

## Thermal similarity in two and three dimensions: The Debye temperatures of bulk and adsorbed monolayer He<sup>4</sup>

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The Debye temperatures for two- and three-dimensional systems are compared using an isotropic elastic model that includes the effect of finite initial stress and assumes the Cauchy conditions. It is shown that the effect of initial pressure on sound speeds, Debye temperatures, and selected elastic properties is determined in both dimensions by the dimensionless product of pressure and compressibility. The model is applied to the observed similarity in Debye temperatures for monolayer and hcp bulk He<sup>4</sup>. Using 0°K compressibility and pressure data, there is essential agreement between the elastic model and the experimental bulk Debye temperatures. The agreement results from the effect of initial pressure, which softens the bulk Debye temperatures by as much as 20% relative to the zero-pressure values for the same compressibility. A large softening also occurs in the two-dimensional extension when applied to the He<sup>4</sup>-graphite adsorption system but, in contrast to the bulk, the two-dimensional spreading pressures are insufficient to produce comparable quantitative agreement with the experimental film Debye temperatures. The idealized model is extended to include a specific substrate effect by separating the total film elastic constants into two parts: An intrinsic (Cauchy) contribution associated with the two-dimensional adsorbate lattice and a secondary contribution identified with the substrate, which lifts the Cauchy conditions on the total elastic constants for the film. The required fractional substrate contribution to the bulk and shear moduli yielding agreement with the experimental film Debye temperatures is examined.

### I. INTRODUCTION

Thermal systems formed by adsorbing helium on expanded graphite are known to exhibit a large variety of phase equilibrium properties depending upon conditions of temperature and areal density.<sup>1,2</sup> Whereas some of these properties appear to be uniquely characteristic of matter constrained upon a structured substrate, other features are notable in their similarity with ordinary bulk helium. For example, Bretz, Huff, and Dash<sup>1,3</sup> have observed that in the solid phases the Debye temperatures of the film ( $\Theta_2$ ) and bulk ( $\Theta_3$ ) are nearly coincident over a substantial range of equivalent mean interatomic separations as determined from the atomic areas and volumes by  $a^{1/2}$  and  $v^{1/3}$ . Although the simplest isotropic-continuum models suggest some correspondence in these temperatures, a similarity as close as that observed (2%) is surprising and intriguing. The Debye temperatures for two- and three-dimensional solids both scale as the ratio of some average sound speed to the average interatomic separation, but only for very special ratios of two- and three-dimensional sound speeds would they be coincident as well.

Previous<sup>4</sup> experimental studies of the helium film on nongraphite substrates have exhibited "solidlike" behavior in the heat-capacity signatures. However, these experiments have never

shown such explicit correlations with the properties of the bulk. Further, these earlier studies have not been interpretable via substrate-independent models over the total coverage range where  $T^2$  signals are observed. On graphite, however, overt requirements for film heterogeneity,<sup>5,6</sup> commensurateness,<sup>7</sup> or other substrate mechanisms<sup>8</sup> to describe the behavior of the Debye temperature with coverage and temperature appear to be absent. From this observation, it is tempting to pursue the apparent similarity in film and bulk by inquiring if similar model assumptions are adequate to describe the similar behavior of  $\Theta_2$  and  $\Theta_3$ . Does mechanical consistency alone in two and three dimensions lead to the observed thermal similarity for these helium systems? Such a dual approach requires (a) a model of the bulk solid yielding  $\Theta_3$  as a function of interatomic separation, and (b) the extension or reformulation of the same assumptions in the context of two dimensions.

Debye temperatures in two and three dimensions are given by

$$\Theta_3 = \frac{2\pi\hbar}{k_B} \left( \frac{3}{4\pi v} \right)^{1/3} \bar{C}_3, \quad (1)$$

$$\Theta_2 = \frac{2\pi\hbar}{k_B} \left( \frac{1}{\pi a} \right)^{1/2} \bar{C}_2, \quad (2)$$

with mean velocities  $\bar{C}_3$  and  $\bar{C}_2$  determined by the

long-wavelength continuum averages

$$3\bar{C}_3^{-3} = (4\pi)^{-1} \int_0^{4\pi} \sum_j C_{j3}^{-3} d\Omega_3, \quad (3)$$

$$2\bar{C}_2^{-2} = (2\pi)^{-1} \int_0^{2\pi} \sum_j C_{j2}^{-2} d\Omega_2. \quad (4)$$

If the required elastic moduli that determine the propagation velocities in Eqs. (3) and (4) are known, then the Debye temperatures<sup>9</sup> may be determined. For the bulk, such detailed elastic information<sup>10-14</sup> exists for a limited range at the largest molar volumes (19–21 cm<sup>3</sup>). In the case of the film, the situation is more primitive: Experimental knowledge of the elastic properties is limited to the compressibility at all areal densities. As a consequence of the limited data, a mechanically consistent model for the Debye temperatures in both systems must be based upon the compressibility alone. Such a model is isotropic and hence unrealistic in detail for the bulk solid, at least at low densities where the direct measurements indicate anisotropic sound speeds. However, it remains an approximation which uses available experimental data and may be compared with measured  $\Theta$ 's over the full range in interatomic separation for film and bulk.

For isotropic solids Eqs. (3) and (4) simplify to the familiar

$$3\bar{C}_3^{-3} = 2C_{t3}^{-3} + C_{l3}^{-3}, \quad (5)$$

$$2\bar{C}_2^{-2} = C_{t2}^{-2} + C_{l2}^{-2}, \quad (6)$$

where in the general case two elastic variables are required to determine the longitudinal and transverse sound speeds  $c_l$  and  $c_t$ . These may be chosen from a variety of possibilities which include Young's modulus, the compressibility, Poisson's ratio, or the conventional Lamé constants  $\lambda$  and  $\mu$  (shear modulus). Although the volume compressibility for the bulk is known and the areal compressibility for the film may be determined from appropriate vapor pressure measurements<sup>15</sup> or from thermodynamic functions obtained from combined heat-capacity and vapor-pressure experiments,<sup>2,16,17</sup> the second variable remains unknown over the total experimental range of atomic separations for both systems. Given the Debye temperature and compressibility, even the isotropic model has too many degrees of freedom to be checked directly against experiment: It could only be assumed, for example, and then used to estimate a second variable like Poisson's ratio.

An assumption which eliminates the above difficulties and which has been used in the bulk<sup>18</sup> to

approximate compressibilities knowing only longitudinal sound speeds is that the Cauchy conditions<sup>19,20</sup> are valid. This further simplification may arise when the atoms of the solid are subject to central force interactions and are located at centers of inversion symmetry. With the Cauchy conditions, Poisson's ratio is prescribed by elasticity theory and the sound speeds (Debye temperatures) depend upon a single elastic variable. Although such an assumption eliminates one elastic degree of freedom in the general isotropic solid, the model retains maximum complexity for the comparison of thermal and mechanical properties when all the elastic information is contained in the compressibility. For this reason it is considered in detail for two and three dimensions. In addition, the role of finite initial stress in determining the thermal properties for solids with large values of the pressure-compressibility product is examined. This effect is substantial for helium in both film and bulk and has been omitted in previous isotropic Cauchy approximations concerned with the bulk solid.

## II. THREE DIMENSIONS AND APPLICATION TO SOLID He<sup>4</sup>

In a three-dimensional isotropic system, the sound speeds are given by

$$C_{l3}^2 = 3(K_3\rho_3)^{-1}(1 - \sigma_3)(1 + \sigma_3)^{-1} = (\lambda_3 + 2\mu_3)\rho_3^{-1}, \quad (7)$$

$$C_{t3}^2 = \frac{3}{2}(K_3\rho_3)^{-1}(1 - 2\sigma_3)(1 + \sigma_3)^{-1} = \mu_3\rho_3^{-1}, \quad (8)$$

where  $\sigma_3$  is Poisson's ratio and  $K_3$  is the compressibility. The Debye temperature from Eqs. (1), (5), (7), and (8) is

$$\Theta_3 = \frac{2\pi\hbar}{k_B} \left( \frac{9}{4\pi V} \right)^{1/3} (\rho_3 K_3)^{-1/2} F_3(\sigma_3), \quad (9)$$

$$F_3(\sigma_3) = \sqrt{3} \left( \frac{1 - \sigma_3}{1 + \sigma_3} \right) \left[ 1 + 4\sqrt{2} \left( \frac{1 - \sigma_3}{1 - 2\sigma_3} \right)^{3/2} \right]^{-1/3} \quad (10)$$

For prescribed  $\sigma_3$ ,  $\Theta_3$  is a function of the compressibility alone and the Debye temperature is determined. Equivalently, known Debye temperatures and compressibilities should give the Cauchy  $\sigma_3$  if the model predictions are consistent with experiment. The same reasoning could be applied to a two-dimensional isotropic system with the Cauchy conditions. Before comparing  $\Theta_2$  and  $\Theta_3$  for such assumptions, however, we reexamine the ability of an isotropic model to describe the bulk data.

Cauchy values of  $\sigma_3 = 0.25$  have been used to estimate the bulk compressibility of solid helium<sup>18,21</sup> from experimental values of  $c_l$  in combination with

Eq. (7), from which we get

$$C_{i3}^2 = \frac{\rho}{5} (\rho_3 K_3)^{-1} . \quad (11)$$

Equation (11) has also been used to approximate sound speeds for monolayer films.<sup>22</sup> However, 0.25 is the Cauchy value of Poisson's ratio obtained from elastic treatments in three dimensions, which assumes that the solid is under zero initial stress. With regard to this assumption, solid helium remains unique by requiring a finite pressure for stable equilibrium at any temperature including 0°K. In addition, from experimental compressibilities and Debye temperatures,<sup>15</sup> the required values of  $\sigma_3$  range from 0.29 to 0.33 as the molar volume varies from 13.7 to 20.7 cm<sup>3</sup>. This combination of factors suggests that if a comparison is to be made between Cauchy elastic theory and the thermal experiments, Eq. (11) should be examined for possible modification resulting from the presence of initial stress. It is known that such a stress does have a significant consequence in the basic elastic relations for a solid: The stress-strain coefficients (elastic moduli) which determine the sound speeds are no longer identical with the second-order elastic constants.<sup>19</sup> It is the elastic constants, however, which remain subject to the Cauchy conditions. As a result of this distinction, it may be shown that the Cauchy value of Poisson's ratio is not fixed at 0.25, but becomes a function of pressure and compressibility. Similarly, sound speeds for a system obeying the Cauchy conditions become a function of pressure in addition to the density and compressibility dependence of Eq. (11). These modified results in the presence of an initial stress arising from hydrostatic pressure are obtained below and then applied to solid helium.

For an isotropic solid subject to initial hydrostatic stress  $t_0 = -p\delta_{ij}$  the stress-strain relations may be cast in the conventional Lamé form (summation convention)

$$T_{ij} = \lambda'_3 e_{kk} \delta_{ij} + \mu'_3 (e_{ij} + e_{ji}) , \quad (12)$$

where  $T_{ij}$  is the excess stress measured with respect to the initial value  $t_0$  and  $\lambda'_3$ ,  $\mu'_3$  are the effective three-dimensional Lamé constants in the presence of initial pressure. The  $e_{ij}$  are small strains from the initial state and have their conventional meanings as elements of the symmetric part of the displacement gradient matrix. The distinction between the effective Lamé constants and the elastic constants  $C_{ij}$  is explicit in the relations<sup>19,23</sup>

$$\lambda'_3(p) = C_{12}^{(3)}(p) + p = \lambda_3(p) + p , \quad (13)$$

$$\mu'_3(p) = C_{66}^{(3)}(p) - p = \mu_3(p) - p , \quad (14)$$

where for vanishing initial stress  $\lambda'_3 = \lambda_3 = C_{12}^{(3)}$  and  $\mu'_3 = \mu_3 = C_{66}^{(3)}$ . The superscripts on the elastic constants indicate that they are quantities for a three-dimensional system and have dimensions of bulk pressure. From standard elastic manipulations on Eq. (12), and using Eqs. (13) and (14), the compressibility and Poisson's ratio are

$$K_3(p) = [\lambda_3(p) + \frac{2}{3}\mu_3(p) + \frac{1}{3}p]^{-1} , \quad (15)$$

$$\sigma_3(p) = \frac{1}{2}[\lambda_3(p) + p][\lambda_3(p) + \mu_3(p)]^{-1} . \quad (16)$$

With the simplification of the Cauchy conditions,<sup>19,20</sup>  $\lambda(p) = \mu(p)$  and both  $K$  and  $\sigma$  depend upon one elastic constant and the initial pressure. Hence they are related to each other via

$$\sigma_3(pK_3) = \frac{1}{4}[1 + \frac{4}{3}pK_3][1 - \frac{1}{3}pK_3]^{-1} , \quad (17)$$

where the pressure dependence increases the value of Poisson's ratio beyond the zero-stress limiting value of  $\sigma_3 = 0.25$ . The corresponding relations for the speed of sound from Eqs. (7), (8), and (17) are

$$C_{i3}^2 = \frac{\rho}{5} (\rho_3 K_3)^{-1} (1 - \frac{8}{9}pK_3) , \quad (18)$$

$$C_{t3}^2 = \frac{3}{5} (\rho_3 K_3)^{-1} (1 - 2pK_3) , \quad (19)$$

where (18) reduces to the zero-stress Cauchy result of Eq. (11) for vanishing pressure. It should be noted that if the Lamé representation in Eqs. (7) and (8) is used to obtain the sound speeds,  $\lambda$  and  $\mu$  must be replaced by the explicitly pressure-dependent  $\lambda'$  and  $\mu'$ , whereas the sound speeds in terms of  $\sigma$ ,  $K$  remain unchanged by the initial stress. The latter preservation of form occurs from Eq. (12) since the compressibility and Poisson's ratio as a function of  $\lambda'$ ,  $\mu'$  have the same functional form as  $K(\lambda, \mu)$  and  $\sigma(\lambda, \mu)$  without initial stress. The Cauchy Debye temperature is given by Eqs. (9) and (10) with  $F_3(\sigma_3) = f_3(pK_3)$ , where from Eq. (17) we have

$$f_3(pK_3) = \frac{3\sqrt{5}}{5} \left(1 - \frac{8}{9}pK_3\right)^{1/2} \times \left[1 + 6\sqrt{3} \left(\frac{1 - \frac{8}{9}pK_3}{1 - 2pK_3}\right)^{3/2}\right]^{-1/3} . \quad (20)$$

For no initial stress, Eq. (20) reduces to Eq. (10) with  $\sigma_3 = 0.25$ .

From Eqs. (17)–(20) the dimensionless product  $pK_3 = -d(\ln V)/d(\ln p)$  determines the corrections to the zero-pressure values of Poisson's ratio, sound speeds, and the Debye temperature. Since  $pK_3$  is the magnitude of the ratio of fractional volume change to accompanying fractional pressure change, it is physically a measure of "squeezability" for the system. The analogous squeeze-

ability parameter appears in the two-dimensional extension of the present model in Sec. III. For the bulk, the dependence of selected elastically determined properties on the pressure-compressibility product is shown in Fig. 1 (upper curves), where the solid sound speeds are relative to a liquid of compressibility  $K$  but no shear modulus, and the Debye temperatures are relative to those values  $\Theta_0$  that would be obtained without initial pressure. We note that the transverse modes disappear when  $\rho K_3 = 0.5$ . This is expected from Eq. (17) because when  $\rho K_3 = 0.5$  Poisson's ratio also has its maximum value of 0.5 corresponding to conservation of volume and fluidlike behavior for the longitudinal extension with free lateral surfaces that defines  $\sigma_3$ .

Debye temperature predictions for bulk hcp  $\text{He}^4$  using the stress-dependent Cauchy model [Eqs. (9) and (20)] are compared with experiment in Fig. 2 for the full range of available data. This range extends from 13 to 21  $\text{cm}^3$  in molar volume and corresponds to a  $0^\circ\text{K}$  pressure range of approximately 700 atm. Pressure and compressibility data are used from two different sources: For  $13 < v_m < 16 \text{ cm}^3$  the data of Dugdale and Franck<sup>24</sup> have been used, and for molar volumes  $17 < v_m < 20.5 \text{ cm}^3$  the data of Edwards and Pandorf<sup>21</sup> are used. The combination of large compressibilities and required initial pressure

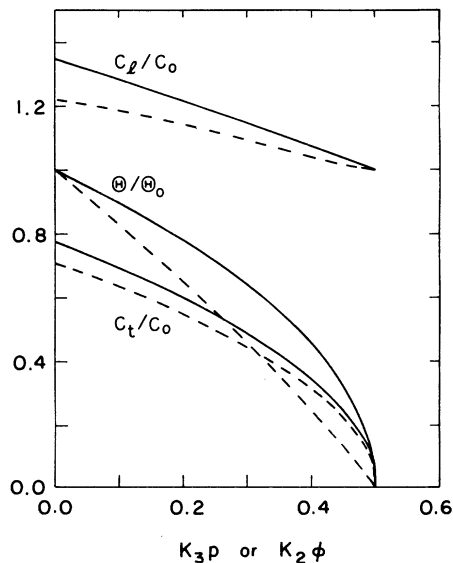


FIG. 1. Dependence of the two- (dashed lines) or three- (solid lines) dimensional Cauchy sound speeds and Debye temperatures on the pressure-compressibility product. The longitudinal and transverse sound speeds  $C_l$  and  $C_t$  are relative to a liquid with  $\rho C_0^2 = K$ , and the Debye temperatures are relative to the value  $\Theta_0$  obtained with no initial pressure.

for helium causes the parameter  $\rho K_3$  to be large and range from approximately 0.1 at 20.5  $\text{cm}^3/\text{mole}$  to approximately 0.2 at 13  $\text{cm}^3/\text{mole}$ . Calculated values of the Debye temperature are shown as solid circles and triangles, and the open circles are experimental Debye temperatures of Ahlers.<sup>25</sup> The theoretical and experimental values agree within the rated precision of the compressibility data, except for molar volumes near 17  $\text{cm}^3$ . This latter deviation reflects the failure of the two sets of compressibility data to extrapolate smoothly in the region at the extreme high and low volumes for the respective measurements. Comparison with Debye temperatures calculated by neglecting initial stress (dashed line) indicates that the explicit pressure dependence softens the Debye temperature relative to the zero-pressure value by as much as 20% at the smallest molar volumes. It is this stress softening that makes the elastic "Cauchy" Debye temperatures nearly coincident with the "thermal" experimental values.

A comparison which separates the single assumption of isotropy and the dual assumptions of isotropy plus Cauchy conditions follows from the relative behavior of the thermal Poisson's ratio [obtained from experimental<sup>15</sup>  $K_3$ ,  $\Theta_3$ , and Eq. (9)] and the Cauchy elastic Poisson's ratio calculated

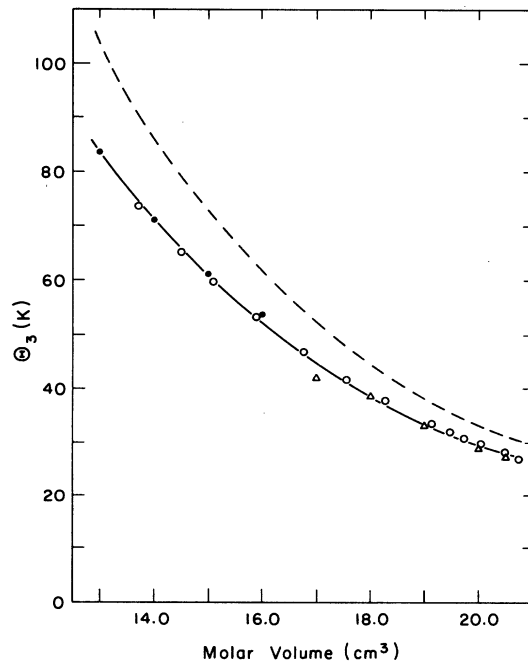


FIG. 2. ●: theoretical bulk helium Cauchy Debye temperatures including initial pressure in Eqs. (9) and (20); △: same but using  $K_3$  of Ref. 21; ○: experimental Debye temperatures of Ref. 25; ---: Cauchy elastic Debye temperatures neglecting initial pressure.

from Eq. (17). This comparison is made in Fig. 3, where it may be seen that with the required inclusion of initial stress the model describes the two characteristic features of the thermal data: the (20–25)% enhancement of Poisson's ratio from the zero-stress Cauchy value of 0.25 and the 10% variation of  $\sigma_3$  with pressure (molar volume). It may be noted that, although initial pressure decreases the Debye temperature for a given compressibility, it increases Poisson's ratio. We conclude that if the bulk is approximated as an isotropic system, then the resultant values for the elastic constants are consistent with the simultaneous assumption of the Cauchy conditions.

Since both longitudinal and transverse sound speeds are contained in the calculated Debye temperatures, the effect of initial pressure on these modes is examined separately in Fig. 4. Although these results are calculated from the elastic model equations (18) and (19), the agreement of the thermal and elastic Poisson's ratio in Fig. 3 indicates that the same speeds would be obtained using the experimental Debye temperature and Eqs. (7)–(9). From Fig. 4, for a given compressibility, the pressure depresses both sound speeds but with a larger relative and absolute effect on the transverse modes. The dominance of these slow modes in determining the Debye temperature indicates that  $\Theta$  is a more sensitive indicator of initial stress than are the longitudinal sound speeds. Indeed, Edwards and Pandorf<sup>21</sup> and Vignos and Fairbank<sup>26</sup> obtained "fair agreement" with experiment for the compressibility using experimental longitudinal speeds in Eq. (11), where the effect of initial stress is neglected. It is interesting to note, however, that when pressure effects are included the compressibilities determined from

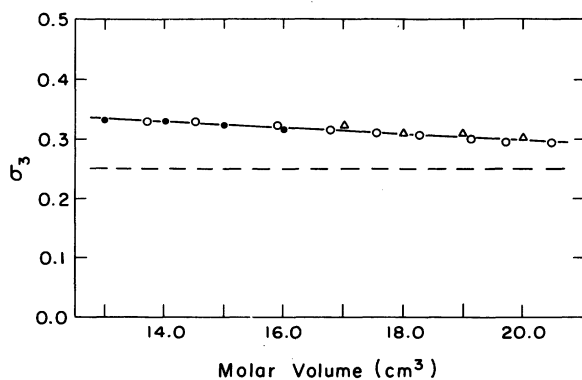


FIG. 3. ●: theoretical Cauchy Poisson's ratio including initial pressure in Eq. (17) with  $K_3$  of Ref. 24; △: same but using  $K_3$  of Ref. 21; ○: thermal Poisson's ratio from Eqs. (9) and (10), the Debye temperatures of Ref. 17, and  $K_3$  of Refs. 21 and 24; ---: Cauchy Poisson's ratio neglecting initial pressure.

Eq. (11) would be decreased by the factor  $(1 - 8pK_3/9)$  from Eq. (18). This correction of (10–12)% in the region of interest would bring into closer relative agreement the values of compressibility determined in Ref. 21 by experiment, from the Debye temperature in combination with the longitudinal speed of sound, and from elastic theory assuming the Cauchy conditions.

### III. TWO DIMENSIONS: APPLICATION TO MONOLAYER He<sup>4</sup>

We return now to the comparison between bulk solid and the solid phase of monolayer helium adsorbed on graphite. Since the Cauchy model describes the bulk  $\Theta_3$  provided initial stress is included, we apply the same assumptions in a two-dimensional extension and examine the dependence of  $\Theta_2$  on film compressibility  $K_2$  and spreading pressure  $\phi$ . As with the bulk, this dependence arises from calculation of sound speeds using the appropriate stress-strain relations. Assuming an idealized planar solid, Eq. (12) may be carried directly into two dimensions with implicit simplifications resulting from summation over one less coordinate:

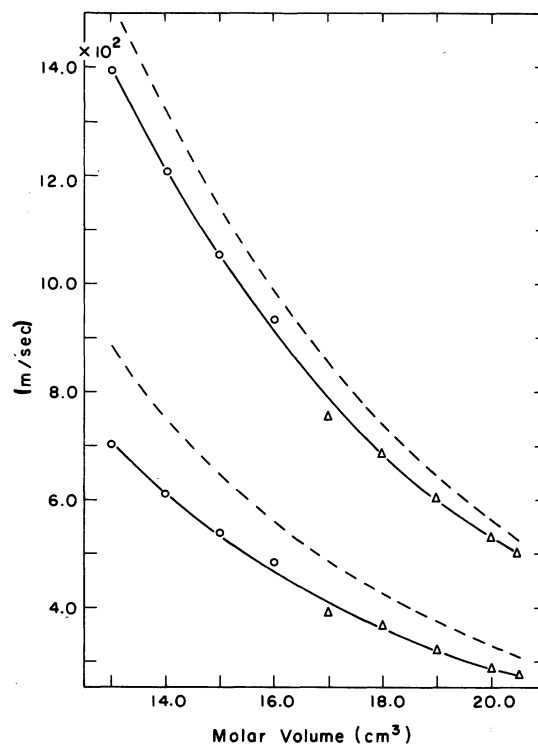


FIG. 4. Theoretical bulk longitudinal (upper pair) and transverse (lower pair) Cauchy sound speeds using  $K_3$  of Ref. 24 (○) and Ref. 21 (△). The upper dashed curves in each pair are the sound speeds neglecting initial pressure.

$$T_{ij} = \lambda'_2 e_{kk} \delta_{ij} + \mu'_2 (e_{ij} + e_{ji}) . \quad (21)$$

$T_{ij}$  is the excess surface stress measured with respect to the initial value  $t_0 = -\phi \delta_{ij}$  and

$$\lambda'_2(\phi) = C_{12}^{(2)}(\phi) + \phi = \lambda_2(\phi) + \phi , \quad (22)$$

$$\mu'_2(\phi) = C_{66}^{(2)}(\phi) - \phi = \mu_2(\phi) - \phi . \quad (23)$$

The same subscripts that would appear for the corresponding quantities in the bulk are used on the elastic constants, but the superscripts indicate that they are two-dimensional quantities with physical dimensions of spreading pressure or surface tension (force per unit length). The sound speeds may be obtained from the equations of motion involving the stress equation (21) by requiring plane-wave propagation:

$$C_{12}^2 = (\lambda'_2 + 2\mu'_2) \rho_2^{-1} , \quad (24)$$

$$C_{42}^2 = \mu'_2 \rho_2^{-1} . \quad (25)$$

Equations (24) and (25) have the same dependence on  $\lambda'_2$  and  $\mu'_2$  as the corresponding bulk expressions as a function of  $\lambda'_3$  and  $\mu'_3$ . However, as indicated below, the speed of sound when expressed in terms of the compressibility and Poisson's ratio has a different form than in the bulk.

For a two-dimensional system subject to an initial hydrostatic compression  $\phi$ , the compressibility may be defined as the ratio of fractional change in area to excess applied spreading pressure relative to the initial state  $\phi$ . For this uniform deformation the excess stress is given by  $T_{11} = T_{22} = -\delta\phi$ ,  $e_{11} = e_{22}$  from Eq. (17) and hence we get

$$\begin{aligned} K_2(\phi) &= -A^{-1} \frac{\partial A}{\partial \phi} = -\frac{2e_{11}}{T_{11}} = [\lambda'_2(\phi) + \mu'_2(\phi)]^{-1} \\ &= [\lambda_2(\phi) + \mu_2(\phi)]^{-1} . \end{aligned} \quad (26)$$

Comparison of Eqs. (26) and (15) indicates that, although there is an explicit dependence of the bulk compressibility on initial pressure, there is no such dependence in two dimensions. In addition, the functional dependence of the compressibility on  $\lambda$ ,  $\mu$  also depends upon dimensionality. Similar distinctions exist for Poisson's ratio when an initial stress is present. Applying an excess longitudinal stress while maintaining free lateral perimeters, Poisson's ratio is the resulting quotient of fractional transverse displacement and fractional longitudinal displacement. From Eq. (21) this strain ratio is

$$\begin{aligned} \sigma_2(\phi) &= \frac{-e_{22}}{e_{11}} = \lambda'_2(\phi) [\lambda'_2(\phi) + 2\mu'_2(\phi)]^{-1} \\ &= [\lambda_2(\phi) + \phi] [\lambda_2(\phi) + 2\mu_2(\phi) - \phi]^{-1} . \end{aligned} \quad (27)$$

The two-dimensional Poisson's ratio of Eq. (27)

may be compared with the corresponding bulk expression of Eq. (16), where it is again apparent that the dependence both on the Lamé constants and initial stress is a function of dimensionality.

With the simplification of the Cauchy conditions,  $\lambda_2 = \mu_2$  and we have

$$K_2(\phi) = [2\lambda_2(\phi)]^{-1} , \quad (28)$$

$$\sigma_2(\phi) = \frac{1}{3} [1 + \phi/\lambda_2(\phi)] [1 - \phi/3\lambda_2(\phi)]^{-1} . \quad (29)$$

The relation between the compressibility and Poisson's ratio, analogous to Eq. (17), is

$$\sigma_2(\phi K_2) = \frac{1}{3} (1 + 2\phi K_2) (1 - \frac{2}{3}\phi K_2)^{-1} . \quad (30)$$

Whereas the Cauchy limiting value of Poisson's ratio with no initial stress in three dimensions is 0.25, from Eq. (16), the loss of one lateral dimension increases this limiting value to 0.33 for a two-dimensional system from Eq. (30). Although the zero-stress value of Poisson's ratio differs in two and three dimensions, the qualitative effect of initial stress is the same: Poisson's ratio increases.

From Eqs. (24)–(27) the two-dimensional sound speeds are given by

$$C_{12}^2 = 2(\rho_2 K_2)^{-1} (1 + \sigma_2)^{-1} , \quad (31)$$

$$C_{42}^2 = (\rho_2 K_2)^{-1} (1 + \sigma_2)^{-1} (1 - \sigma_2) . \quad (32)$$

Combining Eqs. (2), (31), and (32), the Debye temperature is

$$\Theta_2 = \frac{2\pi\hbar}{k_B} \left( \frac{2}{\pi a} \right)^{1/2} (\rho_2 K_2)^{1/2} F_2(\sigma_2) , \quad (33)$$

where

$$F_2(\sigma_2) = \sqrt{2} [(1 - \sigma_2)(1 + \sigma_2)^{-1}(3 - \sigma_2)^{-1}]^{1/2} . \quad (34)$$

Comparison of Eqs. (31)–(34) with the corresponding bulk expressions indicates that both the sound speeds and the Debye temperature have different dependences on  $\sigma$  and  $K$  in two and three dimensions. When the Cauchy conditions are assumed  $F_2(\sigma_2) = f_2(\phi K_2)$ , where

$$f_2(\phi K_2) = \frac{1}{4} \sqrt{6} [(1 - 2\phi K_2)(1 - \frac{2}{3}\phi K_2)(1 - \phi K_2)^{-1}]^{1/2} .$$

The Cauchy sound speeds are given by

$$C_{12}^2 = \frac{3}{2} (\rho_2 K_2)^{-1} (1 - \frac{2}{3}\phi K_2) , \quad (36)$$

$$C_{42}^2 = \frac{1}{2} (\rho_2 K_2)^{-1} (1 - 2\phi K_2) . \quad (37)$$

As with the bulk system, the Cauchy Debye temperatures and sound speeds depend upon the initial stress through the dimensionless pressure-compressibility product. Although the effect is a monotonically decreasing function of this product in both cases, the magnitude is a function of dimensionality. This may be seen in Fig. 1 where Eqs. (33)–

(37) are shown in graphic form for comparison with the corresponding three-dimensional results. For any value of the pressure-compressibility product, the enhancement of the longitudinal sound speed relative to a liquid and arising from the presence of a shear modulus is less in two dimensions than in three. Also, since the transverse modes are more strongly influenced by the initial stress and because they are fully weighted in a two-dimensional calculation of the Debye temperature, the stress softening of  $\Theta$  for a given value of the pressure-compressibility product is greater in two dimensions. However, the transverse modes disappear in both two and three dimensions when the product has the same maximum value of  $\frac{1}{2}$ . We note that the dimensionless character of the product  $K_2\phi$  or  $K_3p$  makes this squeezability parameter a natural variable for comparing the elastic properties in film and bulk. In two dimensions, as in three, the maximum corresponds to fluidlike behavior, but with a (maximum) Poisson's ratio of 1.0 which yields conservation of area when the system is stretched longitudinally with free lateral perimeters. For the more general isotropic case without the Cauchy conditions, the maximum Poisson's ratio and zero transverse sound velocity occur when the effective shear moduli  $\mu'$  of Eqs. (14) and (23) vanish. This may be seen from Eqs. (8) and (16) or Eqs. (27) and (32), which also yield the expected fluidlike behavior for vanishing shear modulus when there is no initial pressure.

The 0 °K spreading pressures of Elgin and Goodstein<sup>2,16,17</sup> may be used to generate compressibilities for comparison of Eqs. (33) and (35) with the Debye temperatures of Bretz, Huff, and Dash.<sup>3</sup> For atomic areas  $8.9 \text{ \AA}^2 < a < 11.5 \text{ \AA}^2$  the spreading pressure is given by

$$\phi = 5.5(10/a)^6 + 0.81 \text{ dyn/cm}, \quad (38)$$

which is estimated to be accurate to 2%. In this range of atomic areas, the squeezability parameter  $K_2\phi$  varies from 0.18 to 0.21, increasing with decreasing density in contrast with the corresponding quantity  $K_3p$  in the bulk. The comparison between the model and the experimental Debye temperatures is shown in Fig. 5, where the estimated uncertainties are largest at the extreme ranges of validity for Eq. (38). As in the bulk, there is a large depression in the Debye temperature relative to the zero-pressure values, suggesting that initial stress may strongly influence  $\Theta_2$ . However, this softening is insufficient to produce comparable agreement between the thermal results and the model predictions where the same general assumptions have been applied in two dimensions. The discrepancy with the experimental observations is about 10% at  $a = 10 \text{ \AA}^2$ , the point of maximum ac-

curacy using Eq. (38), and is larger for other atomic areas. In contrast, over the range of bulk molar volumes corresponding to the film densities where Eq. (38) is valid, the bulk agreement with the three-dimensional model is within 2%.

Because of the dual assumptions, it is not possible to consider separately isotropy and the Cauchy conditions as sources of the discrepancy with experiment. If it were assumed that the film is close packed, then the rotational symmetry would make planar propagation isotropic and the inconsistency must arise from the Cauchy conditions. However, only at much lower coverages where subsidiary evidence<sup>1,3</sup> suggests registry with the hexagonal substrate, is there any information on film structure. With regard to failure of the Cauchy conditions, either the absence of central forces or the failure of the adsorbate atoms to be located at centers of symmetry would be sufficient for invalidation. We note that any active role for the substrate in contributing to the failure of the Cauchy conditions has been omitted in this section, where strict mechanical similarity with the bulk model of Sec. II has been retained.

In Fig. 6 are shown for bulk comparison purposes the thermal sound speeds resulting from the assumption of isotropy using Eqs. (31)–(34), and also the elastic sound speeds calculated from Eqs. (36) and (37) assuming both isotropy and the Cauchy conditions. It is interesting to note that the predicted stress depression of the sound speeds is

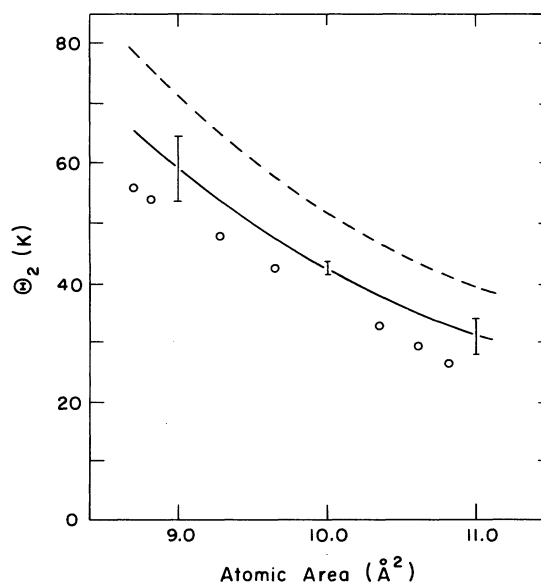


FIG. 5. ---: theoretical film Cauchy Debye temperatures neglecting initial spreading pressure  $\phi$  with  $K_2$  from Eq. (38); —: same but including initial spreading pressure  $\phi$ ;  $\circ$ : film Debye temperatures from Refs. (1) and (3).

larger than that observed for the bulk although, as expected from above, insufficient to produce agreement with the thermal results. There are presently no experimental sound speed measurements for adsorbed helium which could be compared with either of the above estimates. Such information would be useful in drawing further conclusions beyond the previous contrasting observations on the relative properties of film and bulk in the idealized Cauchy model.

#### IV. TWO-DIMENSIONAL SOLID WITH SUBSTRATE

In Sec. III the film was treated as an idealized Cauchy solid without substrate effects. It is possible, however, to estimate the required effect of a substrate for a specific model which retains the solid properties assumed in Sec. III. This is most simply done for the case where the deviations from the idealized model are ascribed to the substrate and where it is required that the intrinsic adsorbent contribution to the elastic constants remains Cauchy. In this extension the film contribution to the elastic properties would be that of a Cauchy solid, but the substrate presence lifts the Cauchy conditions on the total elastic constants. The modification is reminiscent of the electron gas contribution to the bulk modulus in metals,<sup>27</sup> which

also lifts the Cauchy conditions, but in the surface application the substrate is allowed to influence both the shear and bulk moduli. Formally, the substrate is included by dividing the elastic constants of the film into two parts: the intrinsic Cauchy contribution from a two-dimensional lattice and a substrate contribution not subject to the Cauchy conditions. The required magnitude for such a substrate contribution may be determined by requiring agreement between the model and the observed Debye temperatures. It should be noted, however, that this extension, consistent with the approach of Sec. III, is not a general characterization of possible substrate influences. It is a particular modification permitting a magnitude estimate for the required non-Cauchy contribution in a specific case where this contribution is interpretable as a substrate effect.

Allowing the substrate to influence both elastic constants for the film, we include in Eqs. (22) and (23) additional contributions to  $\lambda'_2$  and  $\mu'_2$ :

$$\lambda'_2 = \lambda_l + \lambda_s + \phi = \lambda_l + \phi, \quad (39)$$

$$\mu'_2 = \mu_l + \mu_s - \phi = \mu_l - \phi, \quad (40)$$

where the subscripts  $l$  and  $s$  denote the intrinsic film and substrate contributions to the total elastic constants  $\lambda_l$  and  $\mu_l$ . Requiring that the film lattice contributions to the elastic properties behave as a Cauchy solid,  $\lambda_l = \mu_l$ . The Cauchy conditions for the total elastic constants are now lifted by the substrate and assume the modified form

$$\lambda_l - \mu_l = \lambda_s - \mu_s \equiv \Delta. \quad (41)$$

The discrepancy in the Cauchy conditions,  $\Delta$ , is the difference in the two substrate contributions to the total bulk modulus  $B_2 = K_2^{-1} = \lambda_l + \mu_l$ . The elastic relations for the substrate-dependent sound speeds and Debye temperatures may be obtained as in Sec. III. Formally, Eqs. (30)–(37) still apply if  $\phi$  is replaced by  $\phi' = \phi + \frac{1}{2}\Delta$ . Hence the substrate-induced change in Debye temperature relative to that obtained without substrate is

$$\frac{\Theta_0 - \Theta_s}{\Theta_0} = 1 - \frac{f_2 [K_2 (\phi + \frac{1}{2}\Delta)]}{f_2 (K_2 \phi)}, \quad (42)$$

where  $f_2$  is given by Eq. (35). For any experimental  $K_2 \phi$ , a value of  $K_2 \Delta$  may be determined by requiring  $\Theta_s$  to coincide with experiment.  $K_2 \Delta$  is the difference in fractional substrate contributions to the total bulk modulus of the film:

$$K_2 \Delta = \frac{\lambda_s - \mu_s}{B_2} = \frac{B_{s\lambda}}{B_2} - \frac{B_{s\mu}}{B_2}. \quad (43)$$

It may be noted that since the sum  $\lambda_s + \mu_s$  contributes to the total bulk modulus, whereas the difference in these quantities is determined from

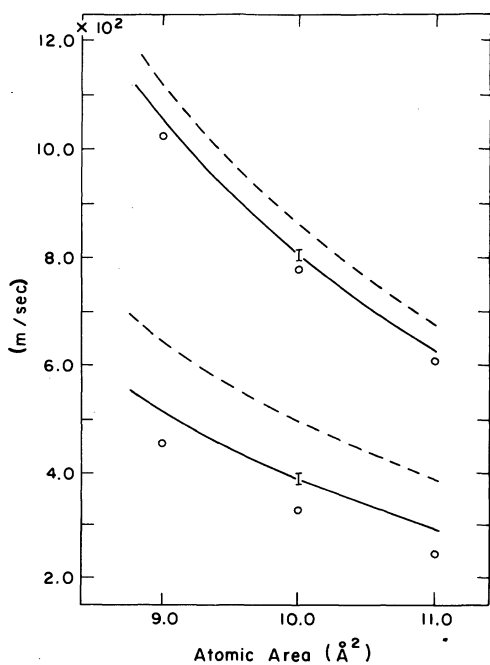


FIG. 6. Longitudinal (upper pair) and transverse (lower pair) two-dimensional sound speeds. ---: neglecting initial pressure with  $K_2$  from Eq. (38); —: including initial spreading pressure; O: thermal speeds from Eqs. (31) and (32) with  $\sigma_2$  from Eqs. (33) and (34).



Eqs. (42) and (43), the substrate need not contribute to both the shear and bulk moduli. For example, for positive  $K_2\Delta$ , if  $\lambda_s = |\mu_s|$ , then there will be no contribution to the total bulk modulus. Similarly, if  $\mu_s = 0$ , then only the bulk modulus or compressibility is influenced by the substrate. In addition, for a substrate effect to exist, the stability conditions on the film must be satisfied. This requires that Poisson's ratio be less than unity or, equivalently, that the effective shear modulus in the presence of initial stress  $\mu_t - \phi$  be positive. From Eq. (30), stability requires

$$2K_2(\phi + \frac{1}{2}\Delta) < 1. \quad (44)$$

Figure 7 shows the solution of Eq. (42) for  $K_2\Delta = 0.19$ , corresponding to atomic areas of  $10 \text{ \AA}^2$ . There are two branches, one dominated by the substrate (upper) and one dominated by the film lattice (lower). The existence of the upper branch for  $\Theta_s = \Theta_0$  suggests that there is a solution for the Debye temperature  $\Theta_s$  that is coincident with  $\Theta_0$ . This would mean an allowed Debye temperature which is dominated by the substrate contribution to the elastic constants even when the experimental Debye temperature agreed with that calculated by the substrate-free model of Sec. III. However, the upper branch does not satisfy the stability condition of Eq. (44) and will not support transverse modes. Eliminating the upper branch on physical grounds, only the lower branch remains for determining the Debye temperature. The possibility of purely longitudinal waves is ruled out since Poisson's ratio is less than unity<sup>15</sup> for the known experimental compressibilities and Debye temperatures; i.e., there is a shear modulus.

The remaining lower branch of Fig. 7 is appropriate for estimating the substrate contribution  $K_2$  for atomic areas of  $10 \text{ \AA}^2$ . From Fig. 5 the fractional change  $(\Theta_0 - \Theta_s)/\Theta_0$  required to produce agreement with experiment is 0.12 and yields  $K_2\Delta = 0.14$  for the substrate influence from Fig. 7. Since  $K_2\Delta$  is the difference in fractional substrate contributions to the total bulk modulus, it is not possible to determine uniquely the two substrate contributions. However, estimates may be made for the cases where (a) the substrate contributes only to the total compressibility or bulk modulus through the shear modulus ( $\lambda_s = 0$ ), (b) the substrate contributes only to the total compressibility or bulk modulus without contributing to the shear modulus ( $\mu_s = 0$ ), and (c) the substrate influences the total shear modulus but not the compressibility or bulk modulus ( $\lambda_s = |\mu_s|$ ). Case (a) corresponds to a negative contribution to the shear modulus of  $\mu_s = -0.14B_2$  and a ratio of substrate to intrinsic film contributions of  $-\mu_s/\mu_1 = 0.24$ . Although the substrate contribution to the shear modulus is neg-

ative, the stability condition Eq. (44) is satisfied since the effective total shear modulus  $\mu_t - \phi$  remains positive along the lower branch. For case (b) the substrate contribution to  $\lambda_t$  is  $\lambda_s = 0.14B_2$  with a substrate to lattice ratio of  $\lambda_s/\lambda_1 = 0.32$ . Although neither elastic constant is dominated by the substrate in these extreme limits, the required fractional contribution to either constant alone to produce agreement in the experimental and calculated Debye temperatures is substantial. In both the above cases the percentage substrate contribution to the bulk modulus is 14%, the contribution being negative when the substrate affects only the shear modulus in (a). For (c) the substrate contribution to  $\lambda_t$  and  $\lambda_t$  is  $\pm 0.07B_2$ , respectively, with fractional contributions  $\lambda_s/\lambda_1$  and  $\mu_s/\mu_1$  of  $\pm 0.14$ , respectively.

We conclude this section by noting that the inclusion of the substrate emphasizes the distinction between a system exhibiting two-dimensional thermal behavior (as manifested by  $T^2$  heat capacities) and a system possessing a negligible substrate effect. Low-temperature  $T^2$  heat capacities are indicative of an excitation spectrum starting at zero frequency and wave number. However, the tendency of substrate potentials to localize adsorbate atoms normal to the surface via binding forces and laterally due to the absence of a perfectly smooth substrate does not eliminate this possibility. Novaco<sup>28</sup> has shown how binding forces normal to the surface may lead to a branch in the planar vibrational spectrum which starts at a finite frequency for surface normal vibrations. A film lat-

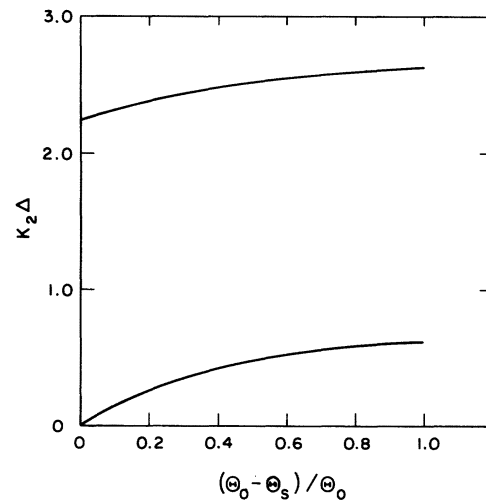


FIG. 7. Required difference in fractional substrate contributions to the total bulk modulus that yields a specified fractional decrease in the ideal (no substrate) Cauchy Debye temperature  $\Theta_0$ . Only the lower curve corresponds to stable film behavior.

tice also supporting modes polarized in the plane of the film, however, may experience decreased average restoring forces<sup>29</sup> from the substrate. Ying<sup>7</sup> has shown that this is generally the case and that when a film is incommensurate with the substrate the lateral averaging may be complete at zero wave number to yield a substrate-dependent vibrational spectrum starting at zero frequency. In the presence of both lateral averaging for the planar polarizations and a finite excitation energy  $\hbar\omega_0$  for long-wavelength normal polarizations, the low-temperature heat capacities ( $kT \ll \hbar\omega_0$ ) would be dominated by the low-lying modes which are polarized in the plane of the surface. The present extension of Sec. III yields an estimate of a possible substrate contribution to the elastic constants which provides the restoring forces for those planar polarizations. Although the modification is specific in form, it does suggest that a substrate-induced contribution to the total elastic properties could further depress the Debye temperatures beyond the already substantial decrease arising from initial stress.

#### V. CONCLUSIONS

The results of a Cauchy isotropic approximation for the solid phase of bulk and monolayer He<sup>4</sup> may be summarized as follows.

(i) Comparison of the elastic and thermal properties for solid helium using a two- or three-dimensional isotropic Cauchy approximation necessitates the inclusion of initial stress effects. Since corrections to the zero-pressure elastic treatment are a monotonically increasing function of the pressure-compressibility product in both dimensions, the large compressibilities of helium make these modifications significant for all pressures in the solid phase.

(ii) The experimental thermal Debye temperatures of hcp He<sup>4</sup> for molar volumes from 13 to 21 cm<sup>3</sup> are in essential agreement with the elastic

isotropic Cauchy Debye temperatures when finite initial stress is included. The agreement results over the full range of Debye temperature despite known anisotropies.

(iii) For bulk helium initial pressure produces a substantial decrease in the isotropic Cauchy sound speeds and Debye temperatures relative to those values when the pressure is neglected. This decrease is most pronounced for the transverse sound speeds and makes these modes or the Debye temperature a more significant indicator of stress effects than the longitudinal sound speed.

(iv) The previous softening effects also occur for submonolayer He<sup>4</sup> adsorbed on expanded graphite when treated by the corresponding two-dimensional elastic model, but agreement with the thermal experiments is not comparable with the bulk comparison. Mechanical consistency alone in a two- and three-dimensional isotropic Cauchy elastic model does not appear to yield the observed experimental similarity in the thermal Debye temperatures for film and bulk.

(v) The extension of the idealized two-dimensional model to include a substrate where only the intrinsic film lattice contribution to the elastic constants remains that of a Cauchy solid will yield the observed Debye temperatures. A 14% substrate contribution to the bulk modulus or either of the Lamé elastic constants at atomic areas of 10 Å<sup>2</sup>, for example, will yield the experimental Debye temperatures.

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