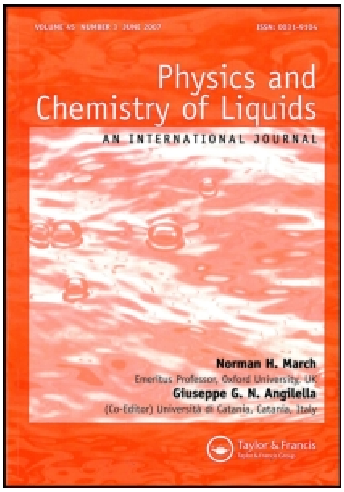

**Physics and Chemistry of Liquids**

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Undercooled State of Liquid Rubidium

R. N. Singh[a]; R. P. Jaju[b]
[a] Physics Department, [b] Computer Science Department, College of Science, Sultan Qaboos University, Sultanate, Oman

**To cite this Article** Singh, R. N. and Jaju, R. P.(1998) 'Undercooled State of Liquid Rubidium', Physics and Chemistry of Liquids, 36: 2, 67 — 74

**To link to this Article: DOI:** 10.1080/00319109808030595

**URL:** http://dx.doi.org/10.1080/00319109808030595

*Phys. Chem. Liq.*, 1998, Vol. 36, pp. 67 – 74
Reprints available directly from the publisher
Photocopying permitted by license only

# UNDERCOOLED STATE OF LIQUID RUBIDIUM

R. N. SINGH[a] and R. P. JAJU[b]

[a]*Physics Department;*
[b]*Computer Science Department, College of Science,*
*Sultan Qaboos University, P. O. Box 36, SQ - 123, Sultanate of Oman*

*(Received 26 April 1997)*

A first principle theoretical scheme which is based on pseudopotential perturbation theory, the thermodynamics of hard sphere systems and the variational method based on Gibbs-Bogoliaubov inequality is used to investigate the specific heat of liquid Rb in the undercooled region ($T < T_m$). $C^l_P$ is found to increase with decreasing $T$ and exhibits a maxima in the vicinity of 60 K. The anomalies in $C^l_P$ in the undercooled region are discussed in terms of structure and volume dependent contributions of energies and entropies.

*Keywords*: Specific heat; Liquid metal Rb

The extended liquid region (both undercooled, $T \ll T_m$, and the expanded state, $T > T_B$) of liquid metals is of considerable significance to understand the structure and the role of basic interactions (i.e. electron – electron, ion – ion and electron – ion) at these extreme conditions. Rubidium and Caesium have low melting temperatures and therefore the extension of liquid region is comparatively easier than other liquid metals. In particular, the experimental data (for review see ref [1]) reveal that the expanded liquid Rb and Cs undergo a metal – nonmetal transition near the liquid – vapour critical point. This could possibly be linked to the significant change in the structure or in the interatomic forces, or both as the density of the fluid is decreased. Similarly the extended liquid region of several liquid metals below $T_m$ also exhibit interesting properties. For example, the heat capacity at constant pressure ($C^l_P$) of several low melting point metals show a temperature dependent $C^l_P$ value in the small temperature range above

$T_m$, and continues into the undercooled state [2–4]. $C_P^l$ of the undercooled liquid metal is a valuable information to understand the structure and energetics of the solidification behaviour of liquid metals at high degrees of undercooling. For want of better knowledge, experimental $C_P^l$ data at $T > T_m$ are normally used [5–6] to construct models to extrapolate it in the region $T < T_m$. But such attempts have proved unsuccessful [7] for low melting point metals.

In this work, we therefore consider a first principle theoretical scheme which is based on pseudopotential perturbation theory, the thermodynamics of hard sphere systems and the variational method based on Gibbs-Bogoliaubov inequality to calculate $C_P^l$ in the undercooled region. Such an approach is free from any adjustable parameters and helps to analyse the role of basic interactions of the metallic systems in the undercooled state. The basic thrust is to establish a suitable link between the forces, the structure and the thermodynamic functions which has been achieved by virtue of the optimization condition i.e.

$$\left(\frac{\partial F}{\partial \sigma}\right)_{\Omega,T} = 0 \tag{1}$$

where $F$ is the Helmholtz free energy at a given temperature $T$ and volume $\Omega$ of the system. $\sigma$ is the hard sphere diameter. Equation (1) also ensures the thermodynamic stability of the system. $F$ can be expressed as

$$F = E - TS \tag{2}$$

$E$ is the internal energy and $S$ is the entropy at temperature $T$. The various interactions likewise electron–electron (e), ion–ion (i) electron–ion (ei) contribute to $E$. Restricting to second order terms of the pseudopotential perturbation expansion, one has

$$E = E_e + E_i + (E_{ei}{}^{I} + E_{ei}{}^{II}) \tag{3}$$

$E_e$ is the contribution due to valence electrons, and $E_i$ arises due to ion–ion interactions. $E_{ei}{}^{I}$ and $E_{ei}{}^{II}$ represent respectively the first and second order perturbation energies due to electron–ion interactions. It may be mentioned that $E_e$ and $E_{ei}{}^{I}$ are volume-dependent terms whereas $E_i$ and $E_{ei}{}^{II}$ involve structure. Detailed expressions of these terms can be obtained from previous works [4, 8]. The structure factors needed for the evaluation of $E_i$ and $E_{ei}{}^{II}$ are calculated from the Percus-Yevic solution for hard sphere fluids which is characterised by the hard sphere diameter ($\sigma$), or, equivalently, by the packing fraction $\eta = \left(\frac{\pi}{6\Omega}\right) \sigma^3$. The same $\sigma$ (or $\eta$) which is required for the calculation of structure factor has also been used to evaluate the entropy, $S$, as needed in equation (2) i.e.

$$S = S_{\text{gas}} + S_\eta + S_{\text{elec}} \tag{4}$$

$S_{\text{gas}}$ is the ideal gas entropy and $S_\eta$ correspond to the packing density $\eta$. $S_{\text{elec}}$ is a correction term which arises due to low temperature specific heat contribution of the electron gas. For detailed expressions of various terms we refer the work of Singh and Singh [8]. Of these, $S_\eta$ is the structure dependent contribution to the entropy.

The basic ingredients for the numerical solution of equations (1) and (2) are the choice of pseudopotential and the electron screening function. We consider the Heine-Abarenkov (HA) [10] form of the potential which consists of a potential well in the core region ($r < r_m$, $r_m$ model radius) and Coulombic ($-Z/r$) in the outside region ($r > r_m$). It is prefered because the model parameters are not fitted to any of the observed properties but are determined independently by matching the wave functions [11]. For electron's screening we consider the exchange and correlation function due to Ichimaru and Utsumi [12] which satisfies the self consistency conditions in the compressibility sum rule and is good at short range correlations.

We have applied it to Rubidium and investigated the role of basic interactions and various energies ($E_e$, $E_i$, $E_{ei}$) and entropies ($S_{\text{gas}}$, $S_\eta$, $S_{\text{elec}}$) contributions in the undercooled region. The optimised values of hard sphere diameter ($\sigma$) calculated from equation (1) for a wide range of $T$ is shown in Figure 1. $\sigma$ increases with decreasing $T$. Among the various energy contributions, $E_e$, $E_{ei}{}^{II}$ and $E_i$ are negative whereas $E_{ei}{}^{I}$ is positive and their magnitude vary as

$$|E_i| > |E_e| > \left|E_{ei}{}^{I}\right| > \left|E_{ei}{}^{II}\right|.$$

The $T$-dependence of these energies is shown in Figures 2(a)–(d). $E_e$ and $E_i$ decrease with decreasing $T$ whereas $E_{ei}{}^{I}$ $E_{ei}{}^{II}$ increase in the undercooled region.

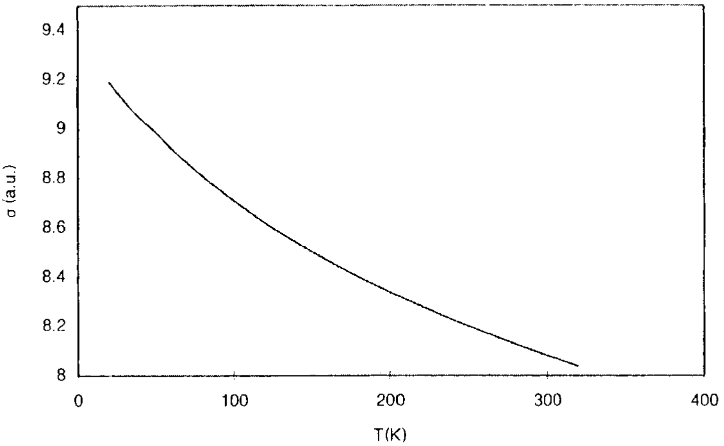

FIGURE 1 $T$-dependence of optimised hard sphere diameter ($\sigma$) in the undercooled region ($T \ll T_m$) of liquid Rb.

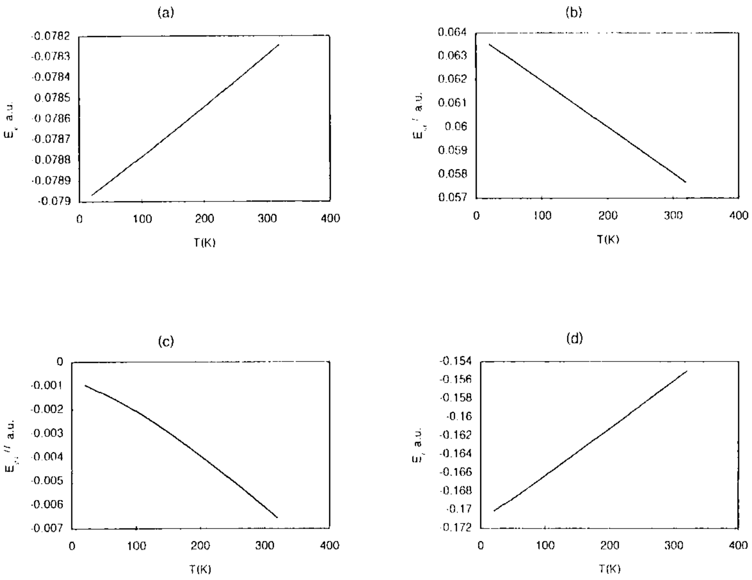

FIGURE 2 $T$-dependence of the various contributions to internal energy in the undercooled region ($T \ll T_m$) of liquid Rb: (a) Electron gas energy, $E_e$; (b) First order energy of electron-ion interactions, $E_{ei}{}^{I}$; (c) Second order energy of electron - ion interactions, $E_{ei}{}^{II}$; (d) Ionic energy, $E_i$.

The optimised values of $\sigma$ determined from the optimisation condition equation (1) in the undercooled state have also been used to estimate the entropy contribution $S_\eta$ as a function of $T$. The temperature dependence of the other entropic terms i.e. $S_{gas}$ and $S_{elec}$ arise due to $T$ and $\Omega$. $S_{gas}$, $S_\eta$ and $S_{elec}$ as a function of $T$ for Rb are plotted in Figures 3 (a)–(c). The plot of total entropy ($S$) is shown in Figure 3 (d). Among these contributions, only $S_\eta$ is structure dependent and is negative, whereas $S_{gas}$ and $S_{elec}$ are volume dependent positive terms. The magnitude of $S_{gas}$ is much larger than $S_\eta$ and $S_{elec}$. All contributions of entropy decrease with decreasing $T$. $\frac{\partial S_{elec}}{\partial T}$ $(= S'_{elec})$ is quite smaller than $\frac{\partial S_{gas}}{\partial T}$ $(= S'_{gas})$ and $\frac{\partial S_\eta}{\partial T}$ $(= S'_\eta)$.

Near the melting temperature the derivatives $S'_{gas}$ and $S'_\eta$ are quite similar, but in the undercooled region, $S'_\eta$ becomes more than double of $S'_{gas}$. We shall see later that these temperature derivatives of entropy terms, affect the values of specific heat considerably in the undercooled region. The calculated values of entropy near the melting temperature

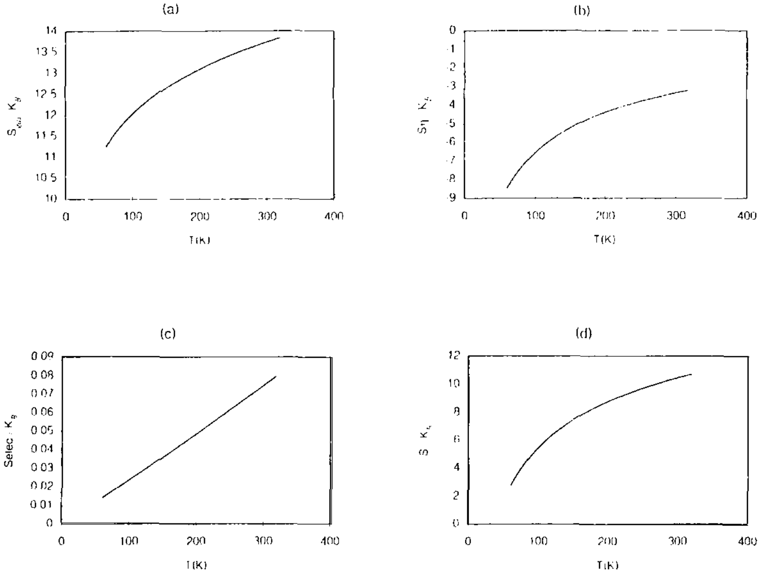

FIGURE 3 $T$-dependence of the entropic contributions in the undercooled region ($T \ll T_m$) for liquid Rb: (a) Electron's gas term, $S_{gas}$; (b) Packing fraction term, $S_\eta$; (c) Low temperature entropy contribution, $S_{elec}$; (d) Total entropy, $S$.

$T_m = 312.64$ K i.e. $S = 10.59\ K_B$ is in good agreement with the experimental value $10.35\ K_B$.

The calculated values of the temperature dependence of the enthalpy and entropy contributions are used to evaluate the specific heat, $C^l_P$, in the undercooled state of liquid Rb. It is quite helpful to investigate the role of various structure and volume dependent terms on $C^l_P$.

$$C^l_P(T) = \left(\frac{\partial H}{\partial T}\right)_P = \left\{\frac{\partial}{\partial T}(E + P\Omega)\right\}_P = \left(\frac{\partial E_e}{\partial T}\right)_P + \left(\frac{\partial E_{ei}}{\partial T}\right)_P + \left(\frac{\partial E_i}{\partial T}\right)_P + P\Omega\alpha_P \tag{5}$$

and

$$C^l_P(T) = T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S_{gas}}{\partial T}\right)_P + T\left(\frac{\partial S_\eta}{\partial T}\right)_P + T\left(\frac{\partial S_{elec}}{\partial T}\right)_P \tag{6}$$

$E_e$ and $E_i$ in equation (5) contribute positively while $E_{ei}$ has negative contributions to $C^l_P$ data. The last term $P\Omega\alpha_P$ ($\alpha_P$, thermal coefficient of expansion) has little contribution. The magnitude of $\frac{\partial E_e}{\partial T}(= E'_e)$ is quite small in comparison to $\frac{\partial E_i}{\partial T}(= E'_i)$ and $\frac{\partial E_{ei}}{\partial T}(= E'_{ei})$. The maximum contribution arises from the ionic term $E'_i$. Further $E'_e$ almost remains constant in the undercooled region. $E'_{ei}$ increases whereas $E'_i$ decreases with decreasing $T$. Near $T_m$, the contributions from $E_e$, $E_{ei}$ and $E_i$ to $C^l_P$ data are 6.555, −110.911 and 136.082 J mol$^{-1}$ K$^{-1}$ respectively, which become, 6.293, −93.867 and 131.887 J mol$^{-1}$ K$^{-1}$ respectively when $T$ is lowered to $T = 100$ K.

Obviously the increase of $C^l_P$ in the undercooled region is controlled by the contributions arising from electron - ion interaction energies. $C^l_P$ values calculated in the undercooled region from equation (5) are plotted in Figure 4. The results indicate that heat capacity of Rb increases with decreasing $T$ in the undercooled region. The caluculated $C^l_P$ from equation (5) exhibits maximum value in the vicinity of 60 K and then decreases.

Near $T_m = 312.64$ K, the calculated value of $C^l_P = 31.73$ J mol$^{-1}$K$^{-1}$ from equation (5) is lower than the experimental [13] value 35.36 J mol$^{-1}$ K$^{-1}$. For the sake of comparison, we have also used the energy equation (5) to calculate $C^l_P$ above $T > T_m$. $C^l_P$ above $T_m$

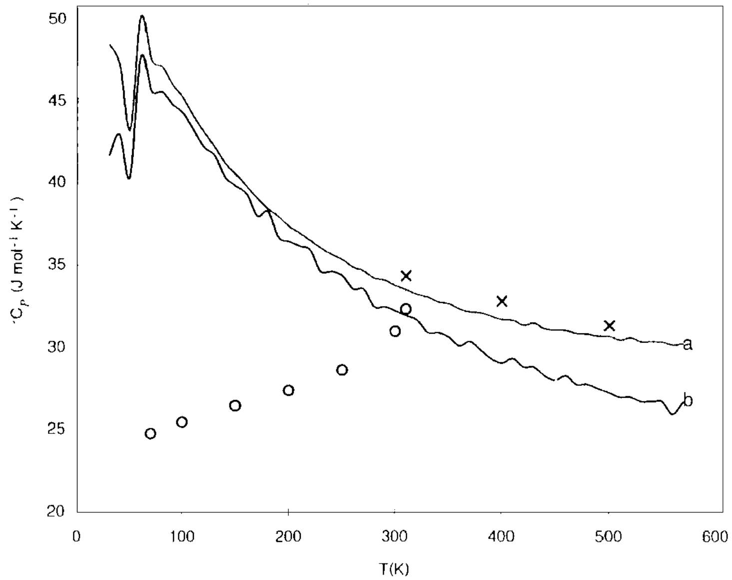

FIGURE 4 Heat Capacity of liquid Rb. (a)-calculated from entropy equation (6), (b)-calculated from enthalpy equation (5). (x x x), (o o o) - experimental values corresponding to crystalline and liquid state.

decreases with increasing $T$ likewise experimental values and tend to attain a constant value in the vicinity of 550 K. However the values calculated from equation (5) decrease faster with increasing $T$ than the experimental result.

$C^l_p$ values calculated from entropy equation (6) for both regions ($T > T_m$ and $T < T_m$) are also plotted in Figure 4. We have observed that all the entropy terms ($S'_{\text{gas}}$, $S'_\eta$ and $S'_{\text{elec}}$), contribute positively to $C^l_p$. The maximum contribution arises from the structure dependent term $S'_\eta$ followed by $S'_{\text{gas}}$ and $S'_{\text{elec}}$. In the undercooled region both $S'_\eta$ and $S'_{\text{gas}}$ increase with decreasing $T$ but $S'_{\text{elec}}$ decreases. It is evident from Figure 4 that $C^l_p$ calculated from equation (6) for Rb in the undercooled region also increases with decreasing $T$. $C^l_p$ calculated from entropy equation (6) are slightly higher than the values obtained from energy equation (5). Likewise earlier, the anomalies in $C^l_p - T$ variation occure around 50 K. The packing fraction $\eta$ for Rb corresponding to maximum in $C^l_p$ is found to be 0.605. $C^l_p$ calculated from entropy equation (6) i.e. $C^l_p(T_m) = 33.53\ \mathrm{J\ mol^{-1}\ K^{-1}}$ at $T = T_m$ is in good agreement with the experimental value $35.36\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

The calculated values of $C^l_p$ at higher temperature ($T > T_m$) from entropy equation (6) also decrease with increasing temperature and $C^l_p - T$ variation is similar to experimental observations.

The present analysis reveals that $C^l_p$ of liquid Rb increases in the undercooled region with decreasing $T$. $C^l_p$ exhibits anomalies i.e. maximum and minimum values in the undercooled region in the vicinity of $T = 60\,\mathrm{K}$. Such anomalies are found to occure due to structure dependent terms. The temperature at which $C^l_p$ is maximum is often interpreted as glass transition temperature ($T_g$) and the temperature of minimum $C^l_p$ as ideal gas transition [14] temperature. The inflection of $C^l_p$ in the undercooled state might be due to structural freezing at a temperature $T_g$ below which atomic mobility in the liquid state is negligible.

## *References*

[1] Winter, R. and Hensel, F. (1989). *Phys. Chem. Liq.*, **20**, 1.

[2] Pesepezko, J. H. and Paik, D. S. (1984). *J. Non-Crystalline Solids*, **61–62**, 113.

[3] Tsuchiya, Y. (1991). *J. Phys. Cond. Matter*, **3**, 3163.

[4] Singh, R. N. and Sommer, F. (1994). *Phys. Chem. Liq.*, **28**, 129.

[5] Hoch, M. and Vornardakis, T. (1976). Ber-Busenges, *Phys. Chem.*, **80**, 677.

[6] Dubey, K. S. and Ramchandra Rao, P. (1984). *Act. Metall.*, **32**, 91.

[7] Sommer, F. (1991). *Mater. Sci. Eng.*, **A113**, 434.

[8] Singh, S. and Singh, R. N. (1994). *Phys. Chem. Liq.*, **27**, 203.

[9] Ashroft, N. W. and Lekner, J. (1966). *Phys. Rev.*, **145**, 83.

[10] Heine, V. and Abarenkov, I. V. (1964). *Phil. Mag.*, **9**, 41.

[11] Ese, O. and Reissland, I. A. (1973). *J. Phys. F. Metal Phys.*, **3**, 2066.

[12] Ichimaru, S. and Utsumi, K. (1981). *J. Phys. Rev.*, **B24**, 7385.

[13] Hultgren, R., Desai, P. D., Hawkins, D. T., Gleissh, M., Kelley, K. K. and Wagman, D. D. (1973). "Selected values of the thermodynamic properties of the elements" *Am. Soc. Metals*, Mtals Parks, Ohio.

[14] Gyeer, A. L. (1995). Intermetallic compounds–Principle and Practice Vol. I, eds. Westbrook, J. H. and Fleischer, R. L., John Wiley and Sons, New York, p. 730.