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COMMENT • OPEN ACCESS

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COMMENT

Comment on 'Gruneisen approach for universal scaling of the Brillouin shift in gases'

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Abstract

I comment on the recent article *Grüneisen approach for universal scaling of the Brillouin shift in gases* by Liang *et al* (2022 *New J. Phys.* **24** 103005). While the result of this article indeed provides a parametrization of measured Rayleigh Brillouin scattering spectra, I argue that the association with the Grüneisen effect is fortuitous. The Grüneisen effect is the change of the specific heat with compression of a gas. For the nontrivial case of the van der Waals gas, it predicts the *decrease* of the velocity of sound with increasing pressure. In solids, which is the context considered in the article by Liang *et al*, the effect is opposite: an *increase* of the velocity of sound with pressure.

1. Rayleigh Brillouin scattering

In a recent paper Liang *et al* [1] associate the Rayleigh–Brillouin spectrum of scattered light in dilute gases with the Grüneisen effect, a phenomenon rooted in solid state physics, which describes the change of phonon frequency due to compression. Alternatively, the Grüneisen effect is the change of specific heat with compression, as quantified by the Grüneisen ratio Γ,

$$\Gamma = \frac{\alpha \kappa_T}{\rho C_V}, \tag{1}$$

with α the thermal expansivity, $\alpha = (1/V)\,\partial V/\partial T|_p$, κ_T the isothermal compressibility, $\kappa_T = [-(1/V)\,\partial V/\partial p|_T]^{-1}$ and C_V the heat capacity per unit mass at constant volume. Inspection of Rayleigh–Brillouin spectra at different pressures, such as illustrated in figure 1, teaches that the side-band peak shifts to higher frequencies with increasing pressure. As the peak frequency was interpreted as the frequency of sound at the scattering wavelength $(2\pi/k_{sc})$ of light, the apparent velocity of sound increases with increasing pressure, suggestive of the analogous situation in solids.

In the context of solid-state lattice phonons, the corresponding dimensionless Grüneisen ratio is $\Gamma = -\mathrm{d}\ln\Theta_0/\mathrm{d}\ln V$, with Θ_0 the Debye temperature which is proportional to $\hbar\omega$, the quantized phonon energy, so that

$$\Gamma = -\frac{\mathrm{d}\ln\omega}{\mathrm{d}\ln V}. \tag{2}$$

The change of the phonon frequency ω with volume is due to the anharmonicity of the atomic interaction potential. Clearly, the context of the Einstein–Debye theory of phonon dispersion is very different from the microscopic physics of gases. In gases, a nontrivial Grüneisen ratio only exists for van der Waals molecules. For monatomic real gases $\Gamma = \frac{2}{3}V_m/(V_m - b)$, with V_m the molar volume and b the finite eigenvolume of the molecules [2]. In a monatomic *ideal* gas, Γ takes on the trivial value $\Gamma = 2/3$.

The marriage between two contexts—the phonon dispersion relation and sound dispersion in a gas—led Liang *et al* [1] to propose equation (2) as a relation between the sound frequency and pressure in Rayleigh–Brillouin scattering. With the additional assumption that the Grüneisen ratio Γ itself is

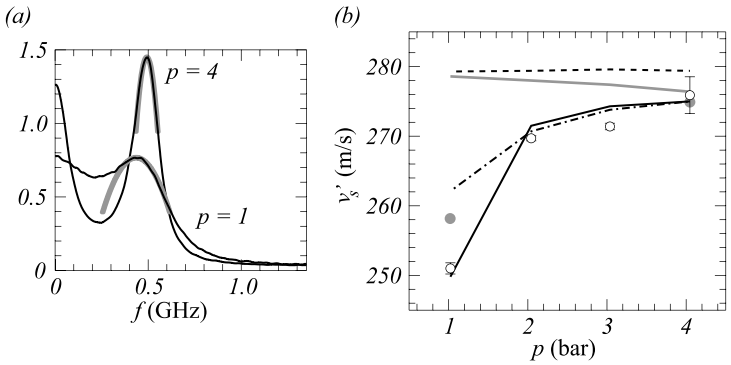

Figure 1. (a) Rayleigh Brillouin spectrum of CO_2 at 1 and 4 bars [3]. Only the right sideband is shown. The temperature is $T = 295$ K, laser wavelength $\lambda = 532$ nm, scattering angle $\theta_{sc} = 55.5°$, so that the scattering wavevector is $k_{sc} = 1.099 \times 10^7$ m^{-1}. The gray lines indicate a quadratic fit to the region around the peak frequency which was used to pinpoint the peak (the Brillouin shift f_B). (b) Open circles with error bars: v_s' determined from f_B in (a) as $v_s' = f_B/k_{sc}$. The error bars correspond to half the sum between left and right sideband frequencies. Gray dots: using a model spectrum of three Lorentzians, with parameters determined in a least squares procedure. Full line: v_s' from peak positions of the Tenti model for these spectra [3, 5]. Dash-dotted line: Grüneisen model, $v_s' = 2\pi f_B/k_{sc}$, $f_B = f_{B\,0} \exp(-\gamma_0 V_m/V_{m0})$, with V_{m0} the molar volume at $T = 295$ K and $p = 1$ bar, and $f_{B\,0}$ the corresponding ideal gas sound frequency. In agreement with [1], the parameter $\gamma_0 = 0.06$. Gray line: v_s from the CO_2 van der Waals gas, $p = RT/(V_m - b) - a/V_m^2$, with $a = 3.647 \times 10^5$ m^6 Pa kmol^{-1} and $b = 0.04267$ m^3 kmol^{-1}. Dashed line: ideal gas $v_s = (\gamma RT)^{1/2}$, with $\gamma = 7/5$. At large pressure the *apparent* sound velocity asymptotes to the real gas prediction.

proportional to pressure, a formula resulted that successfully describes the shift of peaks in Rayleigh–Brillouin spectra (see figure 1). That this marriage is forced is exemplified by the evaluation of equation 2 for the van der Waals gas; the result $\Gamma = b/(V_m - b)$ is very different from the thermodynamic relation.

Therefore, the Grüneisen effect in a real gas cannot be reconciled with that in solids as embodied by equation 2. In solid-state lattices the Grüneisen effect is associated with the anharmonicity of the atomic interaction potential. Contrary to what is stated in [1] there is no such effect in gases. Real gas molecules engaged in a collision do indeed sense an anharmonic interaction potential (the van der Waals potential), but that only enters into the continuum behavior in the form of transport coefficients.

The increase of the Brillouin frequency f_B—the position of the side band peak in the spectrum—with pressure is illustrated in figure 1 for CO_2 at temperature $T = 295$ K. Shown is the corresponding 'velocity of sound' as defined by $v_s' = 2\pi f_B/k_{sc}$ as a function of pressure. It is compared to the true velocity of sound of the van der Waals gas, which *decreases* with increasing pressure.

Figure 1 also shows f_B from the Tenti model which is known to adequately parametrize Rayleigh–Brillouin spectra [3]. It agrees with the measured Brillouin shift f_B, but it is consistent with the classic continuum equations, without invocation of anharmonicity, and without invocation of a pressure-dependent velocity of sound. As in [1], the peak positions f_B were determined 'through peak reading'. A slightly more refined estimate of f_B can be done through fitting an analytical model to the spectrum [4]. A model with Lorentzians leads to larger f_B at low pressures due to peak overlap and convolution with the experiment function. These results show that at low pressures the peak position f_B cannot simply be related to the velocity of sound.

What remains of [1] is a heuristic formula that reproduces the position of maxima in Rayleigh-Brillouin spectra.

Data availability statement

All data that support the findings of this study are included within the article.

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