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An empirical equation for the enthalpy of vaporization of quantum liquids

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Abstract

An empirical equation for the enthalpy of vaporization of quantum fluids is presented. Dimensionless analysis is used to define enthalpy of vaporization as a function of temperature with a standard deviation of about 1%. Experimental data represented in these variables show two different behaviours and exhibit different maximum values of the enthalpy of vaporization, one corresponding to fluids with a triple point and the other to fluids having a lambda point. None of the existing empirical equations are able to describe this fact. Also enthalpy of vaporization of helium-3, n-deuterium and n-tritium are estimated.

Keywords: Enthalpy of vaporization; Quantum liquids; Empirical equation

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1. Introduction

Since Kamerlingh Onnes in 1908 liquefied helium-4 many of the quantum liquids of low critical temperature have been extensively studied and applied in industrial processes [1,2]. Enthalpy of vaporization is an indispensable physical property for the design and development of refrigeration at low temperatures.

The $\Delta_{\mathrm{vap}}H$ of classical and quantum fluids is zero at the critical point. Classical fluids have a maximum value of $\Delta_{\mathrm{vap}}H$ at the triple point. But in quantum fluids this maximum is shifted to temperatures close to the triple or lambda points. Existing empirical equations for $\Delta_{\mathrm{vap}}H$ such as that of Watson [3] or Fish and Lielmezs [4] give a maximum $\Delta_{\mathrm{vap}}H$ at the triple point or at the lambda point, and therefore these correlations fail at low temperature. The structure of these equations [3,4], a power law of dimensionless temperature, is unable to reproduce the experimental data.

The present work proposes a universal empirical equation for $\Delta_{\mathrm{vap}}H$. The equation is written as a power of dimensionless temperature, but correlates the shift of the maximum of both classes of quantum liquids, and fits the whole coexistence curve with much less dispersion than the equations of Watson or Fish and Lielmezs.

2. Empirical equation for the enthalpy of vaporization of quantum liquids

To construct the empirical equation that fits the experimental data along the coexistence curve, we define the dimensionless variables as follows. For quantum liquids the temperature along the coexistence line varies between the critical temperature T_{c} and the triple temperature T_{t} ($T_{\mathrm{t}} \leq T \leq T_{\mathrm{c}}$), or between the critical and the lambda temperature T_{λ} ($T_{\lambda} \leq T \leq T_{\mathrm{c}}$). Therefore these temperatures must be included in the dimensionless variable t. When the quantum liquid has a triple point we define t as:

$$t = \frac{(T - T_{\mathrm{t}})}{(T_{\mathrm{c}} - T_{\mathrm{t}})} \tag{1}$$

and when the liquid has a lambda point, t is:

$$t = \frac{(T - T_{\lambda})}{(T_{\mathrm{c}} - T_{\lambda})} \tag{2}$$

In both cases the new variable t is bounded between zero and one ($0 \leq t \leq 1$). This definition of reduced temperature is an

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extension of that given by van der Waals. The corresponding dimensionless enthalpies are

$$\Delta h(t) = \frac{\Delta_{\text{vap}} H(T)}{\Delta_{\text{vap}} H_{\text{t}}} \tag{3}$$

$$\Delta h(t) = \frac{\Delta_{\text{vap}} H(T)}{\Delta_{\text{vap}} H_{\lambda}} \tag{4}$$

where $\Delta_{\text{vap}} H_{\text{t}} = \Delta_{\text{vap}} H(T = T_{\text{t}})$ and $\Delta_{\text{vap}} H_{\lambda} = \Delta_{\text{vap}} H(T = T_{\lambda})$ are the values of the enthalpies of vaporization at the triple and the *lambda* points, respectively.

With these dimensionless variables we represent the experimental data for normal hydrogen, para hydrogen and helium-4 [5]. The three curves are represented in Fig. 1. The maximum values are not at $t = 0$, as in the case of classical fluids, but between the boiling temperature and the triple or lambda temperature. These experimental data are well correlated by the following function

$$\Delta h(t) = (1 - t)^{at+b} \tag{5}$$

where a and b are constants obtained by fitting Eq. (5) to the experimental data. For fluids having a triple point,

$$a = 0.44 \quad \text{and} \quad b = -0.137 \tag{6}$$

For fluids with a *lambda* point,

$$a = 0.499 \quad \text{and} \quad b = -0.242 \tag{7}$$

With the variables $\Delta_{\text{vap}} H$ and T, for quantum fluids with a triple point, substitution of Eqs. (1), (3) and (6) into Eq. (5) gives

$$\Delta_{\text{vap}} H(T) = \Delta_{\text{vap}} H_{\text{t}} \left[\frac{(T_{\text{c}} - T)}{(T_{\text{c}} - T_{\text{t}})} \right]^{0.44((T-T_{\text{t}})/(T_{\text{c}}-T_{\text{t}}))-0.137} \tag{8}$$

The correlation for fluids with a lambda point is obtained by the substitution of Eqs. (2), (4) and (7) into Eq. (5) to give

$$\Delta_{\text{vap}} H(T) = \Delta_{\text{vap}} H_{\lambda} \left[\frac{(T_{\text{c}} - T)}{(T_{\text{c}} - T_{\lambda})} \right]^{0.499((T-T_{\lambda})/(T_{\text{c}}-T_{\lambda}))-0.242} \tag{9}$$

The values of T_{c}, T_{t}, T_{λ}, $\Delta_{\text{vap}} H_{\text{t}}$, and $\Delta_{\text{vap}} H_{\lambda}$ depend on the substance, therefore each substance has a different curve of $\Delta_{\text{vap}} H(T)$ versus T. Fig. 2 presents the experimental data for helium-4, normal and parahydrogen and the correlations (8) and (9). A simple inspection shows a good correspondence between the correlations and the experimental data. The dispersion between our correlation and the experiments is of the order of 1%. Table 1 shows the standard deviations ($\text{S.D.} = \sum |\Delta_{\text{vap}} H(T)_{\text{calc.}} - \Delta_{\text{vap}} H(T)_{\text{exp.}}| / N \Delta_{\text{vap}} H(T_{t/\lambda})$) of empirical Eqs. (8) and (9) and that of Watson [3] and Fish and Lielmezs [4]. Our equations correlate the experimental values better than the earlier equations [3,4]. Eq. (5) is not a simple power law of the dimensionless variable as the other empirical equations. Instead, it is a linear power of the same variable in the region $0 \leq t \leq 1$.

Where there are no experimental data for $\Delta_{\text{vap}} H$ we proceed as follows. First we estimate $\Delta_{\text{vap}} H$ at the boiling point via Trouton's rule [6]. Trouton's constants for common liquids lie between $9R$ and $14R$, where R is the gas constant. Hydrogen and helium are not comparable with the simple liquids because of the large size of the "quantum correction" [6]. If we assume that isotopic elements have approximately the same Trouton's constant, then from the experimental data of hydrogen [5],

$$\frac{\Delta_{\text{vap}} H(T_b)}{T_b} \simeq 44\,\text{J/mol K} \tag{10}$$

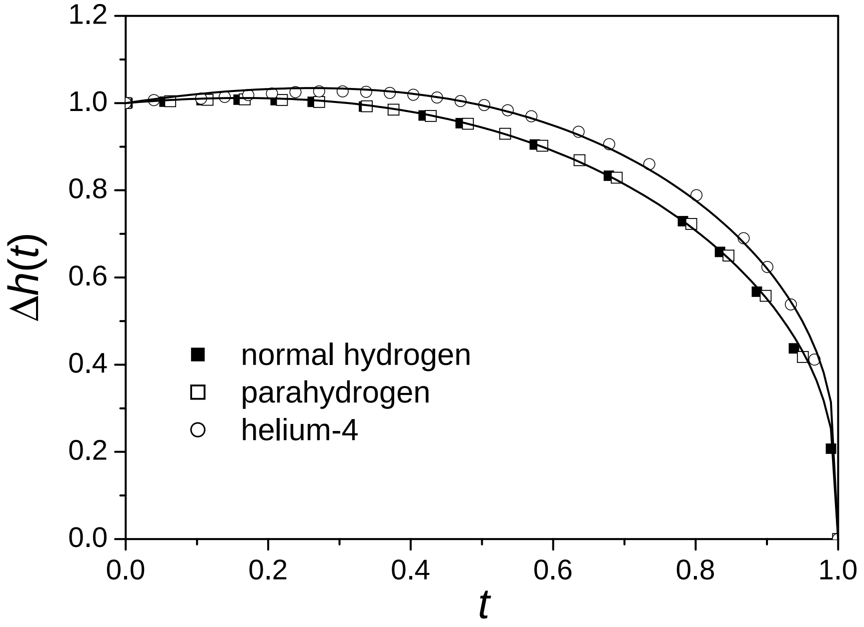

Fig. 1. Reduced enthalpy of vaporization as a function of dimensionless temperature. Points are experimental data [5].

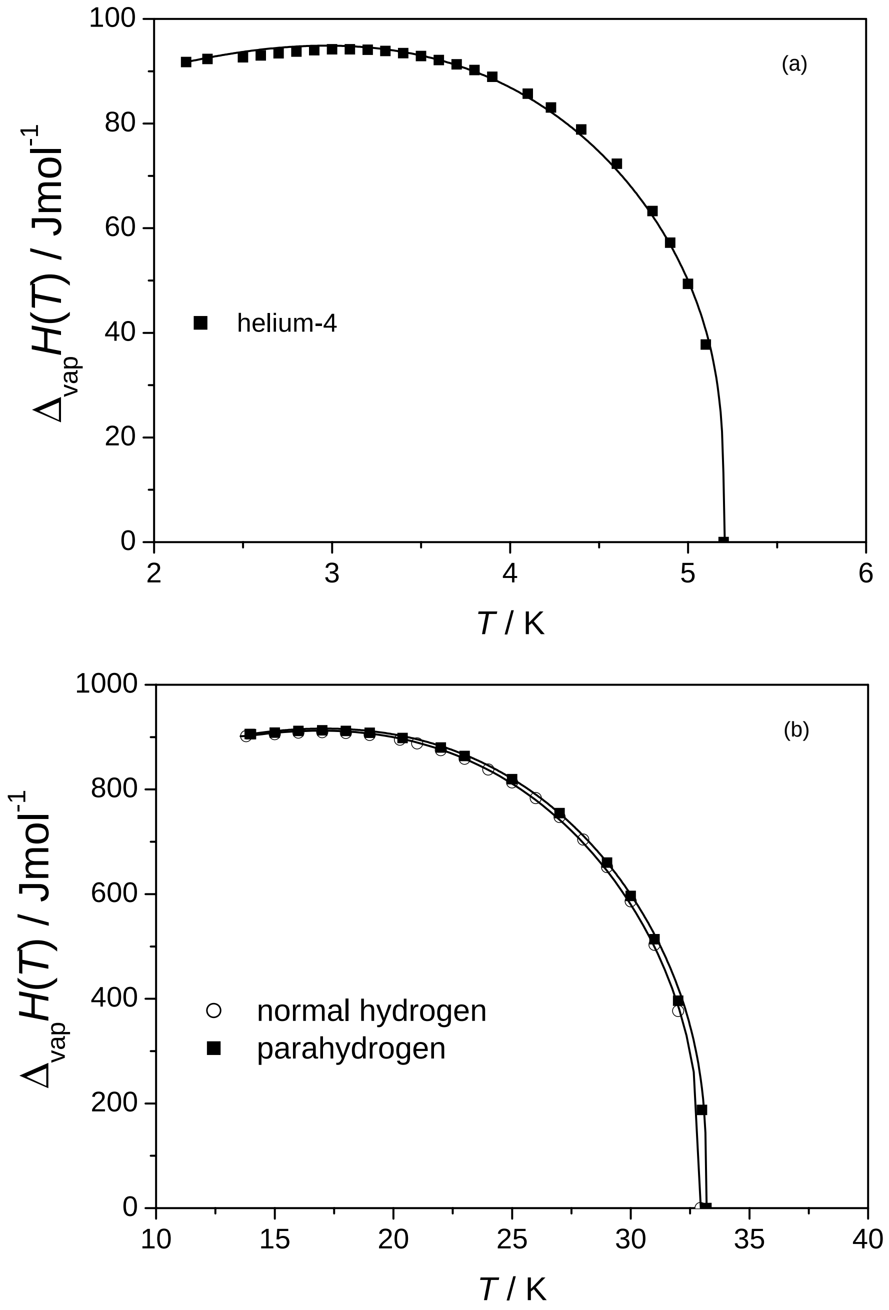

Fig. 2. Enthalpy of vaporization $\Delta_{vap}H$ as a function of temperature, T. Points are experimental data [5], solid lines are plots of Eqs. (8) and (9) with the corresponding values of T_c, T_t, T_λ, $\Delta_{vap}H_t$ and $\Delta_{vap}H_\lambda$. (a) Helium-4, (b) normal and parahydrogen.

Table 1
Standard deviations of empirical equations for the enthalpy of vaporization

Substance	N^a	This work	Watson	Fish and Lielmezs
Normal hydrogen	32	1.215	16.079	5.049
Parahydrogen	26	0.308	13.267	11.945
Helium-4	22	0.573	11.649	15.412

[a] N, number of data points.

Table 2
Values of lambda, triple, boiling and critical temperature for helium-3 [1,2], deuterium and tritium [1]

Substance	T_λ [K]	T_t [K]	T_b [K]	T_c [K]
Helium-3	0.0027		3.2	3.3
n-Deuterium		18.7	23.7	38.4
n-Tritium		20.6	25.0	42.5

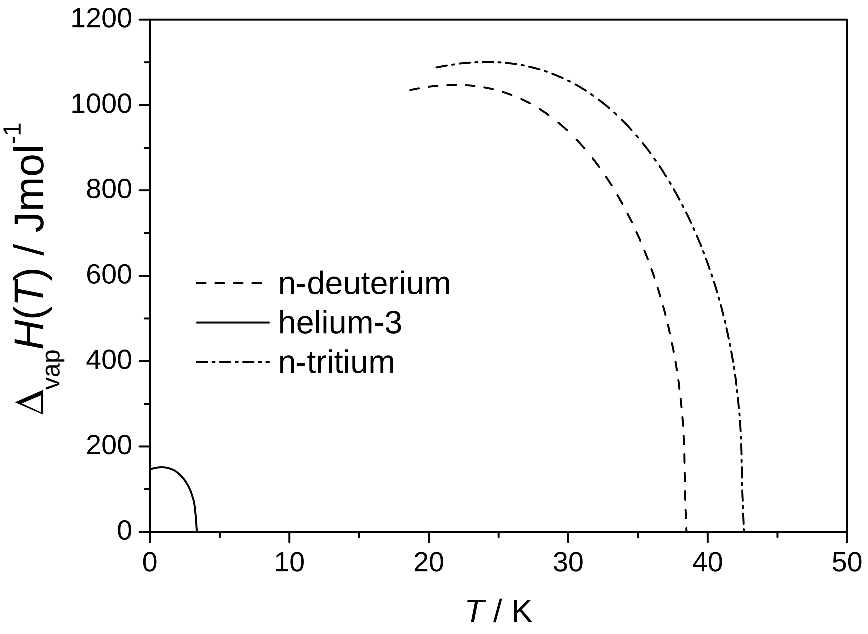

Fig. 3. Enthalpy of vaporization estimated by Eqs. (8) and (9) for n-deuterium, n-tritium and helium-3.

Table 3
Estimated values of $\Delta_{\mathrm{vap}}H(T_b)$ and $\Delta_{\mathrm{vap}}H(T_\lambda)$ for helium-3 and $\Delta_{\mathrm{vap}}H(T_b)$ and $\Delta_{\mathrm{vap}}H(T_{\mathrm{t}})$ for n-deuterium and n-tritium

Substance	$\Delta_{\mathrm{vap}}H(T_b)$ [J/mol K]	$\Delta_{\mathrm{vap}}H(T_\lambda)$ [J/mol K]	$\Delta_{\mathrm{vap}}H(T_{\mathrm{t}})$ [J/mol K]
Helium-3	62.8	146.3	
n-Deuterium	1042.8		1035.1
n-Tritium	1100.0		1088.1

Therefore for n-deuterium and n-tritium, $\Delta_{\mathrm{vap}}H(T_b)$ can be evaluated from Eq. (10) using data given in Table 2 [1,2]. Similarly we can estimate $\Delta_{\mathrm{vap}}H(T_b)$ for helium-3 using the Trouton's constant for helium-4 [5],

$$\frac{\Delta_{\mathrm{vap}}H(T_b)}{T_b} \simeq 19.63\,\mathrm{J/mol\,K} \qquad (11)$$

With these $\Delta_{\mathrm{vap}}H$ values at the boiling temperature and Eqs. (8) and (9) we find $\Delta_{\mathrm{vap}}H$ at the triple and lambda points respectively. These values are displayed in Table 3. With the temperature data of Table 2 and the estimated values of $\Delta_{\mathrm{vap}}H$ given in Table 3 we evaluate $\Delta_{\mathrm{vap}}H$ at any temperature (see Fig. 3).

3. Discussion

Eq. (5) is valid for both quantum and classical fluids. In the case of classical fluids $b = Z_{\mathrm{c}}$ (the universal critical ratio $Z_{\mathrm{c}} = 0.292$ [7]), and $a = b^2$. Therefore, one universal equation without any adjustable parameter [8] is sufficient for these fluids. In quantum fluids, a and b are given by Eqs. (6) and (7), respectively. For these kind of fluids no universal relation exists.

Eq. (5) correlates the experimental data better because of inclusion of a power of the variable. While Watson [3] uses nearly the same dimensionless variable for the temperature, the dimensionless $\Delta_{\mathrm{vap}}H$ is given by $\Delta h(t) = (1-t)^{\alpha}$, with $\alpha = cte$ instead.

Fish and Lielmezs [4] propose an interesting classification of fluids in relation to $\Delta_{\mathrm{vap}}H$ behaviour. They suggest that fluids may be classified into three groups, metallic, organic and inorganic, and quantum liquids. The present analysis indicates that fluids should be classified as classical fluids and quantum fluids with triple and lambda points.

Finally a comment about $\Delta_{\mathrm{vap}}H$ of deuterium, tritium and helium-3. As no experimental data for $\Delta_{\mathrm{vap}}H$ is available for these liquids, we assume the validity of Trouton's rule for isotopic fluids. This assumption allows estimation of $\Delta_{\mathrm{vap}}H$ at the boiling temperature and then, via Eqs. (8) and (9), to obtain $\Delta_{\mathrm{vap}}H$ for the whole coexistence line. The assumption of Trouton's rule is acceptable in light of the known values of Trouton's constant for self-similar substance [9].

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