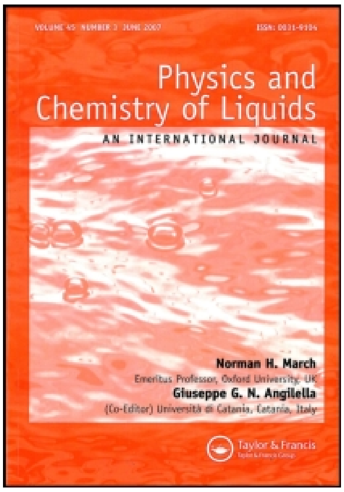

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Jaime Amorós[a]; Suga Ravi[b]
[a] Departamento de Física Aplicada, Universidad de Cantabria, 39005 Santander, Spain [b] Department of Physics, National College, Tiruchirappalli-620001, Tamil Nadu, India

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Correlation among several physicochemical properties of alkali metals in the light of the corresponding states principle

Jaime Amorós[a]* and Suga Ravi[b]

[a]*Departamento de Física Aplicada, Universidad de Cantabria, Avenida de los Castros s/n, 39005 Santander, Spain;* [b]*Department of Physics, National College, Tiruchirappalli-620001, Tamil Nadu, India*

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The objective of this work is to analyse several physicochemical properties (practically all equilibrium properties) for alkali metals (Li, Na, K, Rb and Cs) from the corresponding states principle along the liquid–vapour coexistence line. Selecting the best experimental data, we plot the reduced quantities versus reduced temperature. In all cases, the behaviour of these substances is well correlated. For K, Rb and Cs, a common line adequately represents such behaviour. From the results, we conclude the validity of this principle in the context.

Keywords: alkali metals; correlations; liquid–vapour coexistence line; principle of corresponding states; thermophysical properties

1. Introduction

The evaluation and correlation of physicochemical properties is a matter of great interest in the fields of chemistry, metallurgy, physics and materials science. At present, the values of many quantities are included in a data bank. Others can be calculated from exact thermodynamic relations. The systematisation of this knowledge requires adequate procedures which attempt to search, if it is possible, for a common behaviour which would allow the prediction of results for regions and/or substances barely accessible to experimental treatment.

In this context, the principle of corresponding states (CSP) plays an important role. Such a principle, originally due to van der Waals', postulates that thermodynamic properties of fluids obey two-parameter universal equations when reduced by their critical constants or equivalent parameters. Therefore, the critical temperature and the critical pressure are the two characteristic parameters of the corresponding states method.

This is indeed a good approximation for simple fluids (Ar, Kr, Xe, CH_4 and, partially, Ne) but not for other non-polar or slightly polar 'normal' fluids such as N_2, CO_2, normal paraffins through C_8, etc. The category of normal fluids excludes very light fluids (He, H_2 and, partially, Ne) that are subject to sizable quantum effects, hydrogen-bonded or associated fluids (H_2O and NH_3) and ionic melts or

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*Corresponding author. Email: amorosj@unican.es

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liquid metals. However, even for normal fluids, the thermodynamic properties often deviate from corresponding states by up to 30%.

Successful application of the CSP for correlation of PVT data has encouraged similar correlations of other properties that depend primarily on intermolecular forces. Modifications of the principle are common to improve accuracy or ease of use. Good correlations have been obtained for vapour pressure [1], surface tension [2] and common transport properties such as the coefficients of viscosity [3], thermal conductivity [4] and diffusion [5].

The CSP can be derived from statistical mechanics when severe simplifications are introduced into the partition function [6].

In practice, this hypothesis is valid only for simple fluids, preferably monatomic. The introduction of additional parameters perceptibly improves the results. Pitzer pointed out that by including a third parameter for each substance, the corresponding states approximation can be extended to other fluids [7,8]. Any two substances having the same value of this parameter can then be regarded as having the same thermodynamic properties. Pitzer called the parameter the acentric factor, since it provides a measure of the deviation of the shape of the interaction potential from that for simple fluids. In order to assign numerical values from readily accessible data, he defined his acentric factor w in terms of the reduced vapour pressure $P_\mathrm{r} = P/P_\mathrm{c}$ at a reduced temperature of $T_\mathrm{r} = T/T_\mathrm{c} = 0.7$; thus

$$w = -\log P_\mathrm{r} - 1. \tag{1}$$

In other words, in the van der Waals' picture, the equation of state can be written in the form:

$$f(P_\mathrm{r}, V_\mathrm{r}, T_\mathrm{r}) = 0, \tag{2}$$

whereas in the Pitzer's picture, we write:

$$f(P_\mathrm{r}, V_\mathrm{r}, T_\mathrm{r}, w) = 0 \tag{3}$$

instead of Equation (2).

For simple fluids $w \approx 0$; for typical normal fluids, $w \leq 0.5$. Equations of state based on the acentric factor expansion of corresponding states have been developed, which provide a quite accurate fit to experimental data for normal fluids. Good correlations (1–2%) have been found between the acentric factor and the critical compressibility factor $Z_\mathrm{c} = P_\mathrm{c}V_\mathrm{c}/RT_\mathrm{c}$ [9].

In order to obtain an analytical representation of the Pitzer method suitable for digital computation, Lee and Kesler [10] reformulated the three-parameter corresponding states. In this form, the theory is applicable only to non-polar fluids. However, a more general form [11] using two reference fluids can be applied to a wider range of fluids, including those exhibiting polarity. This form is called the extended corresponding-states principle (ECSP).

Extension of the CSP to polar fluids involves the addition of the fourth parameter to account for polarity effects. While the separation of contributions to the physical properties by size–shape and polarity effects is somewhat artificial, it does provide an approach that has been relatively successful in a number of cases. Furthermore, this type of approach leads to relatively simple generalised expressions that can be used for estimating properties for large classes of compounds.

Although several fourth parameters have been used in the literature, the reduced dipole moment is the choice more adequate. In effect, this quantity is a fundamental electrical property of the molecule. It is often used synonymously with the polarity of a fluid, although higher moments can be significant. The dipole moment is nearly zero for most hydrocarbons.

Recently the CSP has showed an important revival reinforcing their microscopic backgrounds [12,13] and the ECSP has extended its field of application to mixtures [14] and prediction of volumetric properties [15].

However, liquid metals are not usually included. Certainly, they differ from other ionic liquids by the fact that the electronic component requires a quantum mechanical treatment [16]. The long range of the interactions gives rise to a very different behaviour with respect to uncharged liquids [17,18].

There are other substantial differences. In effect, for non-metallic fluids, the liquid–vapour transition is a mere difference of density not affecting the thermodynamic state whereas, for metals, there is moreover a metal–non-metal (MNM) transition due to changes in the electronic structure. The dilute vapours of elemental metals are essentially insulators but an MNM transition occurs, therefore, when a liquid metal vaporises or when it is brought continuously through the region of the critical point into the dilute vapour phase.

The intermolecular potential is created usually from binary interactions. For a dense metallic liquid with a ‘gas’ of delocalised electrons, its valence electron structure is very different from that of an isolated metal atom.

However, the concept of a pair potential can still be useful to describe metallic liquids within a range of ‘normal’ conditions near the triple point. The trick is to construct ‘effective’ potentials that include, in an approximate way, the effects of the conduction electrons as they screen the ‘bare’ Coulomb potential of the positive ions.

From such arguments, some authors [19] have proposed the inadequacy of the CSP to metals. Nevertheless, we have found suitable grounds for its application to alkali metals. The results obtained in this article support reliably this affirmation.

The alkali metals are of major scientific and technological interest. For this reason, a great deal of research has been devoted to their physicochemical properties, despite severe experimental difficulties associated with their high chemical reactivity. From the perspective of fundamental science, the alkali metals occupy a special place. In their normal (high density) phases, they are among the simplest metals: their electronic structure and properties more closely approximate those of the free electron gas than any other elemental groups.

The monovalency of the alkali metals is of central importance for the transition to a non-metallic state. With a single electron per atom, electron–electron interactions are obviously inhibited.

Besides, the study of liquid metals presents interesting specific features with respect to the remaining substances. In effect, whereas for non-metallic elements and compounds, the reduced melting temperature (the ratio between melting point and critical temperature) is about 0.5, for liquid metals it is about 0.15. This fact allows us to investigate an additional range of reduced temperatures with a behaviour that is completely different for some quantities.

This study covers five alkali metals (Li, Na, K, Rb and Cs) along the vapour–liquid saturation line for the following quantities: saturation pressure, density, the ratio between the heat capacities, expansion coefficient at constant pressure, isothermal compressibility coefficient, vaporisation enthalpy, vaporisation entropy, sound velocity, Grüneisen's parameter, internal pressure and static structure factor at long wavelength.

The utilised data were taken predominantly from a standard handbook for alkali metals [20]. Later additional data [21] coincide practically. Other data [22] were also used.

Of course, other researchers have undertaken this type of study previously. Filippov and Blagonravov [23] and Filippov [24,25] analysed molar volume or density (Cs and Li), expansion coefficient at the critical point, isothermal compressibility coefficient and critical constants, also evaluated by Fortov *et al.* [26] following a suggestion made for Grosse [27]. The same author [28] verified the validity of CSP for Rb and Cs from the entropy of vaporisation expecting that Li, Na and K will correspond to Rb and Cs. Balasubramanian [29] calculated the acentric factor (Cs, Rb and K), and recently Prakash *et al.* [30] have extended the analysis to transport coefficients (diffusivity and viscosity coefficients). None of these contributions presents all properties and substances investigated by us.

2. Results and discussion

Table 1 shows the values of main properties (molecular weight, melting point, critical temperature, pressure, density and compressibility factor) for all the substances involved in this work.

As already stated, in the simplest version, the CSP requires two independent parameters. However, temperature and pressure are connected along the saturation line and so only one independent variable is needed in our study. We have verified this statement by plotting the reduced saturation pressure P_{sr} (the ratio between saturated pressure P_{s} and critical pressure P_{c}) versus the reduced temperature, as illustrated in Figure 1.There is an evident common behaviour up to the reduced temperature $T_{\mathrm{r}} = T/T_{\mathrm{c}} \approx 0.45$ where T is the temperature and T_{c} is the critical point. The only exception is Li due to (a) the presence of quantum effects (the high Fermi temperature for Li, and to a lesser extent for Na) and (b) the elevated uncertainty of the critical constants of Li [31].The said result is essential for the present application of the CSP.

The corresponding plot for the reduced density, $\rho_{\mathrm{r}} = \rho/\rho_{\mathrm{c}}$, where ρ is the density of the liquid and ρ_{c} is the critical density, is shown in Figure 2. A slight deviation is observed for Li and Na. The points for the remaining substances obviously coincide.

The dimensionless coefficient $\gamma = C_P/C_V$, where C_P and C_V are the heat capacities at constant pressure P and volume V, respectively, as is shown in Figure 3,

Table 1. Main properties of alkaline metals.

Substance	M	T_{m} (K)	T_{c} (K)	P_{c} (MPa)	ρ_{c} (kg m^{-3})	Z_{c}
Li	6.94	453.67	3680	60	126	0.11
Na	22.99	371.02	2503	25.6	207	0.14
K	39.10	336.76	2281	16.4	194	0.17
Rb	85.47	312.46	2106	13.2	347	0.19
Cs	132.91	301.63	2043	11.7	430	0.21

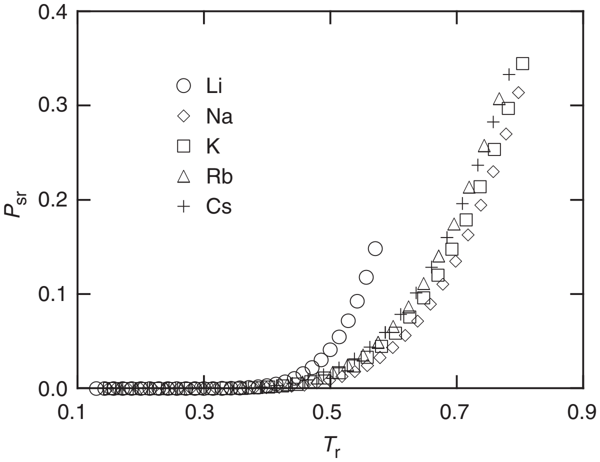

Figure 1. Reduced saturation pressure P_{sr} *vs.* reduced temperature T_r for alkali metals. Data were taken from Equation (4).

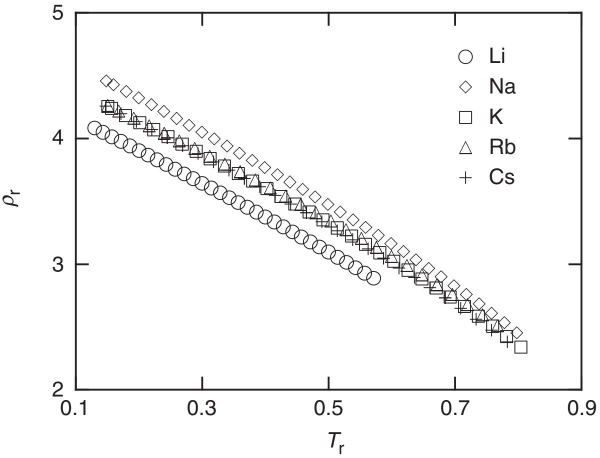

Figure 2. Reduced liquid density of the liquid ρ_r along the saturation line *vs.* reduced temperature T_r for alkali metals. Data were taken from Equation (4).

reveals a similar behaviour at $T_r < 0.5$ with a small deviation for higher reduced temperatures in the case of potassium.

Figure 4 shows the reduced thermal expansion coefficient at constant pressure $\alpha_{Pr} = \alpha_P T_c$, where $\alpha_P = (1/V)(\partial V/\partial T)_P$ and T_c is the critical temperature. All substances present the same behaviour with a small deviation for lithium.

Figure 5 shows the reduced isothermal compressibility coefficient $\beta_{Tr} = \beta_T P_c$, where $\beta_T = -(1/V)(\partial V/\partial P)_T$ is the isothermal compressibility coefficient and P_c is the critical pressure. Upto $T_r = 0.6$, there is a common behaviour. For higher T_r, small deviations appear, probably due to the difficult experimental determination.

The sound velocity was calculated from the expression $u = (\gamma/\beta_T \rho)^{1/2}$ and was reduced according to $u_r = (\gamma \rho_c / \beta_T \rho P_c)^{1/2}$. Figure 6 shows a variation with the same behaviour observed for β_T.

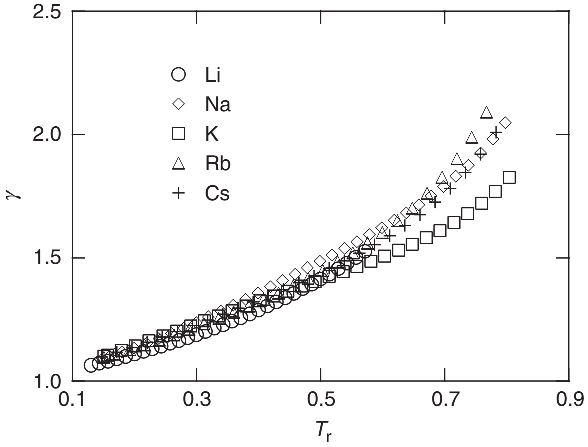

Figure 3. Ratio of the molar heat capacities $\gamma = C_P/C_V$ *vs*. reduced temperature T_r for alkali metals. Data were taken from Equation (4).

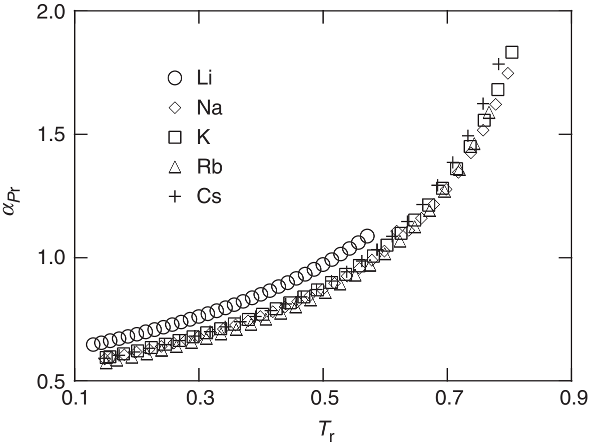

Figure 4. Reduced thermal expansion coefficient α_{Pr} *vs*. reduced temperature T_r for alkali metals. Data were taken from Equation (4).

The reduced vaporisation enthalpy, $\Delta H_{vr} = \Delta H_v / RT_c$, where ΔH_v is the vaporisation enthalpy and R is the molar gas constant, is shown in Figure 7. Small deviations are observed for Li and Na in relation to the rest. The reduced vaporisation entropy, $\Delta S_{vr} = \Delta S_v / R$, where ΔS_v is the vaporisation entropy, shows a very similar trend for all substances, as illustrated in Figure 8.

Grüneisen's equation of state [32] can be written as:

$$PV + g(V) = \Gamma U, \tag{4}$$

where Γ is Grüneisen's parameter or constant, $g(V)$ depends only on the volume, and U is the internal energy. It can easily be shown that

$$\Gamma = \frac{\alpha V}{\beta_T C_V} = \frac{\alpha V}{\beta_S C_P} = \frac{\alpha M u^2}{C_P} \tag{5}$$

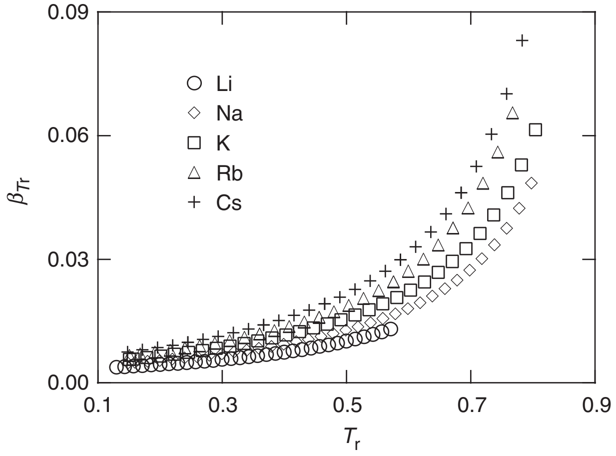

Figure 5. Reduced isothermal compressibility coefficient $\beta_{T\mathrm{r}}$ *vs.* reduced temperature T_r for alkali metals. Data were taken from Equation (4).

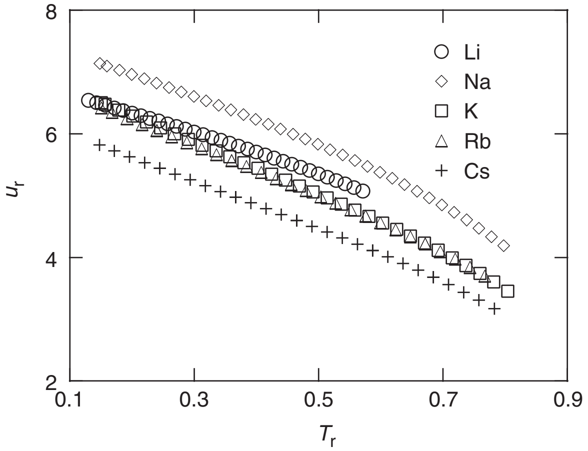

Figure 6. Reduced sound velocity u_r *vs.* reduced temperature T_r for alkali metals. Data were taken from Equation (4).

with

$$\alpha = \left[\frac{C_\mathrm{p}}{MTu^2}\left(\frac{C_\mathrm{p}}{C_\mathrm{v}} - 1\right)\right]^{1/2}. \tag{6}$$

β_S is the adiabatic compressibility coefficient and M is the molar mass. Substitution of α into Equation (5) results in

$$\Gamma = \left[\frac{C_P}{\rho u^2 C_V}\frac{(C_P - C_V)\rho}{MT}\right]^{1/2}; \quad \frac{Mu^2}{C_P} = \left[\left(\frac{1}{C_V} - \frac{1}{C_P}\right)\frac{M}{T}\right]^{1/2} u \tag{7}$$

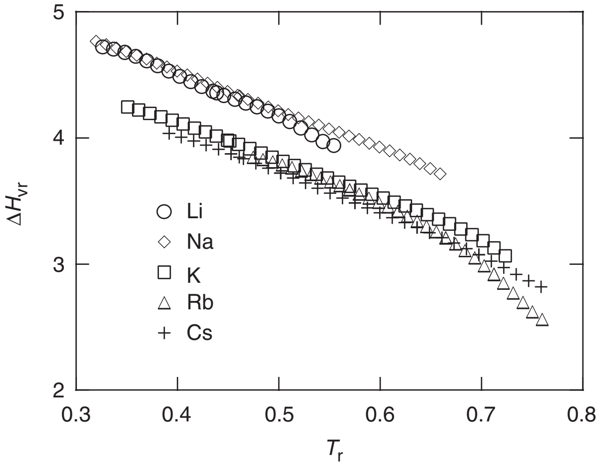

Figure 7. Reduced vaporisation enthalpy ΔH_{vr} *vs*. reduced temperature T_r for alkali metals. Data were taken from Equation (6).

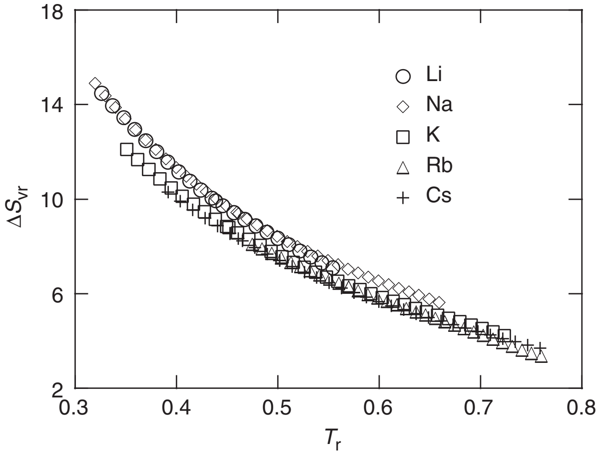

Figure 8. Reduced vaporisation entropy ΔS_{vr} *vs*. reduced temperature T_r for alkali metals. Data were taken from Equation (6).

Figure 9 plots Γ against T_r. Here, a subtler correlation is noticed. Such behaviour is clearly foreseeable given that Grüneisen's theory was introduced for non-metallic monoatomic solids. It is observed that for all substances, Γ first presents an increase, reaches a maximum and then decreases. For a non-metallic substance, the minimum value for T_r is approximately 0.5 and only a downward curve appears. This behaviour reflects the presence of attractive and repulsive forces in the liquid state. When the repulsive/attractive forces are greater, Γ increases/decreases. Besides, the quantum contributions to the repulsive forces extend their range when the molar mass decreases. The height of the maximum is similar for all substances excepting lithium.

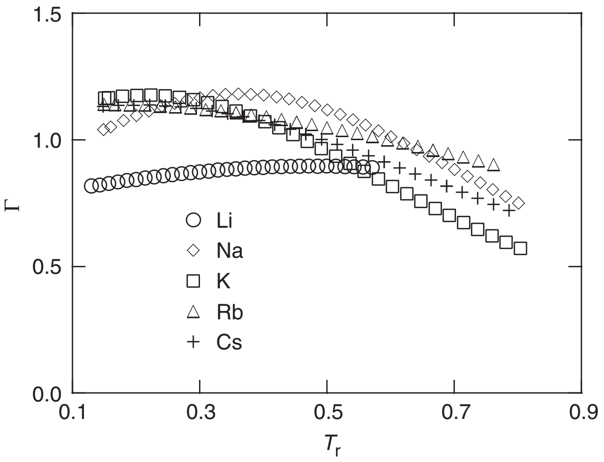

Figure 9. Grüneisen's parameter Γ *vs.* reduced temperature T_r for alkali metals. Data were calculated from Equation (4).

Given that the repulsive forces are practically independent of temperature, whereas the attractive force decreases, at the same density, the repulsive forces are prevailing on the attractive force at higher temperatures. This is easily verifiable in practice. Ar and Na have approximately the same density at the triple point, but the corresponding temperature is four times greater for Na, which shows a clear preponderance of the repulsive forces in contrast with Ar, dominated by the attractive force.

The internal pressure is defined thermodynamically as:

$$P_i = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\frac{\alpha}{\beta_T} - P \tag{8}$$

and plays an essential role, owing to the close relation with the cohesive energy density of matter. As

$$\beta_T = \frac{C_P V}{M u^2 C_V} \tag{9}$$

follows

$$P_i = \frac{u}{V}\left[MTC_V\left(1 - \frac{C_V}{C_P}\right)\right]^{1/2} - P. \tag{10}$$

Obviously this quantity can be connected with Grüneisen's parameter by eliminating some of the basic quantities. This relation is written as

$$P_i = \frac{C_V T \Gamma}{V} - P. \tag{11}$$

Figure 10 shows its variation with the reduced temperature. The earlier discussion involving repulsive and attractive forces can be repeated. The internal pressure is very high for Li due to quantum effects and decreases progressively when the mass increases. The transit to the prevalence of the attractive forces occurs for T_r

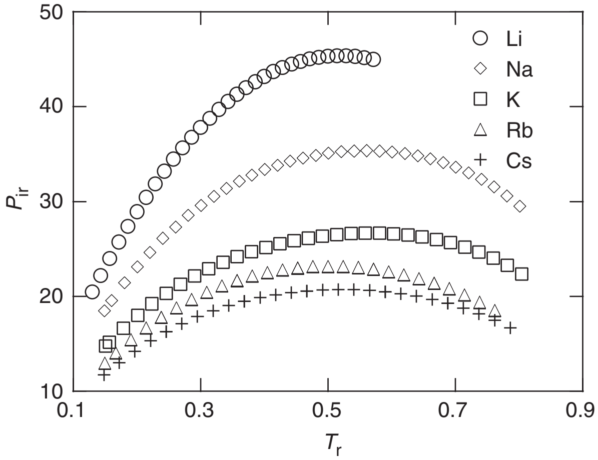

Figure 10. Reduced internal pressure P_{ir} *vs*. reduced temperature T_r for alkali metals. Data were calculated from Equation (5).

in a very similar way. The internal pressure is not uniform because the cohesive forces depend on electronic density, which is different in each case.

The static structure factor is crucial for determining the structure of a substance. For liquids it has an additional significance owing to its relation with the radial distribution function [33]. From the Ornstein–Zernike relation [34] it follows that:

$$\beta_T = \frac{1}{nkT} \lim_{Q\to 0} S(Q), \tag{12}$$

where Q is the wave number, $S(Q)$ is the static structure factor, k is the Boltzmann constant and n is the numerical density. Therefore, its value for the long wavelength limit is

$$S(0) = nkT\beta_T = \frac{N}{V}kT\beta_T = \frac{RT}{V}\beta_T = \frac{\beta_T}{\beta_{\text{id}}}, \tag{13}$$

where $\beta_{\text{id}} = (1/P) = (V/RT)$ and N is the Avogadro constant. Substituting β_T to Equation (5), we obtain

$$S(0) = \frac{C_P RT}{C_V M u^2}. \tag{14}$$

It is also possible to relate directly $S(0)$ to Γ and P_{i} by means of the following expressions:

$$\Gamma = \left[\frac{(C_P/C_V) - 1}{C_V}\frac{R}{S(0)}\right]^{1/2}, \tag{15}$$

$$P_i = \frac{\Gamma}{V}\left[(C_P - C_V)\frac{R}{S(0)}\right]^{1/2} - 1. \tag{16}$$

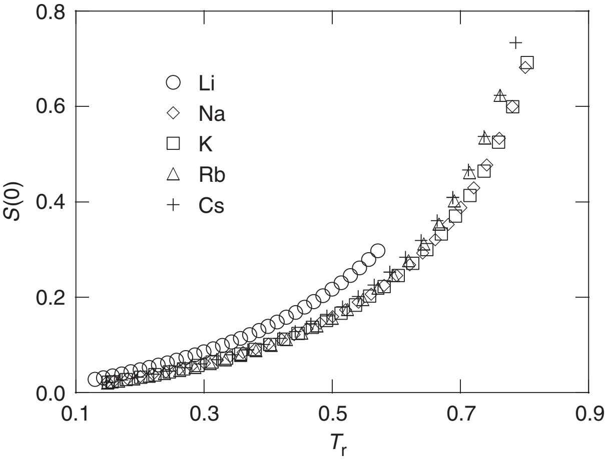

Figure 11. Static structure factor at long wavelength $S(0)$ *vs.* reduced temperature T_r for alkali metals. Data were calculated from Equation (11).

$S(0)$ against T_r is plotted in Figure 11. Lithium shows a moderate deviation and the remaining ones are located on one single line.

3. Conclusions

The application of the CSP to several physicochemical properties along the liquid–vapour coexistence line for the alkali metals Li, Na, K, Rb and Cs gives a satisfactory result. All these properties are well correlated.

Little deviations are observed for Li and to a lesser extent for Na, due to quantum effects in the same way as the behaviour for Ne with regard to Ar, Kr and Xe in the context of non-metallic simple liquids.

The peculiarity of the Li behaviour has sound grounds: Balucani *et al.* [35] exclude Li due to its 'quantum character'; González *et al.* [36] estimate that Li is practically immiscible with the other alkalis, which are all miscible among themselves. Also, Li differs from the other alkali metals in having no p-electrons in its core. Day *et al.* [37] found good experimental agreement for the static structure factor S(Q) of Na and K but only a qualitative agreement for Li.

A very strong correlation exists for the ratio of the heat capacities (γ) and the reduced vaporisation entropy (ΔS_v). With the exception of Li, for the reasons quoted above, a correlation exists also for the reduced values of the saturation pressure (P_s), the density of the liquid (ρ), the cubic expansion coefficient (α_P) and the static structure factor [$S(0)$]. In the case of the vaporisation enthalpy (ΔH_v), the correlation line of Li and Na is slightly higher than the line for K, Rb and Cs. The remaining quantities do not show a strong correlation but the variation between them has a solid basis when taking their molar mass into account.

In summary, the results found in this work are excellent for K, Rb and Cs and good (acceptable) for Na (Li and Na). Therefore, the CSP is an important tool for predicting and correlating the physicochemical properties of alkali metals.

References

[1] B.A. Hacker and C.K. Hall, Ind. Eng. Chem. Fundam. **24**, 262 (1985).
[2] G.T. Dee and B.B. Sauer, Polymer **36**, 1673 (1995).
[3] A.S. Teja and P. Rice, Ind. Eng. Chem. Fundam. **20**, 77 (1981).
[4] A.S. Teja and P. Rice, Chem. Eng. Sci. **36**, 417 (1981).
[5] A.S. Teja, Ind. Eng. Chem. Fundam. **24**, 39 (1985).
[6] K.S. Pitzer, J. Chem. Phys. **7**, 583 (1939).
[7] K.S. Pitzer, J. Am. Chem. Soc. **77**, 3427 (1955).
[8] K.S. Pitzer, D.Z. Lipmann, R.F. Curl, and C.M. Huggins, J. Am. Chem. Soc. **77**, 3433 (1955).
[9] D.R. Schreiber and K.S. Pitzer, Fluid Phase Equilibr. **46**, 113 (1989).
[10] B.I. Lee and M.G. Kesler, AIChE. J. **21**, 510 (1975).
[11] A.S. Teja, AIChE. J. **26**, 337 (1980).
[12] D. Ben-Amotz, J. Chem. Phys. **117**, 4632 (2002).
[13] R.M. Digilov, Int. J. Thermophys. **23**, 1381 (2002).
[14] A. Nowarski and D.G. Friend, Int. J. Thermophys. **19**, 1133 (1998).
[15] R.S. Pai-Panandiker, C.A. Nieto de Castro, I.M. Marrucho, and J.F. Ely, Int. J. Thermophys. **23**, 771 (2002).
[16] R. Abe, J. Phys. Soc. Jpn **58**, 1307 (1989).
[17] R.G. Chapman and N.H. March, Phys. Chem. Liq. **16**, 77 (1986).
[18] R.G. Chapman and N.H. March, Phys. Chem. Liq. **17**, 165 (1987).
[19] E.M. Apfelbaum, V.S. Vorob'ev, and G.A. Martynov, J. Phys. Chem. B **110**, 8474 (2006).
[20] K. Hornung, in *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, edited by R.W. Ohse (Blackwell, Oxford, 1985), p. 505.
[21] N.B. Vargaftik, Y.K. Vinogradov, and Y.S. Yargin, *Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures* (Begell House, New York, 1996).
[22] W.C. Reynolds, *Thermodynamic Properties in SI* (Stanford University, Stanford, 1979).
[23] L.P. Filippov and L.A. Blagonravov (in Russian). Izv.Vyssh. Uchebn. Zavd. Energetik*a* **9**, 66 (1985).
[24] L.P. Filippov, High Temp. **24**, 254 (1986).
[25] L.P. Filippov, J. Eng. Phys. **50**, 697 (1986).
[26] V.E. Fortov, A.N. Dremin, and A.A. Leont'ev, High Temp. **13**, 984 (1975).
[27] A.V. Grosse, J. Inorg. Nucl. Chem. **22**, 23 (1961).
[28] A.V. Grosse, J. Inorg. Nucl. Chem. **28**, 2125 (1961).
[29] R. Balasubramanian, Int. J. Thermophys. **24**, 202 (2003).
[30] S.G. Prakash, R. Ravi, and R.P. Chhabra, Chem. Phys. **302**, 149 (2004).
[31] H.Z. Hess, Z. Metallkd. **86**, 240 (1995).
[32] E. Mendoza, Eur. J. Phys. **3**, 181 (1982).
[33] Y. Waseda, *The Structure of Non-crystalline Materials* (McGraw-Hill, New York, 1980).
[34] N.H. March and M.P. Tosi, *Atomic Dynamics in Liquids* (Dover, New York, 1989).
[35] U. Balucani, A. Torcini, and R. Vallauri, Phys. Rev. *A* **46**, 2159 (1992).
[36] L.E. González, D.J. González, M. Silbert, and J.A. Alonso, J. Phys. Condens. Matter **5**, 4283 (1993).
[37] R.S. Day, F. Sun, and P.H. Cutler, Phys. Rev. A **19**, 328 (1979).