of these cases the boundaries are transparent, and there are no externally incident radiation.

The present study provides a simple, straightforward, and highly accurate method of analysis for the determination of angular distribution of radiation anywhere in the medium. As an independent check, the results are compared with those calculated with the F_N method [4]; the agreement was very good. Computations require very little computer time. In the tables presented, the number of terms, NT, used in the calculations for convergence are also listed.

Acknowledgment

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The Latent Heat of Vaporization of a Widely Diverse Class of Fluids

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Introduction

The critical region for most fluids is known to possess nonanalytical character that prohibits a power-series expansion of thermodynamic potentials about the critical point in density and temperature [1]. Over the past two decades, an enormous effort has been made to theoretically describe the anomalous thermodynamic behavior of fluids in the vicinity of the critical point. Phenomenological scaling thoery [2–4] and, more recently, renormalization-group theory [5], for example, have illuminated our understanding of the critical-point region. In order to obtain the proper functional form of the latent of vaporization, L, of a pure fluid that is applicable throughout its entire domain of existence (i.e., from the triple point to the critical point), it is clear one must employ results of modern critical-point theories.

Various latent-heat formulae for certain fluids have previously been given, but, in almost all cases, such expressions either have not accurately described the latent heat data over the broad domain of values that is of interest here [6, 7] or are unnecessarily complex in form, often containing a large number of terms [8]. The flaws in all these empirical equations appear to be the result of failure to incorporate the aforementioned modern understanding of the critical region.

Basic Equation

Using the Clausius-Clapeyron equation and results of renormalization-group theory, Torquato and Stell [9] were

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able to formulate the following simple expression for the dimensionless latent heat, λ, of a fluid belonging to the same universality class as the three-dimensional Ising model

$$\lambda = a_1 t^\beta + a_2 t^{\beta + \Delta} + a_3 t^{1 - \alpha + \beta} + a_4 t + a_5 t^2 + a_6 t^3 \qquad (1)$$

Here $\lambda = L/L_t$, L_t is the latent-heat value at the triple point, $t = (T_c - T)/T_c$, T is the absolute temperature, T_c is the critical temperature, and the a_i are system-dependent parameters. The critical exponents, β and α, describe the singularities associated with the difference in coexisting densities and the specific heat at constant volume, respectively. The exponent Δ is Wegner's first gap exponent [10]. Torquato and Stell least-squares fitted this latent-heat formula to the highly accurate latent-heat data of water obtained by Osborne, Stimson, and Ginnings (OSG) [11] and Osborne, Stimson, and Fiock (OSF) [12] for $T_t \leq T \leq T_c$ (T_t being the triple point temperature). Their predicted latent-heat values were found to be in excellent agreement with the OSG and OSF data.

One object of this study is to fit equation (1) to the data of a large number of different substances, such as alcohols, halogen substituted hydrocarbons (Freons), simple nonpolar fluids, polar fluids, and other hydrocarbons, in order to determine the extent of its validity. Such an inclusive tabulation of properties is given by Vargaftik [13] and is the one employed in this investigation. Second, it is of interest to determine whether a least-squares fit of the data of a particular substance may be used to numerically predict, within some acceptable error, the latent heat of another fluid. Both of these problems are addressed in the subsequent section.

Results and Discussion

Vargaftik's data are by no means the most accurate data available for the individual substances contained therein, but he does provide, in a single compilation, relatively reliable tabulations of thermodynamic properties for a widely diverse class of fluids. We consider twenty different fluids and least-squares fit each latent-heat data set associated with a particular system from the triple point to the critical point using equation (1). Following Torquato and Stell, we take $\beta = 1/3$, $\alpha = 1/8$, and $\Delta = 0.79 - \beta \approx 0.4567$ for all the substances. The justification for this is the expectation that all fluids belong to the same universality class [1]. In Table 1, we summarize the results of these fits by giving T_c, T_t, L_t, the coefficients a_i, the maximum percentage deviation $\delta_m \equiv 100 \times |\lambda_i^* - \lambda_i|/\lambda_i^*$, and the standard error

$$\sigma \equiv \left[\sum_{i=1}^{N} (\lambda_i^* - \lambda_i)^2/N \right]^{1/2} .$$

Here N is the number of latent-heat values; λ_i^* and λ_i are the ith measured and predicted scaled latent-heat values.

The fit for carbon monoxide yields $\sigma = 0.00325$, the largest standard error for the group of fluids presented in this study. On average, the predicted scaled latent-heat values for all twenty substances are within 0.8 percent of the data, assuming an average λ value of 0.5 for the entire temperature range and $\sigma = 0.004$. The fits for most of the fluids, moreover, yield λ values that are within 0.2 percent of the data, on average. The maximum percentage deviation, δ_m, is seen to always occur in the near critical region. This result is expected in light of the experimental difficulties one is faced with in the vicinity of the critical point [9].

A plot of λ versus t for each of the twenty substances does not show universal behavior, i.e., a corresponding states principle [14] is not demonstrated. However, a plot of λ versus $\tau \equiv (T_c - T)/(T_c - T_t)$, for all fluids for which Vargaftik reports values of L_t, appears to display a corresponding states principle in that the function $\lambda = \lambda(\tau)$ is

Table 1 Results of least-squares analysis using equation (1) for twenty different fluids for Vargaftik's data [13]. Temperatures are given in K, latent-heat in kJ/kg.

	Ammonia	Argon	Carbon Dioxide	Carbon Monoxide	Ethane
T_c	405.55	150.86	304.19	132.92	305.50
T_t	195.42	83.78	216.55	68.14	89.88
L_t	1473.90	161.80	347.30	235.52	601.19
a_1	0.47057	0.36102	1.35069	1.45169	− 0.64121
a_2	3.04437	23.96446	− 5.95311	− 25.33722	36.15830
a_3	− 8.04468	55.53528	− 20.83607	− 82.04570	66.16418
a_4	2.69778	− 67.19804	21.89009	87.67934	− 90.29894
a_5	5.37598	− 17.88592	11.94955	32.14627	− 14.05575
a_6	− 2.82782	7.40818	− 13.93713	− 14.91833	4.03838
δ_m	0.33581	0.44605	0.15900	1.54475	0.49968
σ	0.00081	0.00085	0.00118	0.00325	0.00086

	Ethanol	Freon-12	Freon-22	Isooctane	Krypton
T_c	521.35	384.95	369.28	544.25	209.39
T_t	158.65	118.15	113.15	165.77	115.76
L_t	1187.32	207.83	294.18	351.78	109.60
a_1	1.34686	0.94297	0.72254	0.67128	1.30503
a_2	− 15.85366	− 4.70274	2.95824	4.96085	− 10.66454
a_3	− 37.48493	− 11.92221	3.42752	7.92755	− 32.53309
a_4	47.15897	15.46468	− 5.36903	− 10.87562	36.43934
a_5	7.37973	0.59654	− 1.17015	− 2.43041	9.54154
a_6	− 1.70348	1.20085	0.81290	− 0.91875	− 2.80368
δ_m	0.26812	0.60933	0.24399	0.03399	0.56980
σ	0.00077	0.00063	0.00020	0.00031	0.00083

	Methane	Methanol	Neon	Nitrogen	n-Nonane
T_c	190.55	513.15	44.40	126.25	595.15
T_t	91.00	175.15	24.50	63.15	219.65
L_t	543.40	1354.16	89.45	212.60	387.81
a_1	0.78206	0.29045	0.88154	1.41557	0.31647
a_2	0.84814	12.12910	9.79304	− 10.94088	13.56551
a_3	− 9.79152	14.11962	24.10286	− 29.52156	22.12327
a_4	6.41067	− 24.69802	− 28.20568	34.51737	− 31.61818
a_5	4.66431	1.28818	− 8.03241	8.43211	− 4.26098
a_6	− 2.04333	− 3.46706	2.70559	− 3.10147	1.05594
δ_m	1.12302	0.74542	0.03090	0.59132	1.71695
σ	0.00073	0.00105	0.00007	0.00083	0.00207

	Oxygen	Propane	1-Propanol	Water	Xenon
T_c	154.77	370.00	536.85	647.27	289.74
T_t	54.35	85.46	147.15	273.16	161.36
L_t	238.70	540.31	946.80	2501.00	96.98
a_1	1.24529	0.32838	1.15023	0.72241	1.13256
a_2	− 4.05385	13.25739	− 14.07059	5.33402	− 3.08280
a_3	− 6.31829	26.78045	− 31.76604	8.97347	− 8.18035
a_4	10.20602	− 34.00190	40.45017	− 11.93143	10.80348
a_5	− 0.81329	− 8.50819	− 8.64866	− 3.31206	− 0.91775
a_6	0.98570	3.84203	4.26884	1.63257	2.42356
δ_m	0.84017	0.25917	1.09955	1.53773	0.17028
σ	0.00074	0.00064	0.00208	0.00028	0.00099

nearly the same for each substance. By using the smallest temperature value given and the associated latent-heat value reported for this temperature, we have used this universal function $\lambda = \lambda(\tau)$ (equation (2) below) in order to estimate the value of L_t for those fluids for which Vargaftik does not provide data. Less than half of the latent-heat values at the triple point given in Table 1 were obtained in this way. In order to test the accuracy of this method, we apply the technique to estimate L_T using ammonia, a substance for which L_T is given. Using the ammonia data at 260 K and 300 K, the predicted L_T are within 0.1 and 1.3 percent of the reported L_T, respectively.

We obtain λ explicitly as a function of τ for water using the coefficients, a_i, of Table 1 for water and equation (1)

$$\lambda = b_1\tau^\beta + b_2\tau^{\beta+\Delta} + b_3\tau^{1-\alpha+\beta} + b_4\tau + b_5\tau^2 + b_6\tau^3 \qquad (2)$$

where

$b_1 = 0.60176 \qquad b_2 = 3.45913 \qquad b_3 = 4.62671$

$b_4 = -6.89614 \qquad b_5 = -1.10643 \qquad b_6 = 0.31522$

Clearly $b_i = a_i[(T_c - T_t)/T_c]^{\theta_i}$, where θ_i is the exponent associated with the ith term, $i = 1, \ldots ,6$. In Fig. 1, we plot

equation (2) for water along with $\lambda - \tau$ values obtained from Vargaftik's data for five other respresentative fluids. Note that τ varies from zero at the critical point to unity at the triple point. The latent-heat curve for water appears to be bounded by nitrogen data from above and carbon dioxide data from below. At $\tau = 0.1$ and $\tau = 0.5$, both nitrogen and carbon dioxide data are within 2 and 5 percent of equation (2), respectively.

Conclusions

A least-squares fit of the latent-heat data of a widely diverse class of fluids is made using equation (1), yielding predicted values that are in excellent agreement with the data throughout a wide range of temperatures. Proper scaling of the temperature allowed us to obtain a universal expression for the scaled latent heat, λ, which may be used to provide good estimates of the latent heat of vaporization of any fluid, given T_c, T_t, and L_t. Equation (2) may also be used to estimate the latent heat in instances when L_t is not given by first using the universal expression to estimate L_t in the manner described above. It is important to note, however, that the universality of equation (2) does not depend upon the
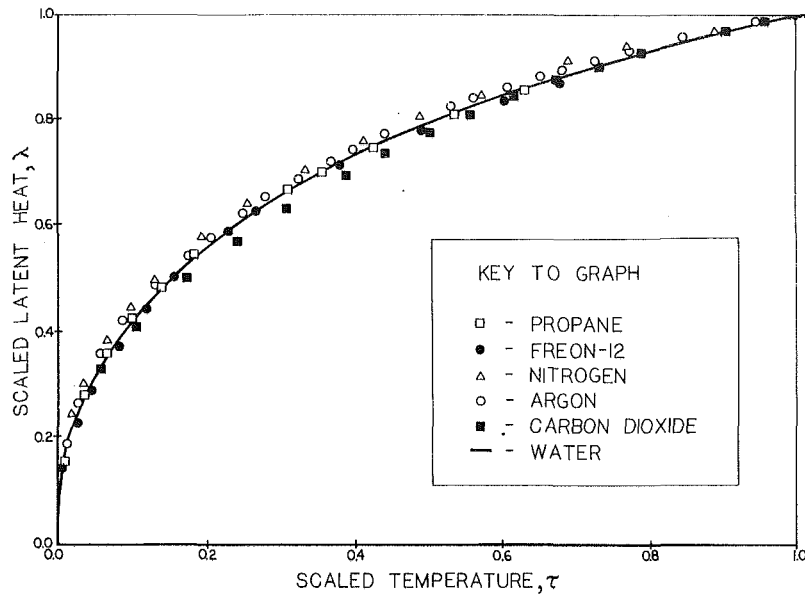
Fig. 1 A plot of the scaled latent heat, λ, versus the scaled temperature $\tau \equiv (T_c - T)/(T_c - T_t)$. The universal curve obtained from equation (1) is shown here along with data for several representative substances (from Vargaftik [13]).

constant latent heat, L_O, used to scale the actual latent-heat value, i.e., we could scale L with cL_T (where c is some constant such that $0 < c \le 1$) instead of L_T and obtain universal behavior, but in this general case, $0 \le L/L_0 \le 1/c$. We have chosen $c = 1$ in this study for convenience. Although the latent-heat values provided by Vargaftik are not numerically the most accurate, the data are sufficiently reliable to demonstrate the existence of a universal equation. For future work, it is suggested that more precise correlations be obtained by using better data.

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