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ANALYSIS BASED ON THE GENERALIZED LENNARD-JONES POTENTIAL

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Abstract

We have used the generalized Lennard-Jones potential to study the equation of state, thermal pressure and thermodynamic properties of different types of materials. The results have been discussed and compared with those reported in the literature.

Keywords: Generalized Lennard-Jones potential, Temperature dependent parameters, Boltzmann constant, Thermal pressure coefficient, Thermodynamic properties.

INTRODUCTION

The generalized Lennard-Jones cohesive energy relation can be written as [1]

$$\varepsilon = A(r)^{-m} - B(r)^{-n} \quad (1)$$

where r is the interatomic distance and A, B, m and n are constants. Common choices are n=6 (for induced dipole interaction) and m=12. After some manipulation, the constants A and B may be replaced by more physically meaningful parameters and equation (1) may be written as;

$$\varepsilon(r)=\frac{\varepsilon_0}{m-n}\left[n\left(\frac{V}{V_0}\right)^{-m/3} - m\left(\frac{V}{V_0}\right)^{-n/3}\right] \quad (2)$$

where ε_0 is the binding free energy (which reduces to the binding energy U_0 at 0 K) . Differentiating equation (2) with respect to the volume yields;

$$P =\frac{3B_0}{m-n}\left[\left(\frac{V_0}{V}\right)^{\frac{m}{3}+1} - \left(\frac{V_0}{V}\right)^{\frac{n}{3}+1}\right] \quad (3)$$

where B_0 is connected to the parameters of equation (2) by $B_0 = \varepsilon_0 mn/9V_0$ Equation (3) is Gilvary EOS [2]. This EOS has one more adjustable parameter than the UEOS. Further differentiations yield:

$$B =\frac{3B_0}{m-n}\left[\left(\frac{m}{3}+1\right)\left(\frac{V_0}{V}\right)^{\frac{m}{3}+1} - \left(\frac{n}{3}+1\right)\left(\frac{V_0}{V}\right)^{\frac{n}{3}+1}\right] \quad (4)$$

and

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$$B' = \frac{\left(\frac{n}{3}+1\right)^2\left(\frac{V_0}{V}\right)^{-\left(\frac{m}{3}+1\right)} - \left(\frac{m}{3}+1\right)^2\left(\frac{V_0}{V}\right)^{-\left(\frac{n}{3}+1\right)}}{\left(\frac{n}{3}+1\right)\left(\frac{V_0}{V}\right)^{-\left(\frac{m}{3}+1\right)} - \left(\frac{m}{3}+1\right)\left(\frac{V_0}{V}\right)^{-\left(\frac{n}{3}+1\right)}} \quad (5)$$

On putting $V=V_0$ in equation (5) yields

$$B_0' = \frac{m}{3} + \frac{n}{3} + 2 \quad (6)$$

V_{sp} is given by putting B = 0 giving

$$\frac{V_{sp}}{V_0} = \left(\frac{m+3}{n+3}\right)^{\frac{3}{m-n}}, \frac{-P_{sp}}{B_0} = \frac{3}{(m+3)}\left[\frac{m+3}{n+3}\right]^{-\frac{m+3}{m-n}} = \frac{3}{(m+3)}\left(\frac{V_{sp}}{V_0}\right)^{-\left(\frac{n}{3}+1\right)} \quad (7)$$

Equation (2) may be expanded as a power series around V_{sp}. Now β can be calculated by substituting equations (3)-(7). The results show that, at the spinodal, $\beta = 1/2$ as required i.e. Gilvarry EOS is suitable for describing the properties of expanded fluids.

In the previous section, the Gilvarry EOS was deduced from a generalized Lennard-Jones potential by a simple algebraic manipulation. Such an approach may be justified at low temperature, where the thermal pressure is small relative to the zero-temperature binding energy, so that all temperature effects may be represented by temperature-dependent parameters in the potential. However, this is not rigorous in the sense that if an ensemble of molecules are interacting via a Lennard-Jones potential (equation (1)), equation (3) may not be deduced from this theoretical set up by means of a statistical-mechanics analysis. Unfortunately, an exact analytical EOS, based on the Lennard-Jones potential, does not exist yet. This difficulty is overcome by the use of empirical EOSs, in which adjustable parameters are fitted to the results of the computer simulations, and the development of semi-theoretical EOSs, based on the perturbation of some known EOS. An example of the second, more theoretical approach is the very accurate EOS due to the Kolafa and Nezbeda[3] for Lennard-Jones potential. Another, particularly simple, EOS of this type was developed by Hess [4]. Hess started from modified hard-spheres approximations for a fluid of particles interacting only via the repulsive part of the Lennard-Jones potential, which he denoted WCA. The attractive part of the potential entered the EOS via the second virial coefficient. The resulting expressions are:

$$\varepsilon(r) = k_B T\left\{\frac{\left[\frac{B^{WCA}}{V}\right]}{1-\left[\frac{V_{eff}}{V}\right]} + \left[\frac{\left[\frac{V_{eff}}{V}\right]}{1-\frac{V_{eff}}{V}}\right]^2\right\} + \frac{k_B T}{V}\left[B^{LJ} - B^{WCA}\right] \quad (8)$$

where k_B is the Boltzmann constant, V_{eff} is an effective hard-sphere volume and B^{WCA} and B^{LJ} are the second virial coefficients of the WCA and Lennard-Jones potentials. V_{eff}, B^{WCA} and B^{LJ} are functions of the temperature.

Expression (8) for the free energy is analytical for$V > V_{eff}$. Thus, in principle, the Hess EOS may be used for locating the spinodal, although the spinodal volume cannot be evaluated analytically. It should be noted that equation (8) may be used only for relatively high temperatures, since it does not include any 'cold' part. V_{sp} and P_{sp} are the volume and divergence pressure along a certain pseudospinodal curve (PSC) respectively and $\kappa^*$and β are, respectively an amplitude and pseudocritical exponent that characterize the pressure behaviour of the isothermal compressibility $K_T=B^{-1}$ through universal relation [5, 6]

$$K_T(P)=k^*[P - P_{sp}]^{-\beta} \quad (9)$$

β being a universal constant close to 0.85 [6, 7],which will be used here.

The PSC represents the mechanical-stability limit for given phase of a substance. Here it can be considered at a negative hydrostatic pressure at which solid rupture. It was stated [8] that the shape of PSC in variable determine the ratio (α_P/K_T) in solids (i.e. thermal pressure coefficient $\gamma_V =(dP/dT)_V$) over the wide range of pressure. This followed from the fact that both quantities follow the same power law in the pressure i.e.

$$\alpha_P(P) = \alpha^*(P - P_{sp})^{\beta} \quad (10)$$

with a value of β about 0.85 also, unlike liquids, where diverges following a mean-field exponent[23].

The previous statement can be written as follows [8]

$$\left(\frac{dP}{dT}\right)_V=\left(\frac{\alpha_P}{K_T}\right)=\left(\frac{\alpha^*}{k^*}\right)=\left(\frac{dP_{sp}}{dT}\right) \quad (11)$$

The coefficients are related to zero pressure quantities through the following relations.

$$B_0= [1/\kappa^*][-P_{sp}]^{\beta} \quad (12)$$

$$B_0^{'} = \frac{\beta B_0}{(-P_{sp})} \quad (13)$$

$$\frac{V_{sp}}{V_0} = \exp\left[\frac{\beta B_0^{'}}{(\beta-1)}\right] \quad (14)$$

It has been observed that both $\kappa^*$and V_{sp} are usually temperature independent within their estimated uncertain over a wide range of temperatures. Thus it follows from equation (10) and (11) that the thermal expansion coefficient at P = 0 can be calculated $\alpha_{P0} =(dP_{sp}/dT)/B_0$. Finally, according to equation (10)-(14) the temperature dependence of α_{P0},V_0, B_0 and $B_0^{'}$ should be only determined by the shape (on temperature) of the PSC.

The Mie-Grüneisen equation is widely used in the correlation shocks-wave experiments as well as to generate the EOS from P-V-T measurement [9]. This equation expresses the pressure as a function of volume and temperature as

$$P(V,T) = -\left(\frac{\partial U_{coh}}{\partial V}\right)_{T=0} + \left[\frac{\gamma^G}{V}\right] E_{vib}(T) \quad (15)$$

where U_{coh} is the cohesion or binding energy and ε_{vib} is the vibrational energy which is only temperature dependent. The second term of equation (15) is called the thermal pressure. Assuming that the ratio $\left[\gamma^G/V\right]$ is temperature independent, a widely used approximation which is in good agreement with experiment (15), can be written according to the equation (11) and (15),

$$\left[\frac{dP}{dT}\right]_v = \left(\frac{\gamma^G}{V}\right) C_V = \left[\frac{dP_{sp}}{dT}\right] \quad (16)$$

where C_V is the isochoric heat capacity. Integration of the second equality in equation (16) between zero temperature and a generic temperature T yields the PSC as a function of temperature so the generic form of the Mie-Grüneisen equation is recovered

$$P_{sp}(T) = P_{sp}^0 + \left[\frac{\gamma^G}{V}\right] E_{vib}(T) \quad (17)$$

where P_{sp}^0 plays the role of the rupture (negative) pressure of the solid at 0K. Here only E_{vib} is temperature dependent in equation (17), so it derives the temperature variation of PSC. Thus provided $E_{vib}(T)$ is known ,the EOS of any solid can be determined from four experimental quantities only:V_0, B_0, B_0' and$\gamma_0^G(V_0)$ evaluated at a single reference temperature T_{ref} .

In order to obtain an analytical approximation to the EOS, let account for $E_{vib}(T)$ using the Eintein's expression (so the characteristics temperature, θ_E is also required as an input parameter). The PSC can be therefore written as follows;

$$P_{sp}(T) = P_{sp}^0 + \left[\frac{\gamma^G}{V}\right] 3Nk_B\theta_E \left\{\left(\frac{1}{2}\right) + \frac{1}{\left[\exp\left(\frac{\theta_E}{T}\right)-1\right]}\right\} \quad (18)$$

where k_B and N are Boltzmann constant and the number of particles respectively. The established universal EOS model [10] can applied to all classes of solids and compared also with the EOS of Vinet et al [11]. This EOS has been proved reliable above the Debye temperature .It was pointed out that their predictions at high temperature require the thermal expansion coefficient at the reference temperature as an additional input. The temperature dependence of several thermodynamic properties are according to equation (10)-(14).

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