Grüneisen Parameter for Gases

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The Grüneisen ratio (Γ), i.e. the ratio of the linear thermal expansivity to the specific heat at constant pressure, quantifies the degree of anharmonicity of the potential governing the physical properties of a system. While Γ has been intensively explored in solid state physics, very little is known about its behavior for gases. This is most likely due to the difficulties posed to carry out both thermal expansion and specific heat measurements in gases with high accuracy as a function of pressure and temperature. Furthermore, to the best of our knowledge a comprehensive discussion about the peculiarities of the Grüneisen ratio is still lacking in the literature. Here we report on a detailed and comprehensive overview of the Grüneisen ratio. Particular emphasis is placed on the analysis of Γ for gases. The main findings of this work are: *i)* for the Van der Waals gas Γ depends only on the co-volume b due to interaction effects, it is smaller than that for the ideal gas (Γ = 2/3) and diverges upon approaching the critical volume; *ii)* for the Bose-Einstein condensation of an ideal boson gas, assuming the transition as first-order Γ diverges upon approaching a critical volume, similarly to the Van der Waals gas; *iii)* for ^{4}He at the superfluid transition Γ shows a singular behavior. Our results reveal that Γ can be used as an appropriate experimental tool to explore pressure-induced critical points.

I. INTRODUCTION

It is well known from daily life that upon increasing or decreasing the temperature of a solid, in general, its volume changes. The formation of ice, namely the phase transition of water from liquid-to-solid, consists a classical example of volume change. It is worth to mention that in the case of water, in particular, a negative thermal expansion is observed upon freezing, thus leading the ice to fluctuate in the surface of the liquid. In general terms, in the case of solids, regarding solely the phononic excitations, the phenomenon of thermal expansion is a direct consequence of the deviation of the lattice potential from the so-called harmonic approximation, i.e. temperature changes bring terms of the lattice potential U with power higher than two into play, for instance $U(x) = ax^2 - bx^3 - cx^4$, being a, b and c positive constants and x the average atomic displacement from the equilibrium position and, as a consequence $< x >$ is not longer zero[1]. Thus, as an effect of such anharmonic contributions to the lattice potential, once the temperature is varied the solid continuously either shrinks or dilates in order to achieve the optimal volume where its total free energy (F) is minimized, namely $\partial F/\partial < x > = 0$. The situation is quite distinct in the immediate vicinity of a generic phase transition, where besides such anharmonic terms contributing to the lattice potential other sorts of excitations like charge, spins and orbital as well as critical fluctuations itself[2] can contribute dramatically to the volume change of the solid. From the experimental point of view, such volume changes cannot, in many cases, be detected directly by means of standard x-ray structural data analysis due to the relatively low-resolution intrinsic to this kind of experiments, i.e. $\Delta l/l \simeq 10^{-8}$, here l refers to the sample length, see e.g.[5]. In this sense, high-resolution measurements of the thermal expansivity can be considered a quite powerful thermodynamic experimental tool for investigating volume changes associated with phase transitions. Indeed, employing such an experimental technique phase transitions involving distinct types of excitations, i.e. lattice, charge, magnetic and orbital degrees of freedom can be precisely detected. For instance, ultra-high resolution expansivity measurements have been recently employed to detect and explore subtle lattice effects accompanying the charge-ordering transition in molecular solids[6,7], spin-liquid-like lattice instability[8], the Mott metal-to-insulator transition[2,3,9,10], magnetic[11], multiferroic[12] and superconducting transition as well[13]. Analogously, the bulk properties of a solid can be obtained by means of high-resolution specific heat measurements[14]. Indeed, high-resolution specific heat measurements constitute one of the most powerful experimental tools to access fundamental excitations in solids, like the effective charge carrier mass and the entropy changes associated with a phase transition[15], just to mention a few examples. In his seminal paper of 1908[16], E. Grüneisen reported on a formal connection between both quantities, i.e. thermal expansion and heat capacity, which leads to the birth of the so-called *Grüneisen Ratio*, abbreviated to GR hereafter. The GR (Γ) is generally defined as the ratio of the linear thermal expansivity (α) to the specific heat at constant pressure (c_p), namely:

$$\Gamma = \frac{\alpha}{c_p}. \tag{1}$$

It is straightforward to write Eq. 1 in the following way:

$$\Gamma = V \frac{(\partial P/\partial T)_V}{(\partial E/\partial T)_V} = -\frac{1}{T} \frac{(\partial S/\partial p)_T}{(\partial S/\partial T)_p}, \tag{2}$$

where V, P, T, E and S refer, respectively, to the specimen volume, pressure, temperature, energy and entropy.
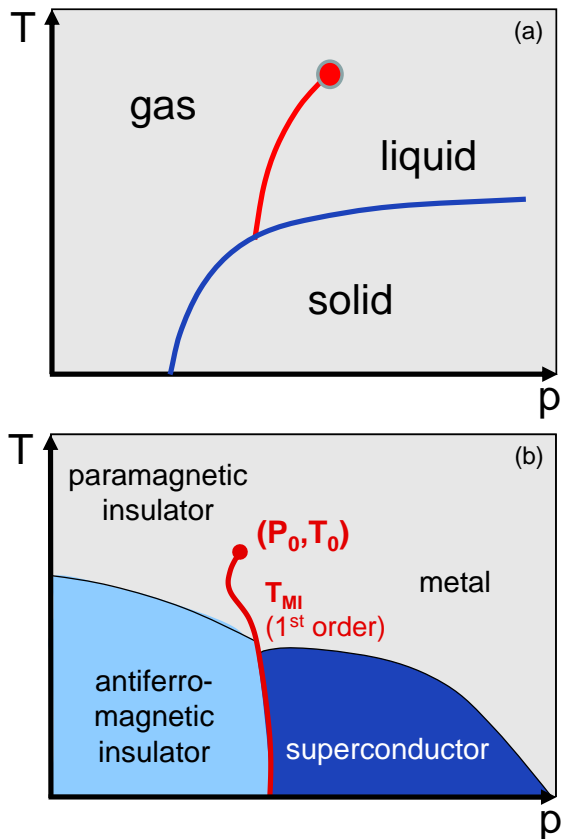
FIG. 1. (a) Schematic universal pressure (p) versus temperature (T) phase diagram for a generic substance, being solid, liquid and gaseous phases indicated explicitly. (b) Schematic proposed universal pressure versus temperature phase diagram of molecular conductors of the κ-(BEDT-TTF)$_2$X serie[2–4]. The red solid lines in (a) and (b) represent a first-order phase transition line which separate the paramagnetic/antiferromagnetic insulating from the metallic/superconducting phased and ends in a critical point (indicated by red bullets in (a) and in (b)), indicated by (P_0, T_0). Details about the behavior of the GR close to the critical-end point are presented in the main text.

For completeness, it is worth recalling that $(\partial E/\partial T)_V$ is the specific heat at constant volume.

More generally, the GR is roughly constant when a single energy scale E^s, for instance the exchange coupling constant in a magnetic system or the electrical polarization in a conventional ferroelectric, governs the physical properties of the system of interest. In such cases, for the sake of completeness, it is worth mentioning that the entropy $S \propto f(T/E^s)$ and the GR are given by:

$$\Gamma = \left(\frac{1}{V_m E^s}\right)\frac{\partial E^s}{\partial p}, \tag{3}$$

see e.g. [17] and references cited therein for details. However, from the definition of the GR (cf. Eqs.1 and 2) one can directly infer that for *any* pressure-induced critical point the GR should diverge. This is a direct consequence of the entropy accumulation in the immediate vicinity of a critical point. Indeed, it is nowadays well established that the GR shows a singular behavior upon approaching a quantum critical point[17,18] and close to a finite-temperature critical end-point[2–4] as well (see Figs. 1 and 2). Hence, the GR can considered the *smoking gun* for exploring pressure-induced critical points (see Figs. 1 a), b) and Fig. 2), no matter the nature of the phase transition. While the GR has been largely explored in solid state physics, since measurements of the specific heat and thermal expansion measurements are quite accessible, very little is known about its behavior for gases. This is most likely due to the difficulties posed to carry out both thermal expansion and specific heat measurements in gases with high accuracy as a function of pressure and temperature. To the best of our knowledge, the only report about the GR for gases is found in Ref. [19]. Also in classical textbooks discussions on the GR are quite limited, see e.g. Refs. [20,21]. Interestingly enough, recently the GR was identified as the scaling exponent γ in supercooled liquids[22]. As discussed by the authors of Ref. [22] the scaling exponent γ quantifies the slope of the interatomic potential and its relative contribution of temperature and volume. Hence, as pointed by the authors in Ref. [22] a direct connection between γ and the GR exists, characterizing thus both quantities as a *gauge* for the level of the anharmonicity of the potential. In this contribution we introduce the fundamental physical concepts associated with the GR in a didactic way and report on a systematic analysis of the GR for gases. We show that for the Van der Waals gas the GR depends only on the co-volume b due to interaction effects, it is smaller than that for the ideal gas (GR = 2/3) and diverges upon approaching the critical volume. For the Bose-Einstein condensation of an ideal boson gas, assuming the transition as first-order the GR diverges upon approaching a critical volume, similarly to the Van der Waals gas. Furthermore, for ^{4}He at the superfluid transition the GR shows a singular behavior at the transition. Hence, we show, for the first time, the particularities of the GR for various gaseous systems. The paper is divided as follows: after this brief introduction, which comprises the first section, we discuss the most relevant textbooks thermodynamic quantities of interest for this work followed by an analysis of the GR for well-known systems like the ideal, Van der Waals and ultra-relativistic gases; ^{4}He and the Bose-Einstein condensation (BEC). Our aim is to give an overview of the GR and its relevance in the exploration and understanding of the above-mentioned systems in a comprehensive fashion.

II. THERMODYNAMIC QUANTITIES

The Grüneisen-Relation, discussed in the introduction of this work, was originally[16] presented as follows:

$$\beta(T) = \Gamma_{eff} \cdot \frac{\kappa_T}{V_{mol}} \cdot c_V(T), \tag{4}$$

where $\beta(T)$ and V_{mol} refers, respectively, to the volumetric thermal expansion coefficient and molar volume; Γ_{eff} is the so-called effective Grüneisen parameter, κ_T stands for the isothermal compressibility. It is worth mentioning that the GR (Eq. 4) holds true for solid, liquid and gases. Although this work is focused on the properties of the GR for gases, for the sake of completeness, in the following we discuss briefly the lattice Grüneisen parameter, obviously present only in solid-state. In the frame of the Debye-model, the lattice (or phononic) Grüneisen parameter Γ_{pho} reads:

$$\Gamma_{pho} = -\frac{d\ln\Theta_D}{d\ln V}, \qquad (5)$$

where Θ_D stands for the Debye temperature of the solid. A simple analysis of Eq. 5 reveals that the bigger the lattice Grüneisen parameter, the higher the volume dependence of the vibration modes of the lattice. Strictly speaking, as above-mentioned, the lattice Grüneisen parameter is a measure of the volume dependence of the anharmonicity of the lattice vibrations, which in turn is responsible for the lattice contribution to the thermal expansion in a solid. In general terms, the vibrational free energy, entropy, specific heat and thermal expansion originate from sums of contributions f_i, s_i, c_i and α_i from independent vibration modes of frequency $\omega_i(V)$, respectively. Hence, the so-called mode Grüneisen parameter is defined in the following way:

$$\Gamma_i = -\frac{d\ln\omega_i}{d\ln V}. \qquad (6)$$

Thus, according to Eq. 6, vibration modes whose frequency, ω_i, decreases or *softens* as the volume of the solid decreases will result in a negative Grüneisen parameter and, from Eq. 4, such vibration modes, in particular, will be responsible for a negative contribution to the overall thermal expansion of the material[23]. As a matter of fact, the so-called mode Grüneisen parameter can be related to the interatomic/intermolecular potential via the elastic force constant, namely $k \equiv d^2U/dr^2$, which in the frame of the harmonic approximation is proportional to ω^2. More generally, in addition to the ordinary phononic background contribution to the thermal expansion of a certain solid material, other contributions, whose origin might be electronic or magnetic, have to be taken into account in an accurate estimate of the GR. This is the case especially at low temperatures, where such contributions may dominate the thermodynamic properties[5]. Hence, in such cases the Grüneisen usually is written in the following way:

$$\Gamma_{eff} = \Gamma_{ph} + \Gamma_{el} + \Gamma_{mag} = \frac{V_{mol}}{\kappa_T}\left(\frac{\beta_{ph}}{c_{ph}} + \frac{\beta_{el}}{c_{el}} + \frac{\beta_{mag}}{c_{mag}}\right), \quad (7)$$

where β_{ph} (c_{ph}), β_{el} (c_{el}) and β_{mag} (c_{mag}) refer to the phononic, electronic and magnetic contributions to thermal expansivity β (specific heat c), respectively, while

Γ_{ph}, Γ_{el} and Γ_{mag} are the respective Grüneisen parameters. Strictly speaking, when various contributions to the GR have to be taken into account the GR reads[24]:

$$\Gamma = \frac{V\sum_i c_i\Gamma_i}{\kappa_T\sum_i \Gamma_i}, \qquad (8)$$

where i refers to the ith contribution to Γ.

At this point, it is useful to discuss the GR in quantitative terms. For the critical temperature of the ordinary metal-to-superconducting phase transition in the molecular conductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ $\Gamma \approx 40$ was obtained[25]. The latter is roughly by a factor of twenty bigger than those obtained for ordinary superconducting materials such as Pb, with a $\Gamma = 2.4$[26] or even bigger than those measured for the well-known high-critical temperature cuprate superconductor YBa$_2$Cu$_3$O$_7$ with $\Gamma = (0.36 \sim 0.6)$[27]. Such a simple comparison reveals the high-sensitivity of the superconducting transition temperature to application of external pressure in the above-mentioned molecular metals, as discussed in quite details in Ref. [28]. Regarding the GR close to P-induced critical points, a huge value of $\Gamma \simeq 100$ was deduced experimentally in the immediate vicinity of a quantum critical point in heavy fermions[18], close to the critical end-point of the metal-to-insulator Mott transition[2,3] and at the $\gamma \leftrightarrows \alpha$ structural phase transition of Cerium[29]. For the sake of completeness, analogously, if the tuning parameter of the phase transition is an external magnetic field (H), the magnetic Grüneisen parameter, frequently also called magnetocaloric effect, reads[17]:

$$\Gamma_H = -\frac{(\partial M/\partial T)_H}{c_H} = -\frac{1}{T}\frac{(\partial S/\partial H)_T}{(\partial S/\partial T)_H}, \qquad (9)$$

where M refers to the magnetization and c_H to the specific heat under constant external magnetic field. Furthemore, it is worth mentioning that is well documented in the literature that for a magnetic field-induced quantum critical point, due to the enhancement of the entropy in the critical region a sign change of Γ_H is expected[30]. The latter consists one of the fingerprints of a magnetic field-induced quantum critical point.

III. APPLICATIONS AND DISCUSSION

Below we discuss the GR ratio for various gases and make a detailed discussion for each particular case of interest.

A. The Ideal Gas

We start with the simplest example. For an ideal gas, well known from textbooks, the equation of state is given by:
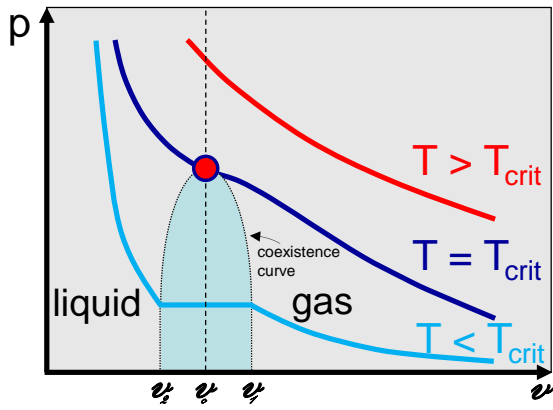
$$pV = nRT, \qquad (10)$$

FIG. 2. Schematic universal pressure *versus* volume phase diagram. The shaded area indicates a phase coexistence region. At $T = T_{crit}$, i.e. at the liquid-to-gas phase transition temperature the system achieves a critical volume and the GR diverges. For details, see discussion in the main text.

and the (internal) energy in turn, reads:

$$E = \frac{3}{2}nRT, \tag{11}$$

where n and R refers to the number of moles and the universal gas constant, respectively. Employing Eqs. 10, 11 and making use of the definition for the GR discussed in the introduction of this work (Eqs. 1 and 2), one obtains $\Gamma = 2/3$. Thus, for the ideal gas Γ is a constant. Analogously, the same result, i.e. $\Gamma = 2/3$, is obtained for the free electron gas at zero temperature, where $E = 3/2VP$. This result can be easily understood by considering the physical definition of the GR, which quantifies the degree of the anharmonicity of the potential. Since for both ideal and free electron gas the intermolecular interaction is not taken into account and thus no phase transition takes place, a constant value for the GR is expected in these cases. With respect to the value 2/3, it is a direct consequence of the number of degrees of freedom in the system. To make this clear, for the ideal gas, remembering that $C_p - C_V = R$, the GR can be written in the following way:

$$\Gamma = \frac{C_p}{C_V} - 1. \tag{12}$$

Now, considering the relation $C_P/C_V = (f + 2)/f$, being f the number of degrees of freedom (for the ideal gas $f = 3$; namely three translational degrees of freedom), from Eq. 12, $\Gamma = 2/3$ is obtained for the ideal gas. For the sake of completeness, below we derive the GR for the ideal gas employing the partition function:

$$Z = \left[V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \right]^N. \tag{13}$$

Making use of the well-known relations, namely:

$$p = \frac{1}{\beta^*} \left(\frac{\partial lnZ}{\partial V} \right)_T, \tag{14}$$

and

$$E = -\frac{\partial lnZ}{\partial \beta^*}, \tag{15}$$

being $\beta^* = 1/k_B T$[31], the GR (cf. Eq. 1) can thus be written as follows:

$$\Gamma = -V \frac{\frac{\partial}{\partial T} \left[\frac{1}{\beta^*} \frac{\partial}{\partial V} (\ln Z) \right]}{\frac{\partial}{\partial T} \left[-\frac{\partial}{\partial \beta^*} (\ln Z) \right]}, \tag{16}$$

making the inner derivatives, one obtains:

$$\Gamma = -V \frac{\frac{\partial}{\partial T} \left[\frac{1}{\beta^*} \frac{N}{V} \right]}{\frac{\partial}{\partial T} \left[-\frac{3N}{2\beta^*} \right]} = \frac{V \left[\frac{Nk_B}{V} \right]}{\frac{3}{2} k_B N}, \tag{17}$$

we then achieve the same value obtained for the GR, namely:

$$\Gamma = \frac{2}{3}, \tag{18}$$

employing the equation of state as discussed above.

B. The Van der Waals Gas

In the case of the Van der Waals gas, the equation of state reads:

$$\left(P + \frac{n^2 a}{V^2} \right)\left(V - nb \right) = nRT, \tag{19}$$

where a and b stand for the cohesion pressure and co-volume, respectively; while n refers to the number of particles of the gas investigated. The Van der Waals gas energy is given by:

$$U = U_{ideal\ gas} - \frac{n^2 a}{V}. \tag{20}$$

Making the derivatives of Eqs. 19 and 20 the GR for the Van der Waals gas is obtained:

$$\Gamma = \frac{2}{3} \cdot \frac{V}{(V - nb)}. \tag{21}$$

Interestingly enough, as can be directly inferred from Eq. 21, the GR depends solely on the co-volume. This means that the cohesion pressure is not relevant and the GR for the Van der Waals is governed only by the radius of the gas particles. Yet, from Eq. 21, one can deduce that measuring the Grüneisen parameter of a real gas, the co-volume b of the investigated gas can be immediately obtained. Furthermore, upon pressurizing the gas,

b increases and, in particular, when b achieves the gas cloud critical volume[32] $V_c = nb$ the GR diverges, since the denominator of Eq. 21 tends to zero when $V \to V_c$. As we have done for the ideal gas, for the sake of completeness, below we derive the GR for the van der Waal gas employing the partition function. The latter, for the van der Waals gas, reads:

$$\ln Z = -N \ln N + N + N \ln \left[\frac{(V - Nb)}{\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}} \right] + \frac{N^2 a}{V k_B T} \tag{22}$$

and can be rewritten in the following way:

$$\ln Z = N[1 - \ln N + \ln(V - Nb)] -$$

$$- N \left\{ \frac{3}{2} \left[\ln h^2 - \ln (2\pi m k_B T) \right] \right\} + \frac{N^2 a}{V k_B T} \tag{23}$$

Hence, making use of Eqs. 16 and 23 the GR can be easily calculated:

$$\Gamma = -V \frac{\frac{\partial}{\partial T} \left\{ \frac{1}{\beta^*} \left[\frac{N}{(V - Nb)} - \frac{N^2 a}{k_B T V^2} \right] \right\}}{\frac{\partial}{\partial T} \left[-\frac{3}{2} N k_B T + \frac{N^2 a}{V} \right]}, \tag{24}$$

which simplified, reads:

$$\Gamma = -V \frac{\frac{\partial}{\partial T} \left\{ \frac{k_B T N}{(V - Nb)} - \frac{N^2 a}{V^2} \right\}}{-\frac{3}{2} N k_B}, \tag{25}$$

thus, the GR for the van der Waals gas is obtained, namely:

$$\Gamma = \frac{2}{3} \cdot \frac{V}{(V - Nb)}, \tag{26}$$

which is identical to Eq. 21, deduced starting from the equation of state.

Still considering the Van der Waals gas, it is useful to analyze the behavior of the GR for the Joule-Thomson effect. For the latter, the temperature gradient is given by:

$$\Delta T = -\frac{n^2 a}{c_V V}. \tag{27}$$

Combining Eqs. 21 and 27, the GR (Γ_{JT}) for the Joule-Thomson effect can be obtained, namely:

$$\Gamma_{JT} = \frac{2}{3} \frac{1}{\left(1 + \frac{b c_V \Delta T}{na}\right)}. \tag{28}$$

Interestingly enough, as can be deduced immediately from Eq. 28, in the Joule-Thomson effect the van der Waals GR assumes a value closer to those obtained for the ideal gas, i.e. $\Gamma = 2/3$, when the second term in the parenthesis of the denominator tends to zero.

C. Bose-Einstein Condensation

The Bose-Einstein gas is of particular interest because, in contrast to the Fermi-Dirac gas, it can undergo a phase transition thought the particles do not interact with each other. As well-known from the literature, the Bose-Einstein condensation is a direct consequence of how the particles occupancy takes place in the case of bosons. To make this clear, let us recall the average number $\langle N \rangle$ of particles in an allowed state l:

$$\langle N \rangle = \sum_l \left(\frac{1}{e^{\beta^*(\epsilon_l - \mu)} - 1} \right) = \left(\frac{z}{e^{\beta^* \epsilon_l} - z} \right) = \sum_l \langle n_l \rangle, \tag{29}$$

where $z = e^{\beta^* \mu}$ is an effective pressure, the so-called fugacity. Since $1 \leq e^{\beta^* \epsilon_l} \leq \infty$, i.e. all states are accessible in this range, to keep $\langle N \rangle > 0$, there is a constrain to the fugacity, namely $0 \leq z \leq 1$. In addition, a simple analysis of Eq. 29 reveals that μ should be either zero or negative. Physically, as a consequence of such constrains, one can say that it is *easy* to tot up additional particles to the gas. A particular situation is found when $l = 0$, i.e. $\epsilon_0 = 0$. In such a situation $\lim_{z \to 0} \langle n_l \rangle \to \infty$ and a phase transition into a Bose-Einstein condensation takes place[33]. Here we are interested in estimating the GR for the condensate. In the case of the Bose-Einstein condensation of an ideal boson gas, the specific heat for $T \geq T_c$ is given by[34]:

$$c_v = 1.496 N k_B + 0.341 N k_B \left(\frac{T_c}{T}\right)^{1.5} + 0.089 N k_B \left(\frac{T_c}{T}\right)^3, \tag{30}$$

and, according with Ref. [35] for $T > T_c$

$$\frac{\partial P}{\partial T} = \frac{\partial \left[\frac{N}{V} k_B T \frac{g_{5/2}(z)}{g_{3/2}(z)} \right]}{\partial T}, \tag{31}$$

where $g_{5/2}(z)$ and $g_{3/2}(z)$ are the so-called Bose functions.

At this point, it is worth mentioning that only those particles which do not take part in the condensate contribute to the energy of the Bose gas below T_c[36]. Thus, for $T < T_c$, the specific heat of those particles is given by[34]:

$$c_v = 1.926 N k_B \left(\frac{T}{T_c}\right)^{1.5}; \tag{32}$$

and[36]

$$\frac{\partial P}{\partial T} = \frac{\partial [0.0851 m^{1.5} (k_B T)^{2.5} \hbar^{-3} g]}{\partial T}, \tag{33}$$

where m refers to the mass of the gas particle, g is the degeneracy, $\hbar = h/2\pi$ being h the Planck constant.

Employing Eqs. 30, 31, 32 and 33, the GR of the condensate can be estimated.

It turns out that employing such expressions both below and above the Bose-Einstein condensation temperature GR = 2/3, as in the case of the ideal gas. An alternative equation of state was proposed in Ref. [37] considering that in the ground state the system holds the kinetic energy associated with the gas cloud right at the condensation temperature. The proposed equation of state below the condensation temperature reads[37]:

$$PV = cVT^{5/2} + 0.513\left[1 - (T/T_c)^{3/2}\right]Nk_bT_c, \quad (34)$$

where $c = g_{5/2}(1)k^{5/2}(m/2\pi\hbar^2)^{3/2}$. Thus, making use of Eqs. 32 and 34 the GR follows a linear dependence with T below T_c. In what follows, we discuss the BEC in analogy with a liquid-to-gas phase phase transition. The critical volume (v^*) is given by[38]:

$$v^* = \frac{1}{n^*} = \frac{\lambda^3}{g\xi_{3/2}} = \frac{1}{g}\left[\frac{h}{(2\pi mk_BT)^{1/2}}\right]^3; \quad (35)$$

Considering the transition as being of first order, the Clausius-Clapeyron equation can be used:

$$\frac{dT}{dP} = \frac{\Delta v}{\Delta s} = \frac{T_c(v^* - v_0)}{L} \quad (36)$$

where Δv, Δs and L, refer to the volume change, entropy change and latent heat, respectively.

The GR reads:

$$\Gamma = \frac{Lvc_v}{T_c(v^* - v_0)} \quad (37)$$

From Eq. 37, when $v_0 \to v^* \Rightarrow \Gamma \to \infty$. A similar result from that obtained for the Van der Waals gas.

From the experimental point of view, immense efforts have been put by different groups to measure the thermodynamic properties of a Bose–Einstein condensate. In this regard, we refer to measurements of the specific heat of a weakly interacting gas[39] and the influence of pressure on a Bose–Einstein condensate in two dimensions[40].

D. Grüneisen Parameter in the Vicinity of the ^{4}He λ-Phase Transition

Due to its exotic behavior, the theoretical and experimental investigations of the ^{4}He isotope physical properties have been a topic of great interest since the middle of the 20th century until nowadays. Seminal works include the reports by Fairbank and Kellers on the λ-like (superfluid) transition[41] as well as the detailed report by McCarty[42], who investigated the helium physical properties in a broad range of temperature and pressure. Furthermore, it is worth mentioning experiments of dielectric constant[43], thermal expansion[43] and specific heat[44–46], whose results will serve as the basis for the estimate of the GR to be discussed in the following. Here, for the estimate of the GR under pressure the results of Graywall and Ahlers[47] were employed. The expression for the
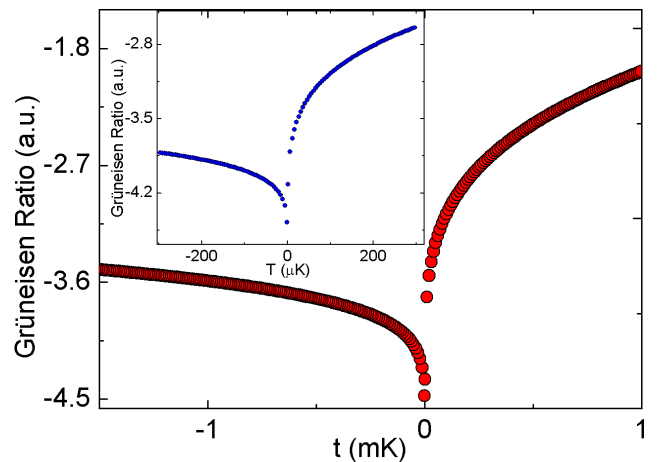

FIG. 3. Grüneisen ratio as a function of the reduced temperature t for ^{4}He in the immediate vicinity of the normal liquid-to-superfluid phase transition, namely for $\sim |t| \leq 1$ mK. Inset: Blowup of the data shown in the main panel, being the Grüneisen parameter shown in the range $|t| \leq 1\,\mu$K.

specific heat in the immediate vicinity of the λ-like transition, reported in the literature by Fairbank and Kellers[41], is given by:

$$c_p = 4.55 - \log_{10}|T - T_\lambda| - 5.20\Delta, \quad (38)$$

here Δ is a phenomenological parameter and it is assumed to be 1 at the normal-liquid phase $(t > 0)$ and 0 at the superfluid phase $(t < 0)$, where t refers to the reduced temperature; T_λ stands for the from normal-liquid-to-superfluid phase transition temperature. We stress that Eq. 38 is in perfect agreement with experimental results[44] in the temperature range $|T-T_\lambda| = |t| \leq 200$ mK. However, in our analysis we stick to the region $|t| \leq 10$ mK, cf. detailed discussion below. Yet, we stress that the expression employed for the specific heat fits was taken from an experiment carried out at constant volume. However, as the range of temperature is quite small, the process can be considerate isobaric as well as isovolumetric. Hence, in this particular case we assume $c_P = c_V$ so that Eq. 1 can be used in our analysis. Regarding thermal expansivity experiments, the work of Niemela and Donnelly[43] provided the data set in the T-range from 1.35 K to 4.9 K. Nevertheless, here the only results within the region $|t| \leq 10$ mK are taken into account. The volumetric thermal expansion data are nicely described by the following expression[43]:

$$\beta(t) = -\frac{(a_1 + b_1) + a_1 \ln|t| + (a_2 + 2b_2)t + 2a_2t\ln|t|}{1 + \sum_{i=1}^{2} a_i t^i \ln|t| + \sum_{i=1}^{7} b_i t^i} +$$

$$(39)$$

$$+ \frac{\sum_{n=3}^{7} nb_n t^{(n-1)}}{1 + \sum_{i=1}^{2} a_i t^i \ln|t| + \sum_{i=1}^{7} b_i t^i},$$
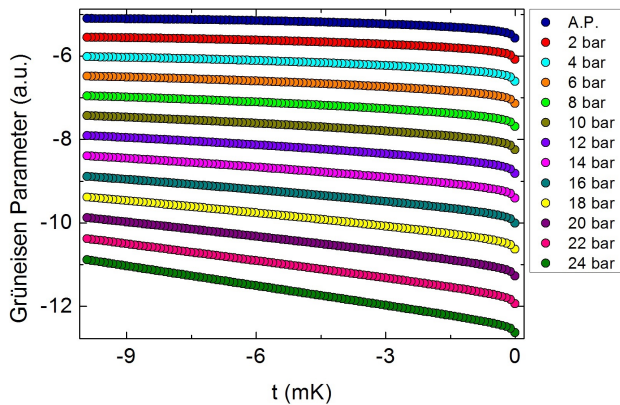
FIG. 4. Grüneisen parameter as a function of the reduced temperature t under various pressures, cf. indicated in the label. The behaviour for saturated pressure value is the same observed in Fig. 3 and increases with the pressure. A.P. stands for ambient pressure.

being, for the sake of completeness, the coefficients a_i and b_i presented in Table 1. Employing Eqs. 38 and 39, the

i	a_i ($T < T_\lambda$)	a_i ($T > T_\lambda$)	b_i ($T < T_\lambda$)	b_i ($T > T_\lambda$)
1	−0.00757537	−0.00794605	0.00379937	−0.0303511
2	0.00687483	0.00507051	0.00186557	−0.0102326
3	-	-	0.00488345	−0.00300636
4	-	-	-	0.00024072
5	-	-	-	−0.00245749
6	-	-	-	0.00153454
7	-	-	-	−0.00030818

TABLE I. Parameters a_i and b_i used for the estimate of thermal expansion expression of ^{4}He (Eq. 39) for $t > 0$ and $t < 0$, after Ref. [43].

GR as a function of temperature can be obtained, being the results in the range $|t| \leq 0.001$ K depicted in Fig. 3. Note that a clear singularity of the GR is observed in the immediate vicinity of the λ transition for the isotope ^{4}He. A blowup of the GR even closer to T_λ together with the normalized Grüneisen parameter is shown in the inset of Fig. 3. It is worth mentioning that for the temperature range $|t| > 1$ mK (not shown), at ambient pressure, the GR does not present singularities, being instead described roughly by a constant function. For the range $t < 0$, i.e. below the superfluid transition, we were able to perform calculations of the GR as a function of temperature and pressure, whose results are presented in Fig. 4. By doing so, we are interested now in following the pressure dependence of the entropy of ^{4}He in the superfluid phase. Hence, we make use of the function for the superfluid helium entropy derived by Greywall an Ahlers[47], which in turn is in good agreement with experimental data published in the literature[48]. Interestingly enough, as can be seen in Fig. 4, the GR is clearly enhanced under pressure. Based on the discussions presented in the introduction of this work the GR can be used as an indirect way to measure the interaction between particles in a gas, fluid or solid. In the model proposed by Tisza[50], the
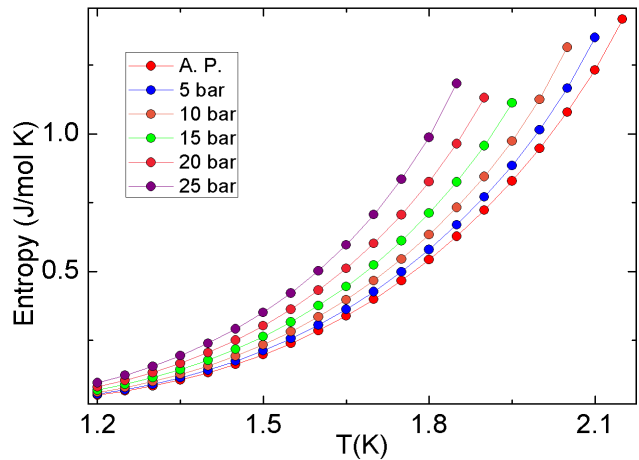

FIG. 5. Entropy as a function of temperature for various values of applied pressures[49]. The entropy enhancement is related to the increase of the interaction between rotons, see main text for details. A.P. stands stands for ambient pressure.

so-called rotons are essentially a bounded pair of Helium atoms which is formed in the superfluid phase. In analogy with a classical rotor, such rotons have translational and rotational degrees of freedom. From the sound velocity data the entropy at the superfluid phase was derived by Maynard[49]. Fig. 5 depicts the entropy as a function of temperature for various pressures. Note that the entropy increases as the applied pressure is increased. Such a behavior is a direct consequence of the enhancement of the interaction between rotons as pressure is applied. The rotons gas is also discussed and presented in details by Pathria in Ref. [35]. Employing the expression of the Helmhotz free energy it is straightforward to obtain the GR of a rotons gas as a function of temperature and pressure (not shown), being the results in perfect agreement with those depicted in Fig 4.

IV. CONCLUSIONS

To summarize, we have derived the Grüneisen ratio for various gases. We have shown that for the ideal gas as well as for the free electron gas a constant value, namely $\Gamma = 2/3$ is found for the Grüneisen ratio. For the Van der Waals gas the Grüneisen ratio diverges when the gas particle co-volume achieves a critical value. We also have shown that Γ for ^{4}He diverges near the so-called λ transition, namely from superfluid to normal liquid. Our analysis show that application of pressure increases the system entropy, in perfect agreement with Tisza's theory based on rotons. Using the textbook Bose-Einstein distribution for gases and considering the boundary conditions for the realization of a Bose-Einstein condensation we have obtained $\Gamma = 2/3$ for the non-interacting boson gas. Yet, an analysis of the Bose-Einstein condensation in analogy with the classical liquid-to-gas transition reveals that when the gas cloud volume achieves the critical, the

Grüneisen ratio diverges. A calculation of the effects of interaction on the Grüneisen ratio for the Bose-Einstein condensation constitute a topic of interest and will be explored in another work.

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[1] C. Kittel, *Introduction to Solid State Physics* (Wiley, 1976).

[2] M. de Souza and L. Bartosch, Journal of Physics: Condensed Matter **27**, 053203 (2015).

[3] M. de Souza, A. Brühl, C. Strack, B. Wolf, D. Schweitzer, and M. Lang, Phys. Rev. Lett. **99**, 037003 (2007).

[4] L. Bartosch, M. de Souza, and M. Lang, Phys. Rev. Lett. **104**, 245701 (2010).

[5] T. Barron, J. Collins, and G. White, Advances in Physics **29**, 609 (1980), http://dx.doi.org/10.1080/00018738000101426.

[6] M. de Souza, P. Foury-Leylekian, A. Moradpour, J.-P. Pouget, and M. Lang, Phys. Rev. Lett. **101**, 216403 (2008).

[7] P. Foury-Leylekian, S. Petit, I. Mirebeau, G. André, M. de Souza, M. Lang, E. Ressouche, A. Moradpour, and J.-P. Pouget, Phys. Rev. B **88**, 024105 (2013).

[8] R. S. Manna, M. de Souza, A. Brühl, J. A. Schlueter, and M. Lang, Phys. Rev. Lett. **104**, 016403 (2010).

[9] M. de Souza, *Thermal Expansion and Transport Properties of Low-Dimensional Organic Conductors*, Ph.D. thesis, Goethe Universitaet Frankfurt (2008).

[10] M. de Souza, A. Brühl, C. Strack, D. Schweitzer, and M. Lang, Phys. Rev. B **86**, 085130 (2012).

[11] R. S. Manna, B. Wolf, M. de Souza, and M. Lang, Review of Scientific Instruments **83**, 085111 (2012).

[12] M. Pregelj, A. Zorko, O. Zaharko, Z. Kutnjak, M. Jagodič, Z. Jagličić, H. Berger, M. de Souza, C. Balz, M. Lang, and D. Arčon, Phys. Rev. B **82**, 144438 (2010).

[13] M. de Souza, A.-A. Haghighirad, U. Tutsch, W. Assmus, and M. Lang, The European Physical Journal B **77**, 101 (2010).

[14] M. de Souza, R. Paupitz, A. Seridonio, R. E. Lagos, and arXiv:1504.07525, .

[15] E. Gopal, *Specific Heats at Low Temperatures*, International cryogenics monograph series (Plenum Press, 1966).

[16] E. Grüneisen, Annalen der Physik **331**, 393 (1908).

[17] L. Zhu, M. Garst, A. Rosch, and Q. Si, Phys. Rev. Lett. **91**, 066404 (2003).

[18] R. Küchler, N. Oeschler, P. Gegenwart, T. Cichorek, K. Neumaier, O. Tegus, C. Geibel, J. A. Mydosh, F. Steglich, L. Zhu, and Q. Si, Phys. Rev. Lett. **91**, 066405 (2003).

[19] P. Harris and L. Avrami, *Some Physics of the Grueneisen Parameter* (Dover, 1972).

[20] L. Landau and E. Lifshitz, *Statistical Physics, Third Edition, Part 1: Volume 5* (Butterworth-Heinemann, 1980).

[21] N. Ashcroft and N. Mermin, *Solid State Physics*, Science: Physics (Saunders College, 1976).

[22] R. Casalini, U. Mohanty, and C. M. Roland, The Journal of Chemical Physics **125**, 014505 (2006).

[23] J. S. O. Evans, J. Chem. Soc., Dalton Trans. **19**, 3317 (1999).

[24] D. Wallace, *Statistical Physics of Crystals and Liquids: A Guide to Highly Accurate Equations of State* (World Scientific, 2002).

[25] J. Müller, M. Lang, F. Steglich, J. A. Schlueter, A. M. Kini, U. Geiser, J. Mohtasham, R. W. Winter, G. L. Gard, T. Sasaki, and N. Toyota, Phys. Rev. B **61**, 11739 (2000).

[26] J. R. S. G. Gladstone, M. A. Jensen, *Superconductivity Vol. 2* (R. D. Parks, 1969).

[27] C. Meingast, B. Blank, H. Bürkle, B. Obst, T. Wolf, H. Wühl, V. Selvamanickam, and K. Salama, Phys. Rev. B **41**, 11299 (1990).

[28] J. K. K.H. Bennemann, *The Physics of Superconductors* (Springer, 2004).

[29] F. Decremps, L. Belhadi, D. L. Farber, K. T. Moore, F. Occelli, M. Gauthier, A. Polian, D. Antonangeli, C. M. Aracne-Ruddle, and B. Amadon, Phys. Rev. Lett. **106**, 065701 (2011).

[30] M. Garst and A. Rosch, Phys. Rev. B **72**, 205129 (2005).

[31] Since β was used to label the volumetric thermal expansion coefficient, in order to avoid confusion we make use of β^* for labelling $1/k_B T$.

[32] A. Sommerfeld, F. Bopp, and J. Meixner, *Thermodynamik und Statistik*, Vorlesungen über theoretische Physik (Deutsch, 1977).

[33] K. B. Davis, M. O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, Phys. Rev. Lett. **75**, 3969 (1995).

[34] F. Y.-H. Wang, American Journal of Physics **72** (2004).

[35] R. Pathria, *Statistical Mechanics*, International series of monographs in natural philosophy (Pergamon Press, 1977).

[36] J. D. W. A. L. Fetter, *Quantum Theory of Many-Particle Systems* (Dover, 2003).

[37] F. Deeney and J. OLeary, Physics Letters A **375**, 1637 (2011).

[38] M. Kardar, *Statistical Physics of Particles* (Cambridge University Press, 2007).

[39] R. F. Shiozaki, G. D. Telles, P. Castilho, F. J. Poveda-Cuevas, S. R. Muniz, G. Roati, V. Romero-Rochin, and V. S. Bagnato, Phys. Rev. A **90**, 043640 (2014).

[40] J.-H. P. W. Cho, S.-W. Kim, New J. Phys. **17**, 013037 (2015).

[41] W. M. Fairbank and C. F. Kellers, Proceedings of a Conference in Critical Phenomena. Edited by M.S. Green and J.V. Sengers, Natl. Bur.Std. Misc. Pub. No. 273, U.S. GPO, Washington D.C. , p71 (1966).

[42] R. D. McCarty, J. Phys. Chem. Ref. Data **2**, 923 (1973).

[43] J. J. Niemela and R. J. Donnelly, J. Low Temp. Phys. **98**, 1 (1995).

[44] R. W. H. O. V. Lounasmaa, Phyl. Mag. **2**, 143 (1957).

[45] H. C. K. J. D. W. C. J. Gorter, Physica **18**, 329 (1952).

[46] P. R. Roach, Phys. Rev. **170**, 213 (1968).

[47] D. S. Greywall and G. Ahlers, Phys. Rev. A **7**, 2145 (1973).

[48] R. D. Maurer and M. A. Herlin, Phys. Rev. **81**, 444 (1951).

[49] J. Maynard, Phys. Rev. B **14**, 3868 (1976).

[50] L. Tisza, Phys. Rev. **72**, 838 (1947).