The Specific Heat of Liquid Metals

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The specific heat of liquid metals is calculated using a fluid of Percus-Yevick plus tail as a reference system together with the Cumming potential in a random-phase approximation. It is shown that the improved semi-empirical hard sphere direct correlation function proposed by Colot et al. leads to a drastic improvement of C_p values over the HS model.

The Hard Sphere (HS) model has been widely used to understand the structural and thermodynamical properties of liquid metals. The advantage of the HS model is that the Percus-Yevick (PY) solution is available for the direct correlation function (dcf). If one uses this solution for liquid metals, their density range is normally such that the PY solution has to be corrected slightly. This is simply because the PY results lead to a slight overestimate of the height of the main peak in the structure factor $S(q)$ and tend to predict a large space between the successive peaks. Verlet and Weis [1] proposed a method to achieve better agreement with the simulation results for the structure factor known as Verlet-Weis (VW) parametrization. A more recent approach to improve this agreement has been made by Colot et al. [2]. The advantage of this method over the VW approach is that the analytic expression for the dcf is presented. This semiempirical expression for the dcf for the HS model with a Yukawa tail gave an excellent fit with the HS Monte Carlo experiments particularly in the high packing fraction range $0.40 \leq \eta \leq 0.74$, as shown in their paper [2] for $\eta = 0.49$. Recently, we have calculated the structure factor of alkali metals using the Percus-Yevick-tail (PYT) reference system of Colot et al. [2] and shown that this improvement plays a significant role in the determination of the structure factor in random phase approximation [3]. In the present paper we present thermodynamical calculations using the same parameters as those obtained by the structure factor calculations and calculate the specific heat (C_p) of liquid metals.

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The specific heat C_p of a system of hard spheres of diameter σ can be expressed as [4]

$$C_p/k_B = \frac{D}{2} + \frac{|Z(\eta)|^2}{\frac{\partial}{\partial \eta}[\eta\, Z(\eta)]} \tag{1}$$

with $D = 3$ in the present case.

The central thermodynamic quantity is the compressibility factor $Z = \beta\, p/\varrho$, i.e. the dimensionless combination of the density (ϱ), the pressure p and $\beta = 1/k_B\, T$, which for hard spheres depends only on the density. The term $\frac{\partial}{\partial \eta}[\eta\, Z(\eta)]$ can be expressed as

$$\frac{\partial}{\partial \eta}[\eta\, Z(\eta)] = \beta \frac{\partial p}{\partial \varrho} = 1 - C(\eta) = S(0)^{-1}. \tag{2}$$

Using the RPA allows us to write the expression for $C(q)$ of the system in terms of the reference potential and its perturbation $\phi_1(q)$:

$$C(q) = C_{PYT}(q) - \beta\, \phi_1(q). \tag{3}$$

For $C_{PYT}(q)$, we use the Colot et al. [2] expression which they obtained by mixing the Percus-Yevick dcf with the dcf of the Yukawa tail producing the simple Fourier transformed dcf

$$C_{PYT}(q) = a\, C_{PY}(q) + [24\, \eta\, b/(q^2 + d^2)]\left[\cos q + \frac{d}{q} \sin q\right]. \tag{4}$$

The parameters $a(\eta)$, $b(\eta)$ and $d(\eta)$ are given by Colot et al. [2]. For $\phi_1(q)$, the Fourier transform of the

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Cumming potential is used [5]

$$\beta\phi_1(q) = -\frac{12\eta}{q}\left[X_1\left(\frac{a_1\sin q+(a_2+q)\cos q}{(a_2+q)^2+a_1^2}\right.\right. \quad (5)$$
$$+\frac{a_1\sin q-(a_2-q)\cos q}{(a_2-q)^2+a_1^2}$$
$$+X_2\left(\frac{a_1\cos q+(a_2-q)\sin q}{(a_2-q)^2+a_1^2}\right.$$
$$\left.\left.\left.-\frac{a_1\cos q-(a_2+q)\sin q}{(a_2+q)^2+a_1^2}\right)\right],$$

where $X_1=\Lambda_1/k_B\,T\sigma$, $X_2=\Lambda_2/k_B\,T\sigma$, $a_1=Z\sigma$ and $a_2=\mu\sigma$ and $q=Q\sigma$. The parameters Λ_1, Λ_2, Z, and μ are defined by Bretonnet [5]. The long wavelength limit of $S(q)$ is given by [3]

$$S(0)=S_{PYT}(0) \quad (6)$$
$$\cdot\{1-[24\eta(X_1a_1+X_2a_2)/(a_1^2+a_2^2)]\,S_{PYT}(0)\}^{-1},$$

where

$$S_{PYT}(0)=[1-a\,C_{PY}-(24\,\eta\,b/d^2)\,(1+d)]^{-1}.$$

Including the perturbation part, $Z(\eta)$ for the PYT system can be solved as

$$Z(\eta)=\frac{P}{\varrho\,k_BT}=\left[1-a+\frac{a(1+\eta+\eta^2)}{(1-\eta)^3}-\frac{12b(1+d)}{d^2}\eta\right.$$
$$\left.-\frac{12\eta(X_1a_1+X_2a_2)}{(a_1^2+a_2^2)}\right]. \quad (7)$$

Here $a(\eta)$, $b(\eta)$, and $d(\eta)$ are treated as constants at a particular temperature. Substituting $a=1$ and $b=0$ we get $Z(\eta)$ and $S(0)$ for HS system.

Firstly, we have calculated the full structure factors of liquid metals at different temperatures using the dcf of Colot et al. in RPA [6]. Minor adjustment is needed to the parameter values of Bretonnet [5] at the melting temperature to obtain an excellent fit to the experimental values. The value of η is obtained by fitting the first peak of the structure factor at different temperatures. At higher temperatures we have established the uniqueness of the set of parameters by keeping the parameters Λ_1, Λ_2, Z, and μ constant and setting the hard sphere diameters as density dependent. The parameters used in the calculations are shown in Table 1. We have now calculated the values of C_p for several liquid metals at different temperatures for the PYT system using (1), (6), and (7), and for the HS system. Bretonnet [5] has calculated the $S(0)$ values for the HS system in RPA. Substituting $S(0)$ and $Z(\eta)$ for $a=1$ and $b=0$ in (1), we obtained C_p for the HS system. The values of C_p presented in Table 2 using the PYT system show a considerable improvement over the HS system. This clearly shows that the value of C_p is drastically affected by the values of $S(0)$ and $Z(\eta)$ and hence by the compressibility, and may be also by the softness in the pair potential. Thus we conclude that the improvement in the direct correlation function may also lead to an improvement in the thermodynamical quantities such as the specific heat.

Table 1. Potential parameters.

Element	Temp. (K)	η	X_1	X_2	a_1	a_2
Li	463	0.493	−0.1028	0.2925	0.9926	6.064
	523	0.470	−0.0923	0.2626	0.9788	5.968
	725	0.441	−0.0672	0.1912	0.9698	5.8432
Na	378	0.465	−0.2656	0.4343	2.1153	5.947
	473	0.4395	−0.2146	0.3508	2.0927	5.836
	573	0.427	−0.1774	0.2900	2.0896	5.780
K	343	0.451	−0.5421	0.7966	3.1113	5.887
	378	0.432	−0.4978	0.7315	3.0745	5.8031
	473	0.431	−0.3940	0.5790	3.1042	5.7986
Rb	313	0.470	−1.4318	1.9173	5.4533	5.9680
	373	0.448	−1.199	1.6063	5.4610	5.8730
Cs	303	0.458	−2.2609	3.3997	7.2658	5.917
	373	0.440	−1.8471	2.7775	7.2245	5.838

Table 2. Calculations of specific heat of liquid metals using HS and PYT system

Element	Temp. (K)	η_{PYT}	C_p (PYT)	C_p (Expt)[7]	C_p(HS)
Li	463	0.493	4.16	3.67	5.05 (470 K)
	523	0.470	3.95	3.63	4.25 (595 K)
	725	0.441	3.72	3.54	4.22 (725 K)
Na	378	0.465	3.91	3.93	4.70 (373 K)
	473	0.4395	3.70	3.77	3.56 (423 K)
	573	0.427	3.63	3.64	–
K	343	0.451	3.81	3.78	4.50 (338 K)
	378	0.432	3.67	3.73	4.33 (373 K)
	473	0.431	3.66	3.69	4.16 (423 K)
Rb	313	0.470	3.99	3.88	–
	373	0.448	3.82	3.82	–
Cs	303	0.458	3.98	3.80	4.51 (303 K)
	373	0.440	3.84	3.72	4.14 (373 K)

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