Grüneisen parameter for strongly coupled Yukawa systems

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The Grüneisen parameter is evaluated for three-dimensional Yukawa systems in the strongly coupled regime. Simple analytical expression is derived from the thermodynamic consideration and its structure is analysed in detail. Possible applications are briefly discussed.

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I. INTRODUCTION

An equation of state (EoS) in the form of a relation between the pressure and internal energy of a substance (often referred to as the Grüneisen or Mie-Grüneisen equation) has been proven very useful in describing condensed matter under extreme conditions. Central to this form of EoS is the Grüneisen parameter, whose thermodynamic definition is

\[ \gamma_G = V \left( \frac{\partial P}{\partial E} \right)_V = \frac{V}{C_V} \left( \frac{\partial P}{\partial T} \right)_V, \]  

(1)

where \( V \) is the system volume, \( P \) is the pressure, \( T \) is the temperature, \( E \) is the internal energy, and \( C_V = (\partial E/\partial T)_V \) is the specific heat at constant volume. Under the assumption that \( \gamma_G \) is independent of \( P \) and \( E \), one can write

\[ PV = \gamma_G(\rho)E + C(\rho)V, \]  

(2)

where \( C(\rho) \) is the “cold pressure”, which depends only on the density \( \rho = N/V \).

Grüneisen parameter depends considerably on the substance in question as well as on the thermodynamic conditions (location on the corresponding phase diagram). In most metals and dielectrics in the solid phase, \( \gamma_G \) is in the range from \( \approx 1 \) to \( \approx 4/3 \). For fluids it is usually somewhat smaller, typically ranging from \( \approx 0.2 \) to \( \approx 2 \). The focus of this paper is on Yukawa model systems, which are often applied as a first approximation to complex (dusty) plasmas, representing a collection of highly charged particles immersed in a neutralizing environment.

In the context of complex plasmas, the Grüneisen parameter can be useful in describing shock wave phenomena observed in various complex plasma experiments. Therefore, it is desirable to have a practical approach allowing to estimate the Grüneisen parameter and related quantities under different experimental conditions (an attempt to estimate \( \gamma_G \) has been previously reported in Ref. 15). In this paper we evaluate Grüneisen parameter for strongly coupled three-dimensional (3D) one-component Yukawa systems.

To be precise, Yukawa systems studied in this work represent a collection of point-like charged particles, which interact via the pairwise repulsive potential of the form

\[ V(r) = \frac{Q^2}{r} \exp(-r/\lambda), \]  

(3)

where \( Q \) is the particle charge (assumed constant), \( \lambda \) is the screening length, and \( r \) is the distance between a pair of particles. Thermodynamics of considered Yukawa systems is fully characterized by the two dimensionless parameters. The first is the coupling parameter, \( \Gamma = Q^2/\alpha T \), where \( \alpha = (4\pi \rho/3)^{-1/3} \) is the characteristic interparticle separation (Wigner-Seitz radius) and \( T \) is the temperature (in energy units). The second is the screening parameter, \( \kappa = a/\lambda \). In the limit \( \kappa \to 0 \), the interaction potential tends to the unscreened Coulomb form, and Yukawa systems approach to the one-component-plasma (OCP).

Simple and reliable analytical expressions for the energy and pressure of strongly coupled Yukawa fluids have been proposed in Refs. 27 and 28. These expressions are based on the Rosenfeld-Tarazona (RT) scaling of the thermal component of the excess internal energy when approaching the freezing transition. These expressions demonstrate relatively good accuracy and are very convenient for practical applications. In this paper they are employed to estimate the Grüneisen parameter of strongly coupled 3D Yukawa fluids. In this way very simple analytical expressions are obtained and analysed.
II. THERMODYNAMIC PROPERTIES

The total system energy $E$ and pressure $P$ are the sums of kinetic and potential contributions. For 3D systems we can write

$$E = \frac{3}{2} NT + U = \frac{3}{2} NT + NT u_{\text{ex}},$$

$$PV = NT + W = NT + NT p_{\text{ex}},$$

where $U$ is the potential energy and $W$ is the configurational contribution to the pressure or virial. These are expressed in terms of conventional reduced (dimensionless) excess energy $u_{\text{ex}}$ and excess pressure $p_{\text{ex}}$, respectively.

It should now be briefly reminded how the excess energy $u_{\text{ex}}$ and pressure $p_{\text{ex}}$ of one-component Yukawa fluids can be evaluated. We only provide the expressions required in subsequent calculations, further details can be found in Refs. [27, 28, and 31]. The reduced excess energy of a strongly coupled Yukawa fluid can be approximated with a good accuracy by the expression

$$u_{\text{ex}} = M_1 \Gamma + \delta \left( \frac{\Gamma}{\Gamma_m} \right)^{2/3},$$

where the first term corresponds to the static energy contribution within the ion sphere model (ISM). The reduced coupling parameter $\Gamma$ is referred to as the fluid Madelung constant and is given by

$$M_1(\Gamma) = \frac{\kappa(\kappa+1)}{(\kappa+1) + (\kappa-1)e^{2\kappa}}.$$

The second term in Eq. (6) is the thermal contribution to the excess energy, which is equal to the ratio $p_{\text{ex}}/u_{\text{ex}}$. This ratio is not very sensitive to the reduced coupling parameter $\Gamma_m(\kappa)$, it can be well described by a simple approximation,

$$\Gamma_m(\kappa) \approx \frac{172 \exp(\alpha \kappa)}{1 + \alpha \kappa + \frac{1}{2} \alpha^2 \kappa^2},$$

where the constant $\alpha = (4\pi/3)^{1/3} \approx 1.612$ is the ratio of the mean interparticle distance $\Delta = \rho^{-1/3}$ to the Wigner-Seitz radius $a$. The value of the constant $\delta$ in Eq. (6) is $\delta = 3.1$, as suggested in Ref. [28].

Using this approximation for the excess energy, the reduced pressure can be readily obtained as

$$p_{\text{ex}} = p_0 + \frac{\delta}{3} \left( \frac{\Gamma}{\Gamma_m} \right)^{2/3} f_2(\alpha \kappa).$$

Here $p_0$ is the static component of the pressure (associated with the static component of the internal energy)

$$p_0 = \frac{\kappa^4 \Gamma}{6(\kappa \cosh(\kappa) - \sinh(\kappa))^2},$$

and the function $f_2$ is defined as

$$f_2(r) = \frac{2 + 2r + r^2 + r^3}{2 + 2r + r^2}.$$
background in the OCP limit, which is absent in one-
component Yukawa systems. Let us prove this mathe-
matically. In the limit of very soft interaction, the energy
and pressure at strong coupling (\( \Gamma \gg 1 \)) are dominated
by their static contributions. The series expansion of the
fluid Madelung energy [Eq. (7)] and the corresponding
static pressure [Eq. (10)] in the limit \( \kappa \rightarrow 0 \) yield
\[
M_f(\kappa) \Gamma \simeq -\frac{9 \Gamma}{10} + \frac{\kappa \Gamma}{2} + \frac{3 \Gamma}{2 \kappa^2} + \mathcal{O}(\kappa^2 \Gamma),
\]
and
\[
p_0(\kappa) \simeq -\frac{3 \Gamma}{10} + \frac{3 \Gamma}{2 \kappa^2} + \mathcal{O}(\kappa^2 \Gamma).
\]
In the absence of explicit thermodynamic contribution
from the neutralizing medium (that is for one-component
Yukawa systems), both \( M_f \) and \( p_0 \) are divergent at \( \kappa \rightarrow 0 \),
but their ratio remains finite and we have \( p_{\text{ex}}/u_{\text{ex}} = 1 \).
The contribution from the neutralizing medium to the
excess energy (in the linear approximation) is
\[
u_m = -\frac{3 \Gamma}{2 \kappa^2} - \frac{\kappa \Gamma}{2}.
\]
Similarly, contribution of the neutralizing medium to the
excess pressure is
\[
p_m = -\frac{3 \Gamma}{2 \kappa^2}.
\]
Adding these contributions we get the familiar results
for the OCP within the ISM model: \( u_{\text{ex}} \simeq -\frac{3 \Gamma}{10} \) and
\( p_0 \simeq -\frac{3 \Gamma}{10} \), which implies \( p_{\text{ex}}/u_{\text{ex}} = 1/3 \). This consid-
eration demonstrates that Yukawa systems in the limit
\( \kappa \rightarrow 0 \) are not fully equivalent to the Coulomb (OCP)
systems with the neutralizing background. Similar ob-
servation has recently been reported in relation to 2D
Yukawa fluids.\(^{36}\)

C. Density scaling exponent

Let us now consider correlations between configura-
tional components of energy \( U \) and pressure \( W \) in more
detail. The density scaling exponent can be defined as\(^{26}\)
\[
\gamma = \frac{\partial W/\partial T}{\partial U/\partial T}. \tag{12}
\]
Substituting \( W \) and \( U \) and making use of the identity
\( T/\partial T = -\Gamma/\partial \Gamma \) the density scaling exponent becomes
\[
\gamma = \frac{p_{\text{ex}} - \Gamma (\partial p_{\text{ex}}/\partial \Gamma)}{u_{\text{ex}} - \Gamma (\partial u_{\text{ex}}/\partial \Gamma)}. \tag{13}
\]
When substituting expressions for \( u_{\text{ex}} \) and \( p_{\text{ex}} \) into
Eq. (13), the terms linear in \( \Gamma \) will cancel out and a very
simple result is obtained
\[
\gamma = \frac{1}{3} f_Z(\alpha \kappa). \tag{14}
\]
This simple expression agrees with the expected be-
behaviour. In the limit \( \kappa \rightarrow 0 \) we get the expected OCP
limiting value \( \gamma = 1/3 \), corresponding to the unscreened
Coulomb interaction. For the “Veldhorst state point”
with \( \kappa = 4.30 \) and \( \Gamma = 4336.3 \) (using the definitions of
\( \kappa \) and \( \Gamma \) adopted in this paper) Eq. (13) yields \( \gamma = 2.07 \)
in good agreement with the result obtained from a direct
MD simulation\(^{38,39}\) \( \gamma = 2.12 \).

Let us also consider another possible derivation of the
density scaling exponent \( \gamma \). For an arbitrary potential
\( V(r) \) an effective IPL exponent (or inverse effective soft-
ness parameter) can be introduced using ratios of deriv-
atives of the potential\(^{35,37}\)
\[
\gamma_{\text{eff}}^{(p)} = -\Delta \frac{V^{(p+1)}(\Delta)}{V^{(p)}(\Delta)} - p, \tag{15}
\]
where \( V^{(p)} \) is the \( p \)-th derivative of the potential, and
\( \Delta \) characterizes mean separation between the particles.
For IPL potentials, \( V(r) \propto r^{-n} \), we get \( \gamma_{\text{eff}}^{(p)} \equiv n \) for
any \( p \) and \( \Delta \). Moreover, for IPL potentials the density
scaling exponent is trivially related to \( n \): \( \gamma = n/3 \) (in 3D).
For other potentials, the effective IPL exponent will gen-
erally depend on \( p \) and also on the exact definition of
\( \Delta \). Previously, \( \Delta = \rho^{-1/3} \) with \( p = 0 \) and \( p = 1 \) were
used to identify universalities in melting and freezing
curves of various simple systems (Yukawa, IPL, Lennard-
Jones, generalized Lennard-Jones, Gaussian Core Model,
etc.)\(^{40,41}\) It was, however, argued that the choice \( p = 2 \)
is more physically justified.\(^{38,39}\) Indeed, it is straightforward
to verify that, for the Yukawa potential, Eq. (16)
with \( p = 2 \) yields \( \gamma_{\text{eff}}^{(2)} = f_Z(\alpha \kappa) \), that is \( \gamma = \gamma_{\text{eff}}^{(2)}/3 \),
similarly to the conventional IPL result. Thus, identical
results for the density scaling exponent \( \gamma \) can be ob-
tained using the two seemingly very different routes: (i)
thermodynamic approach based on explicit knowledge of
the system pressure and internal energy and (ii) effective
IPL exponent consideration, which operates only with
the third and second derivatives of the interaction po-
tential evaluated at the mean interparticle separation.
An interesting related question, whether this is a special
property of the Yukawa interaction or perhaps a more
general result, requires careful consideration and will not
be discussed here.

D. Gruneisen parameter

Because the density scaling exponent does not depend
on the temperature, the Gruneisen parameter can be eas-
ily expressed using \( \gamma \) as:
\[
\gamma_G = \frac{1}{c_V} \left[ 1 + \gamma (c_V - 3/2) \right], \tag{16}
\]
where \( c_V = C_V/N \) is the reduced heat capacity at con-
stant volume. The derivation is straightforward, for de-
tails see e.g. Ref. \(^{42}\).
The Grüneisen parameter evaluated using Eq. \((16)\) is plotted in Figure 2. Clearly, \(\gamma_G\) is not independent of temperature. Let us discuss the main trends observed. In the limit of very weak coupling (ideal gas limit) we have \(c_V = 3/2\) and hence \(\gamma_G = 2/3\), as expected for the ideal gas in 3D. As the coupling becomes stronger, we can apply the RT scaling to get \(c_V \approx 3/2 + (3\delta/5)(\Gamma/\Gamma_m)^{2/5}\). Assuming that the ideal gas contribution to \(c_V\) exceeds that due to strong coupling effects (this is justified for \(\Gamma \lesssim 0.5\Gamma_m\)), the following estimate is obtained

\[
\gamma_G \approx \frac{2}{3} + \frac{6\gamma - 4}{15} \left( \frac{\Gamma}{\Gamma_m} \right)^{2/5}.
\]

This expression indicates that \(\gamma_G\) can either increase or decrease compared to the ideal gas value of 2/3. The bifurcation occurs at \(\gamma = 2/3\), that is at \(\kappa \simeq 1.4\) for Yukawa systems. This behaviour is further illustrated in Fig. 3 which shows the dependence of \(\gamma_G\) on the reduced coupling strength \(\Gamma/\Gamma_m\) (calculated from Eq. \((16)\)) for four different screening parameters. In particular, Fig. 3 documents the existence of a range of screening parameters near the transitional value \(\kappa \simeq 1.4\), where the Grüneisen parameter remains close to its ideal-gas limiting value even in the strongly coupled regime. For \(\kappa \gtrsim 1.4\) the Grüneisen parameter increases with coupling, for \(\kappa \lesssim 1.4\) the tendency is opposite.

On approaching the fluid-solid phase transition from the fluid side, \(c_V\) reaches values slightly above 3/2. In the OCP limit, the accurate analytical EoS predicts \(c_V \approx 3.4\). The same estimate is obtained using the RT scaling (with \(\delta = 3.1\), as adopted here). This corresponds to the following approximation of \(\gamma_G\) for 3D Yukawa melts:

\[
\gamma_G^m \approx 0.56\gamma + 0.29. \tag{17}
\]

The minimum value of \(\gamma_G^m \approx 0.48\) occurs in the OCP limit with \(\kappa \rightarrow 0\) and \(\gamma \rightarrow 1/3\). As \(\kappa\) increases, the density scaling exponent also increases monotonously and so does the Grüneisen parameter, see Fig. 3. Finally, deep into the solid phase, the harmonic approximation is appropriate and we have \(c_V \simeq 3\) (Dulong-Petit law). In this regime \(\gamma_G^s \approx \gamma/2 + 1/3\), comparable to the result for Yukawa melt, Eq. \((17)\).

IV. CONCLUSION

In this paper simple analytical expressions for the density scaling exponent and the Grüneisen parameter of strongly coupled Yukawa fluids in three dimensions have been derived and analysed. It turns out that identical results for the density scaling exponent \(\gamma\) can be obtained using the thermodynamic approach (based on explicit knowledge of the system pressure and internal energy) as well as from an effective IPL exponent consideration (which requires only the third and second derivatives of the interaction potential, evaluated at the mean interparticle separation).

The Grüneisen parameter evaluated here can potentially be useful in the context of shock-waves experiments in complex (dusty) plasmas. It appears in the expressions relating the pressure and density jumps across a shock wave front (known as Hugoniot equations). For a relevant example of experimental analysis and previous estimate of the Grüneisen gamma the reader is referred to Ref. 13.

The results obtained can be useful provided (i) shock-waves are excited in three dimensional particle clouds, (ii) the Yukawa potential is a reasonable representation of the actual interactions between the charged particles under these conditions, (iii) there is no or weak dependence of particle charge on particle density (in the theory described here the particle charge is constant), and (iv) the screening length is not very much smaller compared to the mean interparticle separation. These conditions can (at least partially) be met in complex plasma experiments under microgravity conditions, e.g. in the PK 4 laboratory, currently operational onboard the International Space Station.
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