{t-1} \tag{28}$$

which spontaneously reduce to Eq. (19) and Eq. (24) at respectively the reference state and critical state. Thus, the composite formula Eq. (26) can equivalently reveal the singularity of EoV at the critical state.

The comparison of calculated results and experimental data [41] is shown in Fig. 1. The detailed procedure for calculating the enthalpy of vaporization based on analytical equation of state is briefly summarized in Appendix A. Fig. 1 shows that prediction of enthalpy of vaporization by the composite formula and calculation based on equation of state both agree well with the experimental results. Moreover, both methods are shown to be able to interpret the singular behavior of enthalpy of vaporization at the critical state. It is recognized that the PR equation of state gives more accurate description to the liquid density than SRK equation of state [16,24]. Accordingly, the calculation based on PR equation of state yields improved prediction to the enthalpy of vaporization than that based on SRK equation of state, as indicated in Fig. 1.

It should be noted that the calculation based on EoS does not require the information of reference state, instead its accuracy depends upon the appropriateness of the equation of state in predicting the thermodynamic behavior of the substance because the intermolecular potential energy is quite sensitive to molecular distance and hence the density discrepancy [16,31]. Therefore, the uncertainty in density calculation by means of SRK and PR EoS tends to be amplified when evaluating the intermolecular potential energy and consequently the enthalpy of vaporization, which is indicated by the discrepancy between broken lines and solid symbols, especially for water and methanol. By adopting more accurate EoS, e.g., crossover theory modified EoS, to do the subsequent calculation, it is believed that the predicted enthalpy of vaporization at the reference state might be closer to the experimental data, which merits future work.

2.5. Unified formula for normalized enthalpy of vaporization

It should be emphasized that the appearance of the nondimensional factors $q_{l,R}$ and f_E in Eq. (26) is requested by the physical essence of phase transition, which involves both energy and configuration of the substance in both phases. The configurations of liquid and gas are respectively characterized by q_l And q_g, respectively, and therefore a characteristic coordination number for liquid $q_{l,R}$ must be introduced to appropriately reveal the drastic change in fluid configuration during the vaporization. From the aspect of dimension analysis, the formulation of EoV must contain a characteristic energy. At the molecular level, it refers to the potential well depth ε_0 of the intermolecular potential energy, while in thermodynamics, it is correlated to the EoV at the reference state L_0, and hence is characterized by the factor f_E.

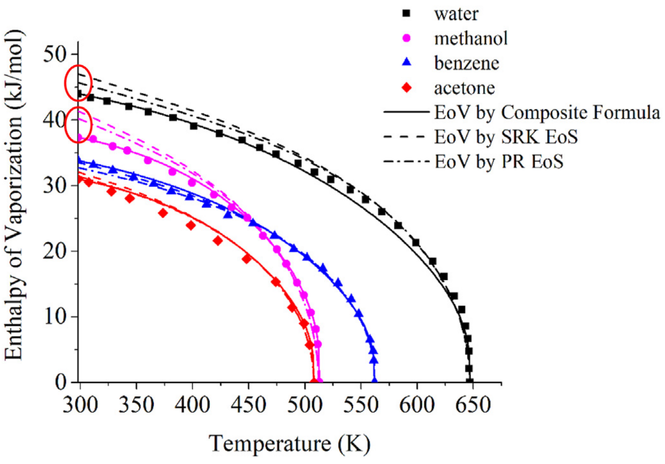

Fig. 1. The enthalpy of vaporization of various fluids that are calculated by composite formula (solid line), calculated by means of equation of state (broken lines) and measured through experiments (solid symbols) [41].

According to the X-ray scattering experimental studies on liquid configurations [34,35], the liquid coordination number changes in a restricted range between 9 and 11 for most concerned fluids. It is also observed that the q_l is slightly smaller than that q_s, which further substantiated the correlation relation between density and coordination number given by Eq. (20). As the reference state is usually specified at the melting point of the fluid, where the molecules are more orderly distributed, the coordination number tends to be greater in magnitude and leads us to specify $q_{l,R}$ as 11. For a variety of fluids, the value of the energy factor f_E, interpreting the non-dimensional reference enthalpy of vaporization, is close to 0.07 when specifying the reference state at the triple point. For instance, the energy factor for water is 0.069, when the reference state is selected at the triple point, i.e., $T = 273\text{K}$ and $p = 1$ atm.

The specification of $q_{l,R} = 11$ and $f_E = 0.07$ shall be inferred as representative values that could characterize common features of a variety of fluids in their molecular arrangement and non-dimensional enthalpy of vaporization at the reference state. With the knowledge of both $q_{l,R}$ and f_E, the normalized EoV can be completely determined as a function of normalized temperature. In Fig. 2, the curve of the normalized EoV given by the composite formula with $q_{l,R} = 11$ and $f_E = 0.07$ is represented by a bold solid line (in red). In the vicinity of this curve, the experimental results, rearranged in the form normalized EoV with respect to normalized temperature, are almost uniformly distributed within a narrow band, indicating that the theoretical calculation using the composite EoV formula, given by Eq. (26) agrees very well with the experimental results. In general, the selection of reference state is flexible. Because of experimental difficulties, the accessible state of the considered substance, where the enthalpy of vaporization can be measured, might be distinct from its thermodynamic triple point. Correspondingly, it leads to a decrement in either coordination number or the energy factor. The reduction in coordination number, at the macroscopic level, can be attributed to the slight expansion effect in liquid according to Eq. (15), while at the molecular level, it can be interpreted that the mobility of the liquid molecule is strengthened, leading to the diminishing configurational order of molecular distribution. According to Eq. (27) and the curves presented in Fig. 2, the reciprocal of energy factor, $1/f_E = L_0/R(T_c - T_r)$, can be regarded as the average slope (in magnitude) of EoV with respect to the temperature over the entire temperature range. When the reference temperature is slightly increased, the geometric characteristic of the curve Eq. (26) leads to an increment in the magnitude of the average slope, i.e. f_E tends to decay accordingly. Altering both coordination number and the energy factor in the composite formula Eq. (26), it shows that the composite EoV formula tends to be surprisingly insensitive to the selection of the reference state.

By selecting the representative values for coordination number and the energy factor and specifying the factors f_ρ and f_c from physical plausibility, the composite formula given by Eq. (26) is free of fitting parameters that may differ for a variety of fluids and thus becomes a unified formula that interprets the normalized EoV in terms of normalized temperature. The calculation of EoV from Eq. (26) requires the knowledge of reference EoV for the calibration

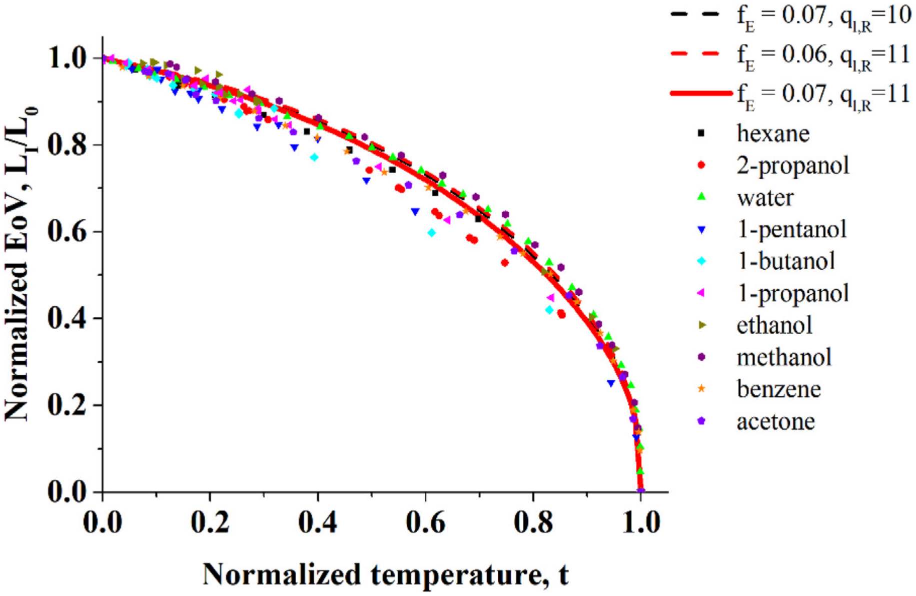

Fig. 2. Comparison of theoretical prediction of EoV by Eq. (26) with experimental results of EoV for various conventional fluids [8–14,38,39,47–49]. The EoV is normalized by its value at the reference state, and the variation of EoV with respect to temperature is rescaled in terms of normalized temperature, defined by Eq. (25).

and the critical temperature to define the normalized temperature, both of which are of direct access in existing experimental results [8–14,38,39] and thermodynamic database [40,41]. The accuracy of the composite formula might be slightly improved by introducing additional adjustable parameters, which may lead to a more complicated mathematical form. However, a rigorous solution must consider the physical mechanisms that bridge the reference state and the critical state. For instance, we suppose that the thermal expansion in liquid would be one of such bridging mechanisms, which, more importantly, plays a significant role in calculating liquid internal energies and heat capacities [50]. At the molecular level, the thermal expansion in liquid may affect the EoV by causing decrement in coordination number of liquid molecules, which leads to a reduction of intermolecular potential energy. Therefore, the EoV falls acceleratingly according to Eq. (11), which merits future study.

3. Conclusions

In this study, a theoretical analysis on the EoV is conducted. Defining the reference state where the EoV is available, an explicit formula for EoV around the reference state is rigorously derived based on fundamental principles of thermodynamics and statistical mechanics, given by Eq. (18). It gives a linear relation between the EoV and temperature, revealing that the larger heat capacity of liquid, due to stronger molecular interaction, can hold more energy as temperature rising and accordingly reduce the value of EoV.

In terms of the critical exponents for heat capacity and density difference, the EoV near the critical state is derived as power functions of temperature deviation, given by Eq. (23). This formula gives accurate prediction to the EoV close to the critical states and is well consistent with the physical recognition that the EoV vanishes acceleratingly as the fluid approaching critical state.

Eqs (18) and (23) separately have their restricted validity range, which may overlap at some intermediate temperature. By appropriately weighing Eqs. (18) and (23), we constitute a composite for normalized EoV in terms of normalized temperature, given by Eq. (26). It can spontaneously reduce to Eqs. (18) and (23) respectively at the reference and critical states and retains all mathematical properties of both constituents. The composite formula becomes free of parameters with the knowledge of reference coordinate number and energy factor, which may change slightly as altering the reference state. However, it is seen that the composite is quite insensitive to the selection of reference state.

It is shown that the EoV predicted by the composite formula agrees well with experimental data within the whole temperature range, i.e., from the reference state to the critical state. On the theoretical aspect, the composite formula reveals the temperature dependence of EoV in an analytical form. On the practical aspect, the composite formula can predict the EoV for various fluids with comparable or even better accuracy than the calculation based on equation of state. Being free of fluid-dependent parameters, it implies that the composite formula is of appropriate functional form that interprets the general variation of EoV with temperature for a variety of fluids. The simple analytical form and its acceptable accuracy ensure the potential of the composite formula in practical applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Dehai Yu: Conceptualization, Methodology, Validation, Writing - original draft. **Zheng Chen:** Conceptualization, Supervision, Writing - review & editing.

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Appendix A

In thermodynamics, the enthalpy of vaporization is defined in terms of internal energy discrepancy

$$L = U_m^v - U_m^l + P_e\left(V_m^v - V_m^l\right) \tag{A1}$$

The differential of internal energy is a function of entropy and molar volume

$$dU = TdS - PdV \tag{A2}$$

By means of Maxwell's relation [19].

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{A3}$$

and integrating over molar volume, the internal energy discrepancy is evaluated by

$$U_m^v - U_m^l = \int_{V_m^l}^{V_m^v} \left[T\left(\frac{\partial P}{\partial T}\right)_{V_m} - P\right] dV_m \tag{A4}$$

The integrand on the right-hand side of Eq. (A4) is evaluated on an isotherm produced by a properly selected equation of state. Substituting Eq. (A4) int Eq. (A1), the EoV is analytically evaluated in terms of PVT data, and hence determined based on equation of state.

$$L = \int_{V_m^l}^{V_m^v} \left[T\left(\frac{\partial P}{\partial T}\right)_{V_m} - P\right] dV_m + P\left(V_m^v - V_m^l\right) \tag{A5}$$

In the present study, we choose both Soave-Redlich-Kwong(SRK) EoS and Peng-Robinson (PR) EoS as candidates to proceed the calculation. The analytical form of SRK EoS is given by

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)}\left[1 + f_\omega\left(1 - T_r^{1/2}\right)\right]^2 \tag{A6}$$

where the parameters are determined by critical properties

$$a = \frac{1}{9\left(2^{1/3} - 1\right)}\frac{R^2T_c^2}{P_c} = 0.42748\frac{R^2T_c^2}{P_c} b = \frac{2^{1/3} - 1}{3}\frac{RT_c}{P_c} = 0.08664\frac{RT_c}{P_c} \tag{A7}$$

and

$$f_\omega = 0.480 + 1.574\omega - 0.176\omega^2 \tag{A8}$$

is an algebraic function of acentric factor ω, which is equal to zero for rigorously spherical molecule, e.g., inert gas.

Substituting Eq. (A7) and (A8) into Eq. (A5), and evaluating the integral analytically, the EoV is presented in terms of PVT data at phase equilibrium state, i.e.,

$$L = \frac{a}{b}(1 + f_\omega)\left(1 + f_\omega - f_\omega T_r^{1/2}\right)\ln\frac{V_m^v\left(V_m^l + b\right)}{V_m^l\left(V_m^v + b\right)} + P_e\left(V_m^v - V_m^l\right) \tag{A9}$$

In the PV-diagram, the coexistence state of liquid and gas is represented by a horizontal line, which, however, cannot be accurately predicted by a cubic equation of state, such as Eq. (A6). To correctly predict various thermodynamic properties by means of EoS, it must satisfy the Maxwell's equal area rule,

$$P_e\left(V_m^v - V_m^l\right) = \int_{V_m^l}^{V_m^v} P(V,T)dV_m \tag{A10}$$

where $P(V,T)$ is evaluated via the adopted EoS. For Soave-Redlich-Kwong EoS, the Maxwell's equal area rule is equivalently written in the form

$$P_e = \frac{1}{V_m^v - V_m^l}\left\{RT\ln\frac{V_m^v - b}{V_m^l - b} - \frac{a}{b}\left[1 + f_\omega\left(1 - T_r^{1/2}\right)\right]^2 \ln\frac{V_m^v\left(V_m^l + b\right)}{V_m^l\left(V_m^v + b\right)}\right\} \tag{A11}$$

Additionally, the Soave-Redlich-Kwong equation must be satisfied at point J for the liquid and at point N for the vapor, i.e.,

$$P_e = \frac{RT}{V_m^v - b} - \frac{a}{V_m^v(V_m^v + b)}\left[1 + f_\omega\left(1 - T_r^{1/2}\right)\right]^2 \tag{A12}$$

and

$$P_e = \frac{RT}{V_m^l - b} - \frac{a}{V_m^l\left(V_m^l + b\right)}\left[1 + f_\omega\left(1 - T_r^{1/2}\right)\right]^2 \tag{A13}$$

The unknowns at phase equilibrium state are determined by simultaneous solution of equation (A11) – (A13). By substituting those solutions into Eq. (A9), the enthalpy of vaporization is finally calculated.

It is argued that the Peng-Robinson EoS gives more reliable estimation to liquid density, and hence may improve the accuracy in the calculation of EoV. The analytical form of PR equation of state is given by

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}\left[1 + f_\omega\left(1 - T_r^{1/2}\right)\right]^2 \tag{A14}$$

with parameters determined by critical properties and acentric factor

$$f_\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$a = 0.45724\frac{R^2T_c^2}{P_c} \tag{A15}$$

$$b = 0.077796\frac{RT_c}{P_c}$$

Following the same procedure as we derive Eq. (A9), he analytical form for EoV based on PR EoS is given by

$$\Delta_{\text{vap}}H = \frac{a}{\sqrt{2}b}(1 + f_\omega)\left(1 + f_\omega - f_\omega T_r^{1/2}\right) \times \left[\operatorname{arctanh}\left(\frac{b + V_m^l}{\sqrt{2}b}\right) - \operatorname{arctanh}\left(\frac{b + V_m^v}{\sqrt{2}b}\right)\right] + P_e\left(V_m^v - V_m^l\right) \tag{A16}$$

where the phase equilibrium quantities are obtained by simultaneously solving Eq. (A17) – (A19)

$$P_e = \frac{1}{V_m^v - V_m^l}\left\{RT\ln\frac{V_m^v - b}{V_m^l - b} - \frac{a}{\sqrt{2}b}\left[1 + f_\omega\left(1 - T_r^{1/2}\right)\right]^2\right.$$

$$\left.\left[\operatorname{arctanh}\left(\frac{b+V_m^l}{\sqrt{2}b}\right)-\operatorname{arctanh}\left(\frac{b+V_m^v}{\sqrt{2}b}\right)\right]\right\} \tag{A17}$$

$$P_e=\frac{RT}{V_m^l-b}-\frac{a}{V_m^l\left(V_m^l+b\right)+b\left(V_m^l-b\right)}\left[1+f_\omega\left(1-T_r^{1/2}\right)\right]^2 \tag{A18}$$

$$P_e=\frac{RT}{V_m^v-b}-\frac{a}{V_m^v\left(V_m^v+b\right)+b\left(V_m^v-b\right)}\left[1+f_\omega\left(1-T_r^{1/2}\right)\right]^2 \tag{A19}$$

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