Full Length Research Paper

The pseudo Grüneisen parameter in dense fluids from distribution functions

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The Grüneisen parameter (in solids) and the pseudo Grüneisen parameter (in liquids) are of high importance in physics, chemistry and material science. The pseudo Grüneisen parameters in dense fluids have been evaluated using three known analytical expressions for radial distribution functions (RDFs). Using such approach not only tests the power of distribution functions theory in predicting the pseudo Grüneisen parameters, but also specifies better expressions in determining these properties. To calculate these quantities, the variation of radial distribution function with density and temperature is required. Therefore, we should have analytical expressions which explicitly present RDF as a function of temperature, density and interparticle distance. It is shown that if an expression properly presents RDFs as a function of interparticle distance, density and temperature, it is possible to calculate the pseudo Grüneisen parameters from analytical distribution functions.

Key words: Radial distribution function, pseudo Grüneisen parameter, statistical mechanics, heat capacity.

INTRODUCTION

Among the quantities of high importance is the Grüneisen parameter, which expresses the dependence of the lattice frequencies on the volume of a crystal. Knopoff and Shpiro (1970) extended the study of the Grüneisen parameter to the liquid state, where Grüneisen parameter takes the name pseudo Grüneisen parameter and can be determined from experimentally measured thermo-dynamic properties of liquid.

The radial distribution function (RDF) acts as a bridge for relating macroscopic thermodynamic properties to interparticle interactions of substances. The RDF is a key quantity in statistical mechanics because it characterizes how the particles correlations in a substance decay with increasing separation.

Analytical expressions for radial distribution functions (RDFs) have most often been used for the evaluation of pressure and internal energy (Goldman, 1979; Matteoli and Mansoori, 1995; Morsali et al., 2005, 2006). In previous

cases as a substitute method, radial distribution functions could have been obtained directly as a function of distance using molecular dynamics (MD) or integral equations. Recently, these expressions have been used for the evaluation of $P-V-T$ differential properties, such as internal pressure, thermal pressure and isothermal compressibility (Morsali et al., 2007).

In this work, the pseudo Grüneisen parameters are evaluated using three known analytical expressions for RDFs (Goldman, 1979; Matteoli and Mansoori, 1995; Morsali et al., 2005). For the evaluation of pseudo Grüneisen parameters, differentials like $\left(\partial g(r,\rho,T)/\partial\rho\right)_{r,T}$ and $\left(\partial g(r,\rho,T)/\partial T\right)_{r,\rho}$ are required where $g(r,\rho,T)$, r, ρ and T are radial distribution function, interparticle distance, density and temperature, respectively. This problem shows our requirement for analytical expressions which explicitly presents RDFs as a function of r, ρ, and T. Until now, this approach (using distribution functions theory) has not been utilized to estimate the values of pseudo Grüneisen parameters.

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distribution functions theory in predicting the pseudo Grüneisen parameters, but also specifies better equations in determining these properties. The results are compared with experimental data for argon (Stewart and Jacobsen, 1989) and an accurate analytic equation of state for the LJ fluid (Mecke et al., 1996).

THEORY

Statistical mechanical equations for the pseudo Grüneisen parameter

The pseudo Grüneisen parameter (Γ) may be defined as:

$$\Gamma = (\partial P / \partial T)_V / (\rho C_V) \tag{1}$$

where C_V is the heat capacity at constant volume.

The temperature dependence of the internal energy (E) is given by the heat capacity at constant volume (C_V) at a given temperature, formally defined by

$$C_V = (\partial E / \partial T)_V \tag{2}$$

where E and $V = 1/\rho$ are internal energy and molar volume, respectively. Heat capacities have been also obtained from density functional theory (Wang et al., 2008; Beyramabadi and Morsali, 2011)
Since

$$E = E^{ig} + 2\pi N \rho \int_0^\infty u(r) g(r,\rho,T) r^2 dr \tag{3}$$

d $u(r)$ are internal energy for ideal gas and interparticle pair potential, respectively; we have:

$$C_V = (3/2)Nk + 2\pi N \rho \int_0^\infty u(r)(\partial g(r,\rho,T)/\partial T)_{r,T} r^2 dr \tag{4}$$

Since

$$P = \rho kT - (2\pi/3)\rho^2 \int_0^\infty (du(r)/dr) g(r,\rho,T) r^3 dr \tag{5}$$

where k is the Boltzmann's constant, we have:

$$(\partial P/\partial T)_V = \rho k - (2\pi/3)\rho^2 \int_0^\infty (du(r)/dr)(\partial g(r,\rho,T)/\partial T)_{r,\rho} r^3 dr \tag{6}$$

Another way to evaluate $(\partial P / \partial T)_V$ is to use internal pressure equation:

$$(\partial P / \partial T)_V = (\pi_T + P)/T \tag{7}$$

where $\pi_T = (\partial E / \partial V)_T$ is internal pressure and using (3), we

have:

$$\pi_T = -2\pi\rho^2 \int_0^\infty u(r)\{g(r,\rho,T) + \rho(\partial g(r,\rho,T)/\partial\rho)_{r,\rho}\} r^2 dr \tag{8}$$

The known expressions for RDF of a LJ fluid

Goldman expression

The first expression was introduced by Goldman (1979). The expression is

$$g(r^*) = g_a(r^*) + g_b(r^*) + g_c(r^*) \tag{9}$$
where

$$g_a(r^*) = 0$$
$$r^* \leq B_1 \tag{10}$$

$$g_a(r^*) = B_2/(r^* - B_1)\exp(-[B_3\{\ln(r^* - B_1) + B_4\}^2])$$
$$r^* > B_1 \tag{11}$$

$$g_b(r^*) = c\exp(-u(r^*)/kT)$$
$$r^* \leq B_9 \tag{12}$$

$$g_b(r^*) = \exp(-[r^* - B_5]^2/B_6)$$
$$B_9 \leq r^* \leq B_5 \tag{13}$$

$$g_b(r^*) = 1$$
$$r^* > B_5 \tag{14}$$

$$g_c(r^*) = 0$$
$$r^* \leq B_5 - 0.25B_7 \tag{15}$$

$$g_c(r^*) = \exp(-B_8 r^*)\sin(2\pi(r^* - B_5 + 0.25B_7)/B_7)$$
$$r^* > B_5 - 0.25B_7 \tag{16}$$

where $r^* = r/\sigma$, $T^* = kT/\varepsilon$, and $\rho^* = \rho\sigma^3$ are reduced interparticle distance, reduced temperature, and reduced density, respectively. $k, \sigma, \varepsilon, r, T,$ and ρ are the Boltzmann constant, length parameter of a potential function, energy parameter of a potential function, interparticle distance, absolute temperature, and density, respectively. B1-B9 and C are adjustable parameters being functions of temperature and density and given in Goldman (1979). These parameters have been presented as polynomials in ρ^* and T^*, using 108 constants. This expression is valid within $0.5 \leq T^* \leq 5.1$ and $0.35 \leq \rho^* \leq 1.1$.

Matteoli and Mansoori expression

Matteoli and Mansoori (1995) have derived an expression for RDF of a LJ fluid as the followings

$$g(y)=1+y^{-m}[g(d)-1-\lambda]+[(y-1+\lambda)/y]\times\{\exp[-\alpha(y-1)]\cos[\beta(y-1)]$$
$$m\geq 1,\quad y\geq 1, \tag{17}$$

$$g(y)=g(d)\exp[-\theta(y-1)^2],\quad y<1 \tag{18}$$

where $y=r/h\sigma$ is dimensionless interparticle distance and h, m, λ, α, and β are adjustable parameters being functions of temperature and density. These parameters have been expanded in terms of ρ^* and T^*, using 21 constants. This expression is valid within $0.6\leq T^*\leq 3.7$ and $0.35\leq\rho^*\leq 0.9$. In this paper, this expression is referred as MM expression.

Morsali et al. (2005) expression

Morsali et al. (2005) derived the following expression for RDF of a LJ fluid:

$$g(r^*)=1+(r^*)^{-2}\exp[-(ar^*+b)]\sin[(cr^*+d)]+$$

$$(r^*)^{-2}\exp[-(gr^*+h)]\cos[(kr^*+l)]\qquad\qquad r^*>1 \tag{19}$$

$$g(r^*)=s\exp[-(mr^*+n)^4]$$
$$r^*\leq 1 \tag{20}$$

where a, b, c, d, g, h, k, l, s, m, and n are adjustable parameters being functions of temperature and density. These parameters have been expanded in terms of ρ^* and T^*, using 65 constants. This expression is valid within $0.5\leq T^*\leq 5.1$ and $0.35\leq\rho^*\leq 1.1$. This expression is referred hereafter as MGMA expression. MGMA expression for RDF is a continuous function of r*, since it consist of two parts, one for r*≤1 (like hard sphere model (Farzi et al., 2011; Tehrani and Jalali, 2011)) and one for r*>1. This expression has been obtained from molecular dynamics calculations on the assumption of Lennard-Jones interaction potential.

RESULTS AND DISCUSSION

The values of $(\partial P/\partial T)_V$ and C_V should be expressed in their reduced form in order to calculate them as functions of reduced density, ρ^*, and reduced temperature, T^*:

$$\left(\partial P^*/\partial T^*\right)_V=\left(\partial P/\partial T\right)_V(\sigma^3/k) \tag{21}$$

$$C_V^*=C_V/Nk \tag{22}$$

The reduced form for $u(r), P, E, C_V, \pi_T$, and $(\partial P/\partial T)$ are

$$u(r^*)=4[(r^*)^{-12}-(r^*)^{-6}] \tag{23}$$

$$P^*=\rho^*T^*-16\pi(\rho^*)^2\int_0^\infty g(r^*)\times[(r^*)^{-4}-2(r^*)^{-10}]dr^* \tag{24}$$

$$E^*=\frac{3}{2}T^*+8\pi\rho^*\int_0^\infty[(r^*)^{-10}-(r^*)^{-4}]\,g(r^*,\rho^*,T^*)\,dr^* \tag{25}$$

$$C_V^*=\frac{3}{2}+8\pi\rho^*\int_0^\infty[(r^*)^{-10}-(r^*)^{-4}]\frac{\partial g(r^*,\rho^*,T^*)}{\partial T^*}dr^* \tag{26}$$

$$\left(\partial P^*/\partial T^*\right)_V=\rho^*-16\pi(\rho^*)^2\int_0^\infty[(r^*)^{-4}-(r^*)^{-10}]\left(\partial g(r^*,\rho^*,T^*)/\partial T^*\right)_{r^*,\rho^*}dr^* \tag{27}$$

$$\pi_T^*=-8\pi(\rho^*)^2\int_0^\infty[(r^*)^{-10}-(r^*)^{-4}]\left\{g(r^*,\rho^*,T^*)+\rho^*\left(\partial g(r^*,\rho^*,T^*)/\partial\rho^*\right)_{r^*,T^*}\right\}dr^* \tag{28}$$

Using internal pressure equation for the evaluation of $\left(\partial P^*/\partial T^*\right)_V$ is more suitable for MGMA expression and leads to less error.

$$\left(\partial P^*/\partial T^*\right)_V=(\pi_T^*+P^*)/T^* \tag{29}$$

Using (21) to (29) and Goldman, MM and MGMA expressions, theoretical values of $\Gamma=(\partial P^*/\partial T^*)_V/(\rho^*C_V^*)$ are obtained. These quantities are compared with experimental data (Stewart and Jacobsen 1989) and Mecke et al. equation of state (Mecke et al., 1996, 1998).

The equations related to Mecke et al. EOS are as follows

$$F=F_H+F_A \tag{30}$$

where F is residual Helmholtz energy. FH accounts for the hard-body interaction and FA for the attractive dispersion forces.

For a system of hard spheres with a packing fraction ξ, the residual Helmholtz energy FH is given according to Carnahan and Starling (1969) as

$$F_H^*/T^*=(4\xi-3\xi^2)/(1-\xi)^2 \tag{31}$$

where $F_H^*=F_H/N\varepsilon$ and

$$\xi = 0.1617(\rho^* / \rho_c^*)\left[0.689 + 0.311(T^* / T_c^*)^{0.3674}\right]^{-1} \quad (32)$$

where $\rho_c^* = 0.3107$ and $T_c^* = 1.328$ are the critical density and temperature, respectively.

FA is presented by the following equation with powers (m_i, n_i, p_i and q_i) and coefficients (c_i) given in Mecke et al. (1996, 1998).

$$\frac{F_A^*}{T^*} = \sum_i c_i (T^* / T_c^*)^{m_i} (\rho^* / \rho_c^*)^{n_i} \exp[p_i (\rho^* / \rho_c^*)^{q_i}] \quad (33)$$

where $F_A^* = F_A / N\varepsilon$.

$F^* = F_H^* + F_A^*$ is reduced Helmholtz energy and the pseudo Grüneisen parameters are derived from it by differentiation.

$$\Gamma = -\frac{(\rho^*)^2(\partial(\partial F^* / \partial T^*)_{\rho^*} / \partial\rho^*)_{T^*}}{T^*\rho^*(\partial^2 F^* / \partial T^{*2})} \quad (34)$$

The experimental data (reduced Helmholtz energy (F^*) for Argon) have been obtained using (10) and (12) of Stewart and Jacobsen (1989).

The pseudo Grüneisen parameters have been calculated using three expressions for RDFs of a LJ fluid at reduced temperature, $T^* = 0.8, 1, 1.2, 1.5, 1.8, 2, 2.5, 3, 3.5, 4, 4.5, 5$ and reduced densities, $0.357 \leq \rho^* \leq 1.1$ (165 points altogether) and compared with those of EOS and experimental data. Although range of validity of Goldman equation $0.5 \leq T^* \leq 5.1$ and $0.35 \leq \rho^* \leq 1.1$ has been reported, but care should be taken when it is applied at high temperatures and low densities (Morsali et al., 2007). Also, due to range of validity of MM expression, $T^* = 3.50 - 5.00$ has been omitted (100 points altogether).

Therefore, initially, the pseudo Grüneisen parameters are evaluated at reduced temperatures of 0.800 to 3.00 (100 points altogether). Figure 1 demonstrates Γ versus ρ^* at $T^* = 2.00, 3.00$. In this figure, theoretical values obtained from Goldman, MM, and MGMA expressions have been compared with those of Mecke et al. EOS and experimental data (Exp.). Table 1 shows the numerical values of Γ at reduced temperatures $T^* = 1.20, 1.80$ and different densities.

As it is seen from Figure 1 and Table 1, Goldman and MGMA expression well predict the values of Γ, both quantitatively and qualitatively, but MM expression is accompanied with many errors, both quantitatively and qualitatively.

If Mecke et al. EOS is taken as the criteria for comparison, the values of average absolute deviations

(AAD) $\quad (AAD = \frac{1}{n}\sum_{i=1}^n 100 \times |\Gamma_{Mecke\,EOS} - \Gamma_{theory}| / \Gamma_{Mecke\,EOS})$ related to Γ in connection with Goldman, MM, and MGMA expressions at range of applied temperatures and densities are 6.38, 34.46 and 2.14, respectively.

If Exp. is taken as the criteria for comparison, the AAD values $(AAD = \frac{1}{n}\sum_{i=1}^n 100 \times |\Gamma_{Exp.} - \Gamma_{theory}| / \Gamma_{Exp.})$ related to Γ in connection with Goldman, MM, and MGMA expressions at range of applied temperatures and densities are 6.40, 37.20 and 3.79, respectively.

The aforementioned description was related to temperatures $0.80 \leq T^* \leq 3.00$. Goldman's expression is not able to reproduce RDFs well at high temperatures and low densities. The MM expression does not apply at temperatures $3.50 \leq T^* \leq 5.00$ and the Goldman's expression should be used with caution (Morsali et al., 2007). Therefore, for temperatures within the range of $3.50 \leq T^* \leq 5.00$, only the errors related to MGMA expression are reported (65 point altogether).

Figure 2 demonstrates Γ versus ρ^* at $T^* = 4.00$. In this figure, theoretical values obtained from Goldman and MGMA expressions have been compared with those of Mecke et al. EOS and experimental data.

If Mecke et al. EOS (Exp.) is taken as the criteria for comparison, The AAD value related to Γ $(AAD = \frac{1}{n}\sum_{i=1}^n 100 \times |\Gamma_{i,Mecke\,EOS(Exp.)} - \Gamma_{i,theory}| / \Gamma_{i,Mecke\,EOS(Exp.)})$ in connection with MGMA expressions at the range of applied temperatures $(3.50 \leq T^* \leq 5.00)$ and densities is 2.96 (9.61).

Generally, the Goldman and MGMA expressions both predict the values of Γ with acceptable errors, but MM expression is not suitable for this purpose. The Goldman and MM expressions are not reliable for the evaluation of Γ at high temperatures and low densities. The MGMA equation well predicts the quantities of Γ within all ranges of temperatures and densities, because MM expression (21 parametrs) reproduces RDFs with an average root-mean-squared deviation (rmsd) of 0.053, while Goldman expression (108 parameters) reproduces RDFs with an average rmsd of 0.034. MGMA expression is capable of producing a balance between the number of parameters (65 parameters) and the accuracy needed for reproducing the Lennard-Jones fluid RDF (rmsd of 0.025). Also, it is able to predict the pseudo Grüneisen parameter in an efficient and reliable way.

Conclusions

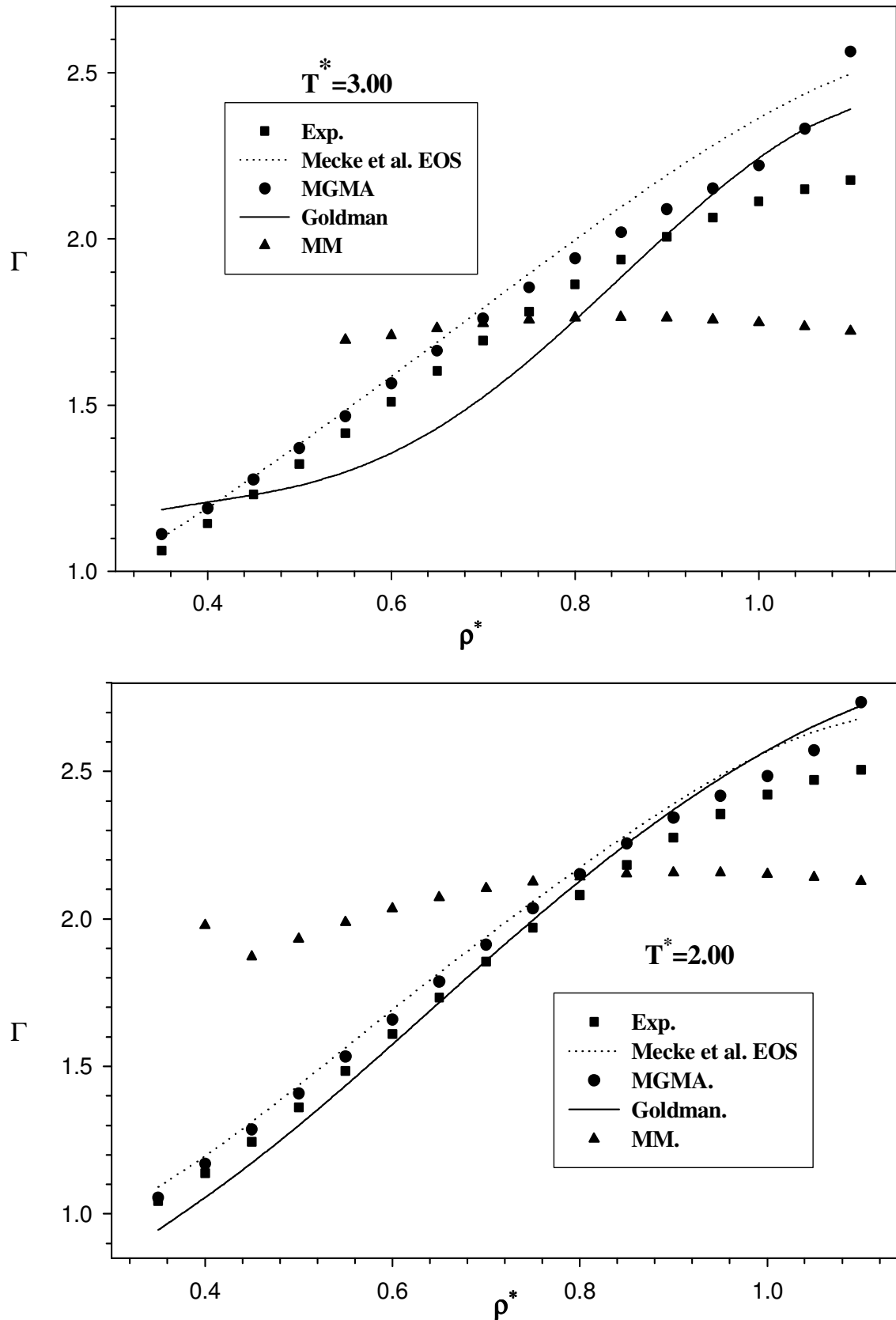By using radial distribution function theory, the pseudo

Figure 1. Γ versus ρ^* at $T^* = 2.00, \ 3.00$. Theoretical values obtained from Goldman (—), MM (▲), and MGMA (●●●) expressions have been compared with those of Mecke et al. EOS (●●●) and Exp. (■).

Table 1. Comparison of numerical values of Γ at $T^* = 1.200, 1.800$.

T^*	ρ^*	$\Gamma_{Exp.}$	$\Gamma_{Mecke\ EOS}$	Γ_{MGMA}	$\Gamma_{Goldamn}$	Γ_{MM}
1.800	0.350	1.022	1.066	1.011	1.050	3.384
1.800	0.400	1.120	1.175	1.146	1.153	1.979
1.800	0.450	1.233	1.300	1.276	1.266	1.871
1.800	0.500	1.360	1.435	1.410	1.391	1.932
1.800	0.550	1.495	1.576	1.545	1.523	1.988
1.800	0.600	1.632	1.716	1.682	1.659	2.035
1.800	0.650	1.768	1.852	1.819	1.798	2.073
1.800	0.700	1.899	1.981	1.956	1.935	2.103
1.800	0.750	2.025	2.105	2.090	2.069	2.126
1.800	0.800	2.145	2.224	2.216	2.198	2.142
1.800	0.850	2.257	2.338	2.330	2.320	2.153
1.800	0.900	2.360	2.445	2.426	2.434	2.157
1.800	0.950	2.450	2.541	2.506	2.538	2.157
1.800	1.000	2.526	2.622	2.578	2.632	2.151
1.800	1.050	2.585	2.685	2.665	2.715	2.142
1.800	1.100	2.625	2.722	2.820	2.787	2.128
1.200	0.550	1.280	1.457	1.011	1.716	2.340
1.200	0.600	1.595	1.717	1.714	1.837	2.417
1.200	0.650	1.856	1.951	1.901	1.961	2.481
1.200	0.700	2.064	2.146	2.086	2.086	2.532
1.200	0.750	2.234	2.307	2.268	2.211	2.573
1.200	0.800	2.382	2.444	2.441	2.335	2.604
1.200	0.850	2.520	2.564	2.597	2.455	2.626
1.200	0.900	2.656	2.668	2.730	2.571	2.640
1.200	0.950	2.792	2.754	2.839	2.681	2.647
1.200	1.000	2.925	2.819	2.931	2.785	2.647
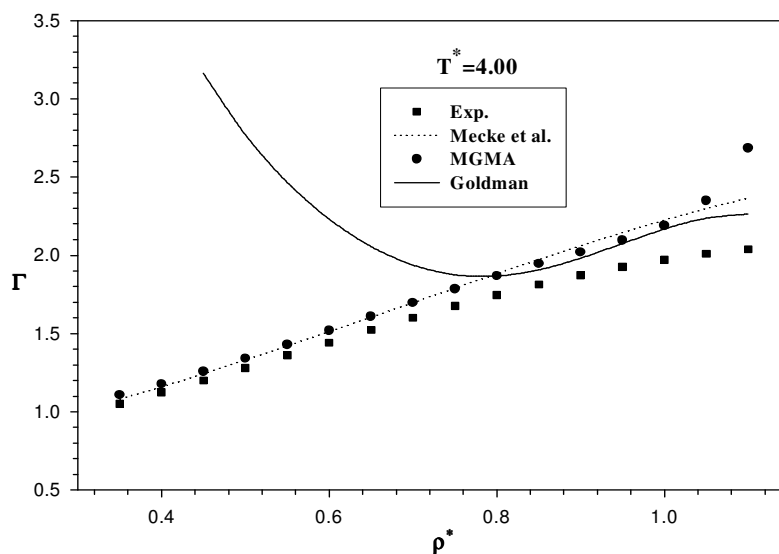
Figure 2. Γ versus ρ^* at $T^* = 4.00$. Theoretical values obtained from Goldman (—) and MGMA (•) expressions have been compared with those of Exp. (■) and Mecke et al. EOS (•••).

Grüneisen parameter was calculated. Three analytical expressions were used for this purpose which presents RDFs as a function of r, ρ, and T. Within the range of lower temperatures, the Goldman and MGMA expressions both predict the values of Γ with acceptable errors, but MM expression is not suitable for this purpose.

The MM expression does not apply at temperatures $3.50 \leq T^* \leq 5.00$ and the Goldman's expression should be used with caution. Within this range, the MGMA expression still well predicts the values of Γ. The reason for this, besides more accuracy of MGMA expression in the reproducing of RDFs (rmsd: 0.025 versus 0.034), is attributable to the number of parameters in these two expressions (65 versus 108). Because of the high number of parameters in Goldman expression, differentiation of this expression causes more errors.

Therefore, if an expression is used which properly presents g(r) as a function of r, ρ, and T, it is possible to calculate the pseudo Grüneisen parameters from RDFs.

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