Pressure-induced softening as a common feature of framework structures that have negative thermal expansion

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I. INTRODUCTION

Almost all materials become stiffer when compressed, as a result of the constituent atoms being squeezed together. It therefore comes as something of a shock that some materials – among them amorphous silica, ZrW₂O₇ and Zn(CN)₂ – actually become softer under compression. Formally, the stiffness is defined through the zero-pressure bulk modulus \( B_0 = V_0 \left( \frac{\partial V}{\partial P} \right)_{T, 0} \), and the change in stiffness is defined through the differential \( B'_0 = \beta B_0 / \partial P \), which is a positive quantity for almost all materials. However, in these cited examples it is found that \( B'_0 \) has a negative value. There is as yet no theoretical explanation for this effect, which can be called “pressure-induced softening”, but in a simulation study of pressure-induced softening in amorphous silica, we drew attention to the role of fluctuations involving whole-body rotations of SiO₄ tetrahedra. Given that the same fluctuations are implicated in the similarly counter-intuitive phenomenon of negative thermal expansion (NTE), and given that the few materials in which pressure-induced softening has been identified also show NTE, we suggest that most NTE materials will show pressure-induced softening, and in this paper we demonstrate the plausibility of this hypothesis.

The basis for linking pressure-induced softening with negative thermal expansion can be understood by considering the relatively simple example of Zn(CN)₂. Its perfect structure has linear Zn–C–N–Zn linkages of bonds along the crystallographic (1, 1, 1) directions. Uniform compression of the perfect structure will force compression of these bonds, which are stiff and will become stiffer on further compression. Hence at a temperature of 0 K, or in a static lattice energy calculation, we might expect to find a positive value of \( B'_0 \). However, on heating thermal fluctuations will cause instantaneous buckling of the Zn–C–N–Zn linkages – a process aided by the fact that the rigid-unit-mode flexibility of the structure allows for localised distortions, so that an external compressive force can be accommodated with relatively low energy cost by further buckling without the need to compress the individual bonds. If we now consider the case of stretching the structure (application of negative pressure), the stretch will first be accommodated by reducing the buckling of the linkages of bonds, but when the buckling has been stretched out the second process is to stretch the individual bonds. This will cost a lot more energy, and the volume change per unit of stretch force will reduce. This means that the bulk modulus will increase on stretching, and hence we have a negative value of \( B'_0 \).

Because the fluctuations that buckle the linkages give rise to a reduction in crystal volume in many framework, and because their amplitude increases with temperature, we have the possibility – perhaps in some cases inevitability – for negative thermal expansion. Thus we might expect pressure-induced softening to be linked to NTE. Put another way, we might expect that many NTE materials will also show pressure-induced softening. In the case of Zn(CN)₂, experimentally it is found to have large NTE, and a negative value of \( B'_0 \), i.e. pressure-induced softening. Our recent simulation study of Zn(CN)₂ is consistent with the experimental data and shows that \( B'_0 \) has a dependence on temperature of the form described above.

In this paper we test the proposal of a direct link between NTE and pressure-induced softening by performing simulation experiments on the full suite of zeolites with cubic lattice symmetry. Zeolites are low-density framework structures built from corner-linked SiO₄ tetrahedra, many of which are found naturally with ionic substitution on the tetrahedral site (e.g. Al for Si) with associated charge-balancing cations (e.g. Na) found in the large pores in the structure. It has long been recognised that some zeolites show NTE, although there has not yet been a systematic study of the set of the cubic zeolites. Here we make two predictions, first that most cubic zeolites will show NTE, and second, based on the preceding discussion, that those that do have NTE will also show pressure-induced softening. This is much easier tested by molecular dynamics simulation than experiment, and for siliceous zeolites we have some good force fields derived from quantum mechanical calculations and...
tested in many independent studies. There are 13 candidate zeolites with crystal structures of cubic symmetry and fully connected SiO$_4$ tetrahedra, all of which are investigated in the current work. For reference for the rest of this paper, we note that all zeolites are assigned a three-letter name, sometimes which relates to a historical name (e.g. ANA for analcime, FAU for faujisite).

The thermodynamic theory to link NTE with pressure-induced softening is derived in Section II. Section III gives the computational method and Section IV presents the main results. Conclusions are drawn in Section V.

II. THERMODYNAMIC BACKGROUND

The Helmholtz free energy of an insulating crystal in the classical high-temperature approximation is written as

$$F = \Phi + \sum_s \ln \left( \frac{\hbar \omega_s}{\tau}\right),$$

(1)

where the first term on the right-hand side is the lattice energy of the crystal at zero temperature. The second term involves the sum over all wave vectors $k$ on all branches of the phonon dispersion curves $j$, with $\omega_s$ as the frequency of each phonon mode denoted by $s = \{j,k\}$. $\tau = k_B T$ is the temperature in the unit of energy.

At equilibrium, the pressure $p$ is obtained as the derivative of the free energy with respect to the crystal volume $V$:

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial \Phi}{\partial V} + \frac{3N \tau}{V} \gamma,$$

(2)

The overall Grüneisen parameter $\gamma$ is defined as the sum over all the mode Grüneisen parameters $\gamma_s = - (V/\omega_s) (\partial \omega_s/\partial V)$:

$$\gamma = \sum_s \gamma_s / (3N)$$

(3)

with $N$ as the total number of atoms in the system. The bulk modulus of the material can be calculated using

$$B = -V \frac{\partial p}{\partial V} = V \frac{\partial^2 \Phi}{\partial V^2} + \frac{3N \tau}{V} \gamma + \frac{3NB \tau}{V} \frac{\partial \gamma}{\partial p},$$

(4)

where we have used

$$\frac{\partial \gamma}{\partial V} = \frac{\partial \gamma}{\partial p} \frac{\partial p}{\partial V} = -B \frac{\partial \gamma}{\partial p}.$$

(5)

Thus,

$$B = \frac{V \partial^2 \Phi/\partial V^2 + (3N \tau/V) \gamma}{1 - (3N \tau/V) (\partial \gamma/\partial p)}.$$

(6)

From Equation 9, we can obtain the first derivative of the bulk modulus with respect to pressure as

$$B' = \frac{\partial B}{\partial p} = \frac{\partial B}{\partial V} \frac{\partial V}{\partial p} \approx -\frac{V}{B} \left( \frac{\partial^2 \Phi}{\partial V^2} + \frac{V \partial^3 \Phi}{\partial V^3} \right) + \frac{3N \tau}{V} \frac{\partial \gamma}{B} + \frac{6N \tau}{V} \frac{\partial \gamma}{\partial p} + \frac{3N \tau B}{V} \frac{\partial^2 \gamma}{\partial p^2},$$

(7)

In Equation 7, we have used the approximation

$$\left| \frac{3N \tau \partial \gamma}{V \partial p} \right| \ll 1$$

(8)

which is generally valid for the zeolites we have studied here, as will be seen in Table 1 in Section V. According to this, from Equation 6 one has

$$B \approx V \frac{\partial^2 \Phi}{\partial V^2} + \frac{3N \tau}{V} \gamma.$$

(9)

Accordingly, we can rewrite Equation 7 in the more compact form

$$B' = B' \big|_{T=0} + \frac{3N \tau}{V} \left[ \frac{\gamma}{B} + 2 \frac{\partial \gamma}{\partial p} + B \frac{\partial^2 \gamma}{\partial p^2} \right],$$

(10)

where the first term on the right-hand side, namely

$$B' \big|_{T=0} = -\frac{V}{B} \left( \frac{\partial^2 \Phi}{\partial V^2} + \frac{V \partial^3 \Phi}{\partial V^3} \right)$$

(11)

is the value of $B'$ at zero temperature obtained in a harmonic-lattice-dynamics calculation. In our case, we will calculate this term for all the cubic NTE zeolites in harmonic lattice dynamics using a force field with the Buckingham potential.

Thus, according to Equation 10, if $B' \big|_{T=0}$ is positive, given that all the rest terms are negative, $B'$ may become negative when the temperature is high enough. In fact, since NTE materials have negative coefficient of thermal expansion, one should have

$$\tau < 0$$

(12)

Accordingly, we can rewrite Equation 7 in the more compact form

$$B' = B' \big|_{T=0} + \frac{3N \tau}{V} \left[ \frac{\gamma}{B} + 2 \frac{\partial \gamma}{\partial p} + B \frac{\partial^2 \gamma}{\partial p^2} \right],$$

(10)
and we will see in Section V, that for all the cubic NTE zeolites,

\[
\frac{\partial \gamma}{\partial p} < 0
\]

\[
\frac{\partial^2 \gamma}{\partial p^2} < 0.
\]

(13)

Note that, if \( \gamma, \frac{\partial \gamma}{\partial p} \) and \( \frac{\partial^2 \gamma}{\partial p^2} \) are in the same order of magnitude, the term containing \( \frac{\partial^2 \gamma}{\partial p^2} \) will contribute dominantly to a negative \( B' \) due to its large coefficient involving the bulk modulus \( B \).

III. COMPUTATIONAL METHODS

The molecular dynamics (MD) simulations were carried out using DL_POLY\textsuperscript{14}. The O–O, Si–O and Si–Si interactions are described by Coulomb interactions and Buckingham potentials \( \phi(r) \) of the form

\[
\phi_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij} r_{ij}^{-6},
\]

(14)

where \( r_{ij} \) is the distance between two atoms of type \( i \) and \( j \), and the parameters \( A_{ij}, \rho_{ij} \) and \( C_{ij} \) for each atom pair type are taken from the force field of Tsuneyuki\textsuperscript{15}. The point charges on the Si and O atoms are (in the units of electron charge) 2.4 and −1.2 respectively. The long-range Coulomb energy was calculated using the Ewald method with precision of \( 10^{-4} \).

Typical simulations, lasting around 30 ps in the production stage with a 10 ps equilibration stage, were performed using time steps of 0.001 ps and the velocity Verlet scheme\textsuperscript{16}. Long-time stability of the structures at high temperature were tested up to 200 ps. Simulations were performed using the Nosé–Hoover constant-pressure constant-temperature ensemble\textsuperscript{17} with relaxation times of 1.0 ps for both thermostat and barostat. The first suite of simulations were performed at constant pressure to search for NTE, followed by a large number of simulations over a range of pressure at a fixed temperature for a large number of different temperature values. Typical sample sizes were \( 6 \times 6 \times 6 \) unit cells.

The calculations of the density of states and the Grüneisen parameters for the studied zeolites were carried out in harmonic lattice dynamics using GULP\textsuperscript{18}. The same potential model as in the MD was used in these calculations.

IV. RESULTS

A. Search for negative thermal expansion in cubic zeolites

Figure\textsuperscript{11} shows the simulated volume–temperature relationships at ambient pressure for all cubic zeolites. Only ANA has positive thermal expansion throughout the temperature range. BSV shows almost zero thermal expansion. The other 11 zeolites have NTE. Three of these undergo phase transitions, and it is their high-temperature phases that show NTE. Figure\textsuperscript{2} shows the simulated volume–pressure relationships at a temperature of 300 K. Inevitably most examples show a pressure-induced phase transition. RWY, SOD and PAU undergo phase transitions at very low pressure (< 0.2 GPa). Thus, from the original pool of 13 zeolites we have 8 useful candidate materials where the transition pressure is not too low and in which we can explore the link between pressure-induced softening and NTE. The key results from these preliminary temperature and pressure scans...
are summarised in Table I. We found that almost all the modes with negative Grüneisen parameters are rigid unit modes (RUMs) in these cubic zeolites. Calculations using the CRUSH code reveal that these RUMs correspond to the rotations and the translations of the SiO$_4$ tetrahedra, with the translational modes occupying the lowest energy band. The big difference between the positive-thermal-expansion ANA and other NTE cubic zeolites is that the low-frequency translational RUMs contribute the most to the NTE of the material, which is similar to the finding in our work on Zn(CN)$_2$. Detailed discussions of the origins of NTE of these cubic zeolites will be given elsewhere.

### B. Pressure-induced softening in NTE-zeolites

From sequences of pressure-sweep simulations over a range of fixed temperatures we have obtained values of $V_0$, $B_0$ and $B'_0$ by fitting isothermal data using the equation of states (EoS). We have explored several EoS formalisms, including 3rd and 4th-order Birch-Murnaghan (BM) EoS, Vinet (Universal) EoS, and Keane EoS. It was found that the 3rd and 4th-order BM EoS have the greater stability. The Vinet and Keane EoSs gave similar results to those of the BM EoS. The 3rd-order BM gave excellent results for most of the studied zeolites, but significant improvements were obtained using the 4th-order BM for AST and MTN. The fitted values of $B_0$ and $B'_0$ at 300 K are given in Table I.

As an example, Figure 3 shows the fitting to isotherms of FAU at different temperatures from 1 to 600 K with a 10 K interval from 10 to 100 K and an 100 K increment from 100 to 600 K, using the 3rd-order BM EoS. The convex-parabola trend seen in the isotherms shows that the volume contracts more rapidly at higher pressure, and this gives the negative value of $B'_0$ at ambient pressure, and its high temperature phase shows NTE. The fitted value of $B'_0$ at 300 K is $-12.6$ MK$^{-1}$.

![Graph showing fitted isotherms of FAU at different pressures and temperatures.](image)

**FIG. 3:** Fitted isotherms of FAU at different temperatures from 1 to 600 K with a 10 K interval from 10 to 100 K and an 100 K increment from 100 to 600 K, using the 3rd-order BM EoS. The convex-parabola trend seen in the isotherms shows that the volume contracts more rapidly at higher pressure, and this gives the negative value of $B'_0$. The fitted value of $B'_0$ at 300 K is $-12.6$ MK$^{-1}$.

**TABLE I:** Calculated coefficients of thermal expansion $\alpha_V$, phase-transition temperature $T'_c$, at ambient pressure, and phase-transition pressure $P'_c$ at 300 K. Because $\alpha_V$ varies with temperature, the averaged values over the temperature range are given. For AST and MTN which only have NTE in their high temperature phases, the values are averaged over 300-1025 K. The bulk modulus at 0 pressure $B_0$ and its first derivative with respect to pressure $B'_0$ of each NTE zeolite is obtained from fitting the 300 K isotherm with the 3rd-order BM EoS. These values are not given for RWY, SOD and PAU because they quickly go through phase transitions on compression.

| Zeolite | $\alpha_V$ (MK$^{-1}$) | $T'_c$ (K) | $P'_c$ (GPa) | $B_0$ | $B'_0$ |
|--------|------------------------|------------|--------------|-------|--------|
| AST    | -13.8                  | 250        | 0.5          | 16(2) | -28(9) |
| FAU    | -8.0$^a$               |            | 2.2          | 51.1(2)$^b$ | -2.6(3) |
| KFI    | -10.0                  | -          | 1.6          | 65.7(5) | -4.4(9) |
| RHO    | -8.3$^b$               | -          | 0.5          | 59(1)  | -4(4)  |
| LTA    | -11.3                  | -          | 1.5          | 61.8(6)$^c$ | -13.0(9) |
| MTN    | -19.3$^c$              | 200        | 1.5          | 27(1)  | -3(2)$^d$ |
| MEP    | -20.8                  | -          | 0.6          | 58(2)  | -30(7) |
| TSC    | -8.2                   | -          | 1.75         | 52.4(2) | -4.9(2) |
| RWY    | -35.2                  | -          | <0.1         | -      | -      |
| SOD    | 13.4                   | 600        | <0.1         | -      | -      |
| PAU    | -11.2                  | -          | <0.2         | -      | -      |
| BSV    | -0.9                   | -          | -            | 56.2(4) | -0.03(37) |
| ANA    | 19.7                   | 800        | 1.2          | 10.3(3) | 0.3(3) |

$^a$Experimental value averaged over 25-573 K is $-12.6$ MK$^{-1}$.

$^b$Averaged value over 0-500 K calculated from lattice dynamics in quasi-harmonic approximation is $-13$ MK$^{-1}$.

$^c$Experiment shows that MTN goes through a phase transition at about 370 K and only its high temperature phase shows NTE. The fitted value averaged over 463-1002 K is $-5.0(0.7)$ MK$^{-1}$.

$^d$Experimental value is 38(2) GPa.

$^e$DFT calculated value is 46 GPa.

$^f$The fitted values of $B'_0$ of AST and MTN using the 4th-order BM EoS are $-108(7)$ and $-37(4)$, respectively.
B\textsubscript{0} expansion shows positive 
almost zero 

Having low frequencies, and these modes contribute the 
most to NTE through their large negative Grüneisen parameter\textsuperscript{3}. Taking the example of FAU, we have obtained the set of mode Grüneisen parameters from the phonon frequencies calculated using expanded and contracted (±0.1\%) unit-cell volumes, and have colored the vibrational density of states according to the value of Grüneisen parameter, as shown in figure \textsuperscript{5} plots of the other NTE zeolites are available in \textsuperscript{27}). It is clear that modes with the most negative Grüneisen parameters — highlighted by red to light violet — are around 1 THz (48 K) and span to the lowest frequency. This suggests that even at low temperature ∼ 50 K, these modes will not be ‘frozen’ out and can still be excited and contribute to NTE and pressure-induced softening of the material. In such a case, the classical MD results at low temperature would not have too much difference from the real quantum picture.

As shown in Table \textsuperscript{1} all the cubic zeolites that have NTE and are stable under compression show pressure-induced softening (negative $B'$). It is interesting to note that BSV having almost zero thermal expansion shows almost zero $B'$, and ANA with positive coefficient of thermal expansion shows positive $B'$.

To show the consistency between the theory in Section II and the MD results, we calculate $B'$ using Equation \textsuperscript{10} and give the values of various terms in Table \textsuperscript{11}. The values of $\gamma$ were obtained from the phonon frequencies calculated using expanded and contracted ±0.05\% unit-cell volumes at zero pressure. The term $\partial^{2}\tau/\partial p$ was calculated as $\partial^{2}\tau/\partial p \approx (\tau_{p} - \tau_{p=0})/p$ for a small $p$ around zero pressure. Combined with the values of $\tau/V\text{at} = N\tau/V$, one can see the validity of Equation \textsuperscript{8}. The volume variation for the calculation of $\gamma$ at each pressure is much smaller relative to the volume reduction at that pressure. $\partial^{2}\tau/\partial p^{2}$ is calculated as

\[ \partial^{2}\tau/\partial p^{2} \approx (\tau_{p=2} - 2\tau_{p=1} + \tau_{p=0})/p^{2} \]

for small pressures $p_{2} > p_{1} > 0$. As we mentioned in Section II, since this term has a coefficient of $B$, it will contribute the most to the negative $B'$ in Equation \textsuperscript{10}.

The values in the last two columns of Table \textsuperscript{11} show a reasonable degree of consistency. The main differences between the two is mainly due to the anharmonic processes that are missing in the calculations of $\gamma$, $\partial\gamma/\partial p$ and $\partial^{2}\gamma/\partial p^{2}$ using harmonic lattice dynamics.

C. Correlation between the pressure-induced softening and NTE

Negative values of $\tau$, $\partial\gamma/\partial p$ and $\partial^{2}\gamma/\partial p^{2}$ can be satisfied by assuming a pressure-induced strain ($e$) dependence for the frequency of the NTE modes, namely

\[ \omega^{2} = \omega_{0}^{2} + Ce > 0, \]  

where $\omega_{0}$ and $C$ are positive constants. Clearly, the frequency of the mode will decrease with more negative strain $e$, i.e. the mode will be softened on compression hence having negative Grüneisen parameter

\[ \gamma = -\frac{1}{2\omega^{2}} \frac{\partial^{2}\omega^{2}}{\partial e} = -\frac{C}{\omega_{0}^{2} + Ce} < 0 \]  

From Equation \textsuperscript{16} we have

\[ \frac{\partial\gamma}{\partial p} = \frac{\partial e}{\partial p} \frac{\partial\gamma}{\partial e} = -\frac{C^{2}}{B(\omega_{0}^{2} + Ce)^{2}} < 0 \]  

\[ \frac{\partial^{2}\gamma}{\partial p^{2}} = \frac{\partial e}{\partial p} \frac{\partial^{2}\gamma}{\partial e^{2}} = -\frac{C^{2}}{B(\omega_{0}^{2} + Ce)^{2}} < 0 \]
TABLE II: Calculated various terms in Equation 10 for all the cubic NTE zeolites, except for AST and MTN which only show NTE in their high-temperature phases. The second column of the table lists the values of $\tau/V_0 = N\tau/V$ at 300 K, with $\tau/V_0$ the average volume per atom in the system. The third column lists the values of the overall Grüneisen parameters, $\bar{\gamma}$. The sixth column lists the values of $B'$ at zero temperature obtained from harmonic lattice dynamics. The seventh column lists the calculated $B'$ using Equation 10. The last column gives the values of $B'$ from molecular dynamics at 300 K.

| Zeolite | $\tau/V_0$ (GPa) | $\bar{\gamma}$ | $\partial\bar{\gamma}/\partial p$ (GPa$^{-1}$) | $\partial^2\bar{\gamma}/\partial p^2$ (GPa$^{-2}$) | $B'$ | $aB'$ | $bB'$ |
|---------|------------------|----------------|---------------------------------------------|---------------------------------------------|------|--------|--------|
| FAU    | 0.16             | -0.40          | -0.27                                       | -0.20                                      | 2.4  | -2.7   | -2.6   |
| KFI    | 0.18             | -0.62          | -0.35                                       | -0.18                                      | 2.6  | -4.1   | -4.4   |
| RHO    | 0.18             | -0.44          | -0.23                                       | -0.16                                      | -0.1 | -5.4   | -4.0   |
| LTA    | 0.18             | -0.85          | -0.60                                       | -0.90                                      | 3.0  | -27.1  | -13.0  |
| MEP    | 0.21             | -1.65          | -1.85                                       | -5.22                                      | -3.1 | -192.1 | -30.0  |
| TSC    | 0.16             | -0.41          | -0.24                                       | -0.10                                      | 0.5  | -2.2   | -4.9   |

$^a$Calculated using Equation 10

$^b$MD results at 300 K.

FIG. 6: Temperature dependence of the cell parameter of FAU at different pressures from MD simulations. The results agree well with the experimental data. The inset shows that the coefficient of thermal expansion ($\alpha$ at 300 K) of the material decreases on compression, i.e. the pressure-enhanced NTE.

and

$$\frac{\partial^2\gamma}{\partial p^2} \approx \left( \frac{\partial e}{\partial p} \right)^2 \frac{\partial^2\gamma}{\partial e^2} = -\frac{2C^3}{B^2(\omega_0^2 + Ce)^3} < 0 \quad (18)$$

Thus, a material with whose mode frequency is reasonably represent by Equation 15 will show NTE with negative $\partial\gamma/\partial p$ as well as negative $\partial^2\gamma/\partial p^2$, and therefore is likely to have negative $B'$ on heating according to Equation 10.

One way in which pressure, elasticity and thermal fluctuations are linked is in the pressure-dependence of the coefficient of thermal expansion, $\alpha$, as shown by

$$- \frac{1}{\alpha} \frac{\partial \alpha}{\partial p} = - \frac{1}{\bar{\gamma}} \frac{\partial \bar{\gamma}}{\partial p} + \frac{1}{B} (1 - B') \quad (19)$$

For all the NTE zeolites (whose $\alpha < 0$) listed in Table II, both terms on the right-hand side of the equation would be positive, resulting in negative $\partial\alpha/\partial p$, i.e. the coefficient of thermal expansion becomes more negative under pressure. This pressure-enhancement of NTE has been confirmed by our MD results. For example, Figure 6 shows both the simulation and the experimental data for FAU. Plots of this kind for the other zeolites are given in the supplemental material.

V. CONCLUSIONS

The main conclusion from this study is that all the cubic zeolites that show NTE and are stable under pressure have negative $B'$. This is a result from simulations and will need experimental verification, but the results are so overwhelmingly positive from simulation that we are confident they reflect the underlying physical processes. This lends strong support to our proposal that many NTE materials are likely to have pressure-induced softening.

The origin of the pressure-induced softening is rooted in the dependence of the frequencies of the NTE phonon modes on strain. With a simple form of frequency having positive dependence on pressure-induced strain, the phonon modes would not only have negative Grüneisen parameters but also have negative first and second derivatives of the Grüneisen parameter with respect to pressure, resulting in NTE as well as pressure-induced softening of the material.

With an increasing number of NTE materials being discovered, we suggest that there should be an increased focus on experimental searches for pressure-induced softening in these materials.
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