# Specific heats of dilute neon inside a long single-walled carbon nanotube

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**Abstract**
An elegant formula for coordinates of carbon atoms in a unit cell of a single-walled nanotube (SWNT) is presented and the potential of neon (Ne) inside an infinitely long SWNT is analytically derived under the condition of the Lennard-Jones potential between Ne and carbon atoms. Specific heats of dilute Ne inside a long (20, 20) SWNT are calculated at different temperatures. It is found that Ne exhibits three-dimensional (3D) gas behaviour at high temperature but behaves as a 2D gas at low temperature. Especially, at ultra-low temperature, Ne inside (20, 20) nanotubes behaves as a lattice gas. A rough method to determine the characteristic temperature $\mathcal{T}_c$ for low density gas in a potential is put forward. If $\mathcal{T} \gg \mathcal{T}_c$, we just need to use the classical statistical mechanics without solving the Schrödinger equation to consider the thermal behaviour of gas in the potential. But if $\mathcal{T} \sim \mathcal{T}_c$, we must solve the Schrödinger equation. For Ne in a (20, 20) nanotube, we obtain $\mathcal{T}_c \approx 60$ K.

## 1. Introduction

Since the discovery of carbon nanotubes [1], the peculiar electronic and mechanical properties of these structures have attracted much attention [2–4]. Experiments have also revealed that they can also be used to store hydrogen [5] and other gases [6]. Many physicists expected that gases in nanotubes or nanotube bundles may display novel one-dimensional (1D) behaviour as a consequence of the remarkable aspect ratio of the length of tubes to their radius. The group led by Cole [7], and other researchers [8], have theoretically studied properties of gases in nanotubes or nanotube bundles. One of the most fantastic properties they found is the specific heat of dilute gas inside single-walled carbon nanotubes (SWNTs) as a function of temperature:

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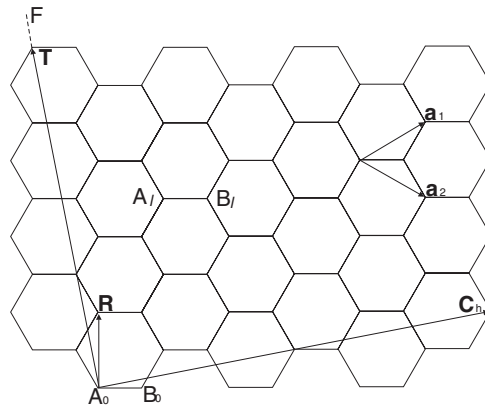[4] Author to whom any correspondence should be addressed.

**Figure 1.** The unrolled honeycomb lattice of an SWNT. By rolling up the sheet along the chiral vector $C_h$, that is, such that the point $A_0$ coincides with the point corresponding to vector $C_h$, a nanotube is formed. The vectors $a_1$ and $a_2$ are the real space unit vectors of the hexagonal lattice. The translational vector $T$ is perpendicular to $C_h$ and runs in the direction of the tube axis. The vector $R$ is the symmetry vector. $A_0$, $B_0$ and $A_l$, $B_l$ ($l = 1, 2, \ldots, N$) are used to denote the sites of carbon atoms.

with increasing temperature it shows the thermal behaviour changing from 1D through 2D to 3D. However, there are still two questions arising: do 1D and 2D behaviours always exist for dilute gas inside an SWNT only if the temperature is low enough, and is classical statistical mechanics (CSM) sufficient to deal with this problem?

In [9], we have given a brief answer to the first question. Here we will exhibit the full calculations and continue to discuss the second question. In recent papers, Šiber *et al* [10] treat the specific heat of dilute He atoms adsorbed in interstitial channels and grooves of carbon nanotube bundles. Here we partially follow their approach.

This paper is organized as follows: in section 2, we give the expressions of the coordinates of carbon atoms in a unit cell of an SWNT. In section 3, we analytically calculate the potential of Ne in a carbon nanotube. As an example, we calculate the potential of Ne in a (20, 20) tube. In section 4, we list the related formula of thermodynamics in statistical mechanics to calculate the specific heat. In section 5, we calculate the specific heats of Ne inside a (20, 20) at different temperatures without considering $\theta$, $z$ effects ($\theta$, $z$ are defined in section 2). In section 6, we calculate the specific heats of Ne inside (20, 20) at low temperature. In section 7, we discuss why we do not use CSM to calculate the specific heat. In this section, we present a rough method to estimate the characteristic temperature, below which the CSM cannot be used. In section 8, we discuss the reliability of our results and give brief conclusions.

## 2. The coordinates of carbon atoms in a unit cell of an SWNT

An SWNT without two caps can be constructed by wrapping up a single sheet of graphite such that two equivalent sites of the hexagonal lattice coincide [11]. To describe the SWNT, some characteristic vectors require introduction. As shown in figure 1, the chiral vector $C_h$, which defines the relative location of two sites, is specified by a pair of integers $(n_1, n_2)$ which is called the index of the SWNT and relates $C_h$ to two unit vectors $a_1$ and $a_2$ of graphite ($C_h = n_1 a_1 + n_2 a_2$). The chiral angle $\theta_0$ defines the angle between $a_1$ and $C_h$. For an $(n_1, n_2)$ nanotube, $\theta_0 = \arccos\left[\frac{2n_1 + n_2}{2\sqrt{n_1^2 + n_2^2 + n_1 n_2}}\right]$. The translational vector $T$ corresponds to the first lattice

point of a 2D graphitic sheet through which the line normal to the chiral vector $\mathbf{C}_h$ passes. The unit cell of the SWNT is the rectangle defined by vectors $\mathbf{C}_h$ and $\mathbf{T}$, while vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ define the area of the unit cell of 2D graphite. The number $N$ of hexagons per unit cell of SWNT is obtained as a function of $n_1$ and $n_2$ as $N = 2(n_1^2 + n_2^2 + n_1 n_2)/d_R$, where $d_R$ is the greatest common divisor of $(2n_2 + n_1)$ and $(2n_1 + n_2)$. There are $2N$ carbon atoms in each unit cell of the SWNT because every hexagon contains two atoms. To denote the $2N$ atoms, we use a symmetry vector $\mathbf{R}$ to generate coordinates of carbon atoms in the nanotube, defined as the site vector having the smallest component in the direction of $\mathbf{C}_h$. From a geometric standpoint, vector $\mathbf{R}$ consists of a rotation around the nanotube axis by an angle $\Psi = 2\pi/N$ combined with a translation $\tau$ in the direction of $\mathbf{T}$; therefore, $\mathbf{R}$ can be denoted by $\mathbf{R} = (\Psi|\tau)$. Using the symmetry vector $\mathbf{R}$, we can divide the $2N$ carbon atoms in the unit cell of the SWNT into two classes: one includes $N$ atoms whose site vectors satisfy

$$\mathbf{A}_l = l\mathbf{R} - [l\mathbf{R} \cdot \mathbf{T}/\mathbf{T}^2]\mathbf{T} \qquad (l = 0, 1, 2, \ldots, N-1); \tag{1}$$

the other includes the remaining $N$ atoms whose site vectors satisfy

$$\mathbf{B}_l = l\mathbf{R} + \mathbf{B}_0 - [(l\mathbf{R} + \mathbf{B}_0) \cdot \mathbf{T}/\mathbf{T}^2]\mathbf{T} - [(l\mathbf{R} + \mathbf{B}_0) \cdot \mathbf{C}_h/\mathbf{C}_h^2]\mathbf{C}_h \qquad (l = 0, 1, \ldots, N-1), \tag{2}$$

where $\mathbf{B}_0 \equiv (\Psi_0|\tau_0) = \left( \frac{2\pi a_{cc} \cos(\theta_0 - \frac{\pi}{6})}{|\mathbf{C}_h|} \Big| a_{cc} \cos\left(\theta_0 - \frac{\pi}{6}\right) \right)$ represents one of the nearest neighbour atoms to $\mathbf{A}_0$ and $a_{cc}$ is the carbon–carbon bond length.

We introduce a cylindrical coordinate system $(r, \theta, z)$ whose $z$-axis is the tube axis. Its $r\theta$-plane is perpendicular to the $z$-axis and contains atom $A_0$ in the nanotube. $r$ is the distance from some point to the $z$-axis, and $\theta$ the angle rotating around the $z$-axis from an axis which is vertical to the $z$-axis and passes through atom $A_0$ in the tube to the point. In this coordinate system, we can express equations (1) and (2) as

$$\mathbf{A}_l = (\rho, l\Psi, l\tau - [l\tau/T]T) \qquad (l = 0, 1, 2, \ldots, N-1), \tag{3}$$

and

$$\mathbf{B}_l = \left( \rho, l\Psi + \Psi_0 - 2\pi\left[\frac{l\Psi + \Psi_0}{2\pi}\right], l\tau + \tau_0 - \left[\frac{l\tau + \tau_0}{T}\right]T \right) \qquad (l = 0, 1, 2, \ldots, N-1), \tag{4}$$

where $\rho = |\mathbf{C}_h|/2\pi$. In equations (1)–(4), the symbol $[\cdots]$ denotes the largest integer smaller than $\ldots$, e.g., $[5.3] = 5$.

## 3. The potential of Ne inside carbon nanotubes

To obtain the potential of Ne inside the nanotube, we firstly consider another simple system shown in figure 2: many atoms distributed regularly in a line form an infinite-atom chain and an atom Q is out of the chain. The interval between neighbour atoms in the chain is $T$, and the site of atom Q relative to atom 0 can be represented by numbers $c_1$ and $c_2$. We take the Lennard-Jones potential $U(R_j) = 4\epsilon[(\sigma/R_j)^{12} - (\sigma/R_j)^6]$ between atom Q and atom $j$ in the chain, where $R_j$ is the distance between Q and atom $j$, and $\epsilon = \sqrt{\epsilon_c \epsilon_{Ne}}$, $\sigma = (\sigma_c + \sigma_{Ne})/2$ with $\epsilon_{Ne} = 35.6$ K, $\sigma_{Ne} = 2.75$ Å, $\epsilon_c = 28$ K and $\sigma_c = 3.4$ Å [7, 12]. We calculate the potential between atom Q and the chain as

$$U_{QC} = 4\epsilon[\sigma^{12}U_6(c_1, c_2) - \sigma^6 U_3(c_1, c_2)], \tag{5}$$
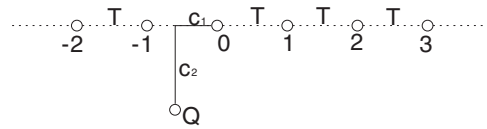
**Figure 2.** An infinite-atom chain and an atom Q out of the chain. Many atoms distributed regularly in a line form the infinite-atom chain. The interval between neighbour atoms in the chain is $T$, and the site of atom Q relative to atom 0 can be represented by numbers $c_1$ and $c_2$.
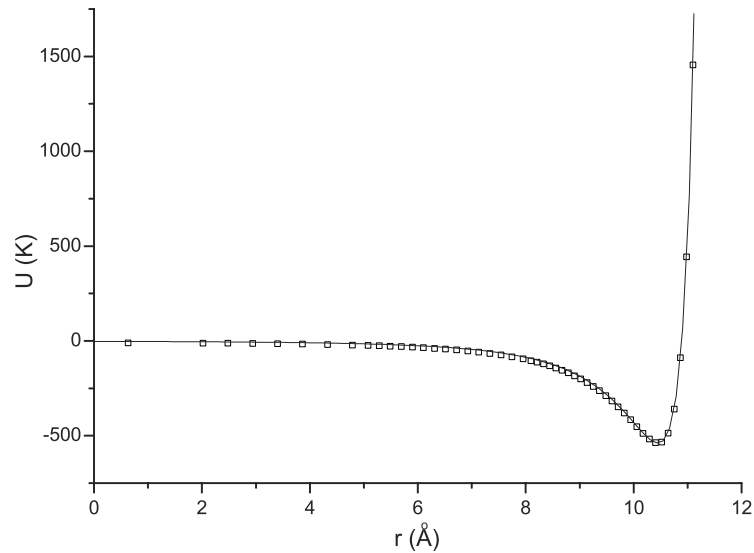


**Figure 3.** The potentials inside the (20, 20) nanotube calculated from equation (7) (squares) and the fit curve (solid curve).

where $U_k(c_1, c_2) = \sum_{n=-\infty}^{\infty} \frac{1}{[(c_1+nT)^2+c_2^2]^k}$ $(k = 1, 2, \ldots)$ which can be calculated through the following recursion [13]:

$$U_1(c_1, c_2) = \frac{\pi \sinh(2\pi c_2/T)}{c_2 T[\cosh(2\pi c_2/T) - \cos(2\pi c_1/T)]}, \tag{6}$$

$$U_{k+1}(c_1, c_2) = -1/(2kc_2)\partial U_k/\partial c_2.$$

The (20, 20) tube, for example, with infinite length, can be regarded as $2N = 80$ chains. Thus the potential of any point Q inside the tube can be calculated as

$$U(r, \theta, z) = \sum_{i=1}^{2N} U_{QC}, \tag{7}$$

where $(r, \theta, z)$ is the coordinates of Q in the cylindrical coordinate system. As an approximation, we neglect the potential varying with $z$ and $\theta$ because we find that it is much smaller than the potential varying with $r$ through calculations, and fit the potential with $U(r) = 4\varepsilon[(\frac{\tilde{\sigma}}{\rho-r})^{10} - (\frac{\tilde{\sigma}}{\rho-r})^4]$, where $\rho = 13.56$ Å is the radius of the tube, $\varepsilon = 390$ K, and $\tilde{\sigma} = 2.63$ Å (see also figure 3). Moreover, we simplify it as

$$U(r) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\tilde{\sigma}}{\rho-r}\right)^{10} - \left(\dfrac{\tilde{\sigma}}{\rho-r}\right)^4\right], & r < \rho - \tilde{\sigma}, \\ \infty, & r > \rho - \tilde{\sigma}. \end{cases} \tag{8}$$

## 4. The basic formulae of thermodynamics in statistical mechanics

When we deal with the thermal behaviour of dilute Ne in a nanotube, we will begin with the free energy $\mathcal{F} = -\mathcal{T} \ln \mathcal{Z}$, where $\mathcal{T}$ is temperature and $\mathcal{Z} = \sum_n e^{-E_n/\mathcal{T}} = \operatorname{tr} \exp(-\mathcal{H}/\mathcal{T})$ is the partition function. We have let the Boltzmann factor be 1 [14]. $E_n$ are the eigenvalues of the Schrödinger equation: $\mathcal{H}\psi_n = E_n\psi_n$. From the free energy, we can derive the specific heat $c_v = -\mathcal{T}(\partial^2 \mathcal{F}/\partial \mathcal{T}^2)_v = \frac{\langle E_n^2 \rangle - \langle E_n \rangle^2}{\mathcal{T}^2}$, where $\langle E_n^2 \rangle = \sum_n E_n^2 e^{-E_n/\mathcal{T}}/\mathcal{Z}$ and $\langle E_n \rangle = \sum_n E_n e^{-E_n/\mathcal{T}}/\mathcal{Z}$.

We call the above statistical mechanics ordinary statistics (OS) and list the corresponding formula in CSM: the free energy $\mathcal{F}_{cl} = -\mathcal{T} \ln \mathcal{Z}_{cl}$, where $\mathcal{Z}_{cl} = \int' e^{-E(p,q)/\mathcal{T}} \, d\Gamma$ is the partition function and here the prime means we integrate only over the regions of phase space which correspond to physically different states of particles. The specific heat $c_{vcl} = -\mathcal{T}(\partial^2 \mathcal{F}_{cl}/\partial \mathcal{T}^2)_v = \frac{\langle E^2 \rangle - \langle E \rangle^2}{\mathcal{T}^2}$, where $\langle E^2 \rangle = \int' E^2 e^{-E(p,q)/\mathcal{T}} \, d\Gamma / \mathcal{Z}_{cl}$ and $\langle E \rangle = \int' E e^{-E(p,q)/\mathcal{T}} \, d\Gamma / \mathcal{Z}_{cl}$.

Under sufficiently high temperature, $\mathcal{F}$ converge to $\mathcal{F}_{cl}$. In other words, the applicable domain of $\mathcal{F}$ is larger than that of $\mathcal{F}_{cl}$. Therefore, the conclusion derived from $\mathcal{F}$ is much more reliable than that derived from $\mathcal{F}_{cl}$. We will use OS in the following discussions if we do not make a special statement.

## 5. Specific heats of Ne gas in an approximate potential

Because we consider dilute Ne, we can neglect the interaction between Ne atoms and write the single-particle Schrödinger equation [15] as $H\psi = E\psi$, where $H = -\frac{\hbar^2}{2\mu}\nabla^2 + U(r)$ and $\psi = \phi e^{i(m\theta + \kappa z)}$. It follows that

$$E = \frac{\hbar^2 \kappa^2}{2\mu} + E_m \qquad (\kappa \in \mathbb{R}, m = 0, \pm 1, \pm 2, \ldots),$$

$$H(r)\phi = E_m\phi, \tag{9}$$

$$H(r) = -\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} - \frac{m^2}{r^2}\right) + U(r),$$

where $m$ is the angular quantum number and $E_m$ is the corresponding energy. Setting $r = (\rho - \tilde{\sigma})\xi$, $\varepsilon_0 = \frac{\hbar^2}{2\mu\rho^2}$ and $\eta = \tilde{\sigma}/\rho$, equations (8) and (9) are transformed into

$$u(\xi) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\eta}{1-(1-\eta)\xi}\right)^{10} - \left(\dfrac{\eta}{1-(1-\eta)\xi}\right)^{4}\right], & \xi < 1, \\ \infty, & \xi > 1, \end{cases} \tag{10}$$

and

$$\mathcal{H}\varphi(\xi) = E_m\varphi(\xi),$$

$$\mathcal{H} = -\frac{\varepsilon_0}{(1-\eta)^2}\left(\frac{d^2}{d\xi^2} + \frac{1}{\xi}\frac{d}{d\xi} - \frac{m^2}{\xi^2}\right) + u(\xi). \tag{11}$$

If we let $|\varphi\rangle = \sum_n a_n |\chi_n\rangle$, we will obtain the secular equation

$$\det(\mathcal{H}_{jn} - E_m\mathcal{S}_{jn}) = 0, \tag{12}$$

where $\mathcal{H}_{jn} = \int_0^1 \chi_j \mathcal{H}(\xi) \chi_n \xi \, d\xi$, and $\mathcal{S}_{jn} = \int_0^1 \chi_j \chi_n \xi \, d\xi$. If we let $\chi_n = J_{|m|}(\nu_n \xi)$, where $J_{|m|}(\xi)$ is the $m$th order Bessel function of the first class and $\nu_n$ is the $n$th zero point of the Bessel function [16], we can calculate $E_{mn}$ ($m = 0, \pm 1, \pm 2, \ldots; n = 1, 2, 3, \ldots$) from equation (12).
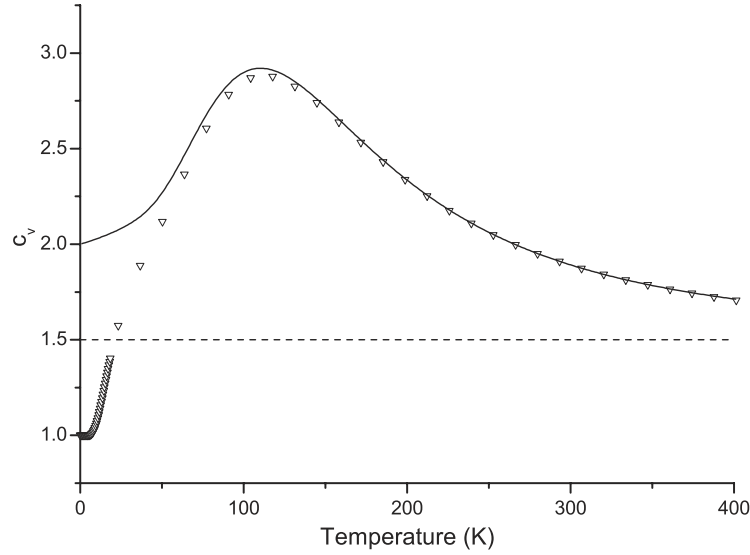
**Figure 4.** The specific heats per atom $c_v$ of Ne inside a (20, 20) nanotube at different temperatures without considering the $\theta, z$ effect. The triangles are the results of OS and the solid curve is that of CSM.

If there are $\mathcal{N}$ Ne atoms inside the tube, we have the free energy $\mathcal{F} = -\mathcal{N}T \ln \mathcal{Z}_1$, where $\mathcal{Z}_1 = \sum_{mn} e^{-E_{mn}/T} \int_{-\infty}^{\infty} e^{-\frac{\hbar^2 \kappa^2}{2\mu T}} \, d\kappa$. We can easily obtain the specific heat per atom as

$$c_v = -\frac{T \partial^2 \mathcal{F}}{\mathcal{N} \partial T^2} = \frac{1}{2} + \frac{\langle E_{nm}^2 \rangle - \langle E_{nm} \rangle^2}{T^2}, \tag{13}$$

where

$$\langle E_{nm} \rangle = \frac{\sum_{mn} E_{mn} e^{-E_{mn}/T}}{\sum_{mn} e^{-E_{mn}/T}}$$

and

$$\langle E_{nm}^2 \rangle = \frac{\sum_{mn} E_{mn}^2 e^{-E_{mn}/T}}{\sum_{mn} e^{-E_{mn}/T}}.$$

In figure 4, the $\bigtriangledown$ symbols reflect $c_v$ varying with the temperature $T$, which implies Ne atoms inside a (20, 20) tube behave as a 3D gas at high temperature (specific heat approaches 3/2) and a 2D gas at low temperature (specific heat is 1). Therefore, we can naturally assume that all atoms are in the valley of potential $U(r)$ at low temperature, i.e. lie on the shell $S^*$ with radius $\varrho = \rho[1 - (5/2)^{1/6}\eta]$.

At high temperature, the Ne atoms may evaporate from the nanotube, but our model cannot recover this effect because our potential is infinite near the surface of the carbon nanotube.

## 6. Specific heats at low temperature

Now we consider the thermal property of Ne inside the nanotube at low temperature in detail. We assume that all atoms lie on the shell $S^*$ with radius $\varrho = \rho[1 - (5/2)^{1/6}\eta]$ at temperature lower than some critical temperature which depends on the energy difference between the two lowest energies of radial excitations. From equations (5)–(7) we can easily calculate the

potential $U_s(v, z)$ on $S^*$, where $v = \varrho\theta$. The Hamiltonian of a single particle can be expressed as $H' = -\frac{\hbar^2}{2\mu}(\frac{\partial^2}{\partial v^2} + \frac{\partial^2}{\partial z^2}) + U_s(v, z)$.

In fact, $U_s$ has periodic structure. If we denote $\alpha_1 = (2\pi\varrho/N, \tau)$, $\alpha_2 = (0, T)$ and $\gamma_l = l_1\alpha_1 + l_2\alpha_2$, we have $U_s(\mathbf{r} + \gamma_l) = U_s(\mathbf{r})$, where $l_1, l_2 \in \mathbb{Z}$ and $\mathbf{r} = (v, z)$. On the one hand, we have the Bloch theorem [17]:

$$H'\Phi(\kappa, \mathbf{r}) = E_\kappa\Phi(\kappa, \mathbf{r}),$$
$$\Phi(\kappa, \mathbf{r} + \gamma_l) = e^{i\kappa\cdot\gamma_l}\Phi(\kappa, \mathbf{r}), \tag{14}$$

which suggests that $\Phi(\kappa, \mathbf{r}) = \sum_j a(\kappa + \mathbf{G}_j)e^{i(\kappa+\mathbf{G}_j)\cdot\mathbf{r}}$, where $\mathbf{G}_j = j_1\beta_1 + j_2\beta_2$ with $j_1, j_2 \in \mathbb{Z}$, $\beta_1 = (N/\varrho, 0)$ and $\beta_2 = (-\tau N/(T\varrho), 2\pi/T)$. From equation (30), we obtain the secular equation

$$\det(\mathcal{H}_{lj} - E_\kappa\delta_{lj}) = 0, \tag{15}$$

where $\mathcal{H}_{lj} = \frac{\hbar^2}{2\mu}(\kappa + \mathbf{G}_j)^2\delta_{lj} + \mathcal{U}_{lj}$, $\mathcal{U}_{lj} = \frac{1}{\Omega_0}\int_{\Omega_0} e^{i(\mathbf{G}_l-\mathbf{G}_j)\cdot\mathbf{r}}U_s(\mathbf{r})\,d\mathbf{r}$ and $\Omega_0 = |\alpha_1 \times \alpha_2|$.

On the other hand, the periodic boundary condition along the circumference of the shell $S^*$ suggests that we just need to consider the first Brillouin zone which consists of $\kappa = (m_v/\varrho, \kappa_z)$ where $m_v \in \mathbb{Z}$, $0 \leqslant m_v < N$ and $\kappa_z \in \mathbb{R}$, $0 \leqslant \kappa_z < 2\pi/T$.

From equation (15), we can calculate the energy $E_{m_v,\kappa_z}$, and then the free energy $\mathcal{F} = -\mathcal{N}T\ln\mathcal{Z}_1^{\text{Note }5}$, where $\mathcal{Z}_1 = \sum_{m_v}\int_0^{2\pi/T} e^{-E_{m_v,\kappa_z}/T}\,d\kappa_z$. Moreover, the specific heat per atom is [14]

$$c_v = -\frac{T\partial^2\mathcal{F}}{\mathcal{N}\partial T^2} = \frac{\langle E'^2\rangle - \langle E'\rangle^2}{T^2}, \tag{16}$$

where

$$\langle E'\rangle = \sum_{m_v=0}^{N-1}\int_0^{2\pi/T} E_{m_v,\kappa_z}e^{-E_{m_v,\kappa_z}/T}\,d\kappa_z/\mathcal{Z}$$

and

$$\langle E'^2\rangle = \sum_{m_v=0}^{N-1}\int_0^{2\pi/T} E_{m_v,\kappa_z}^2 e^{-E_{m_v,\kappa_z}/T}\,d\kappa_z/\mathcal{Z}.$$

In figure 5, the $\triangledown$symbols reflect $c_v$ varying with the temperature $T$, which implies Ne atoms inside a (20, 20) tube behave as a lattice gas [18] at ultra-low temperature (specific heat is zero) and a 2D gas at low temperature (specific heat approaches unity). There is no 1D gas inside a (20, 20) tube, which is quite different from our usual notion.

## 7. Why not use CSM?

At sufficiently high temperature, $\mathcal{F}$ converges to $\mathcal{F}_{cl}$. If a carbon nanotube, for example a (20, 20) tube, just a geometric tube with diameter $d \approx 2$ nm, the characteristic temperature $T_c = h^2/(2\pi md^2) = 0.04$ K. We just need to use the CSM if $T \gg T_c$. However, here the carbon nanotube provides potential to Ne. In the potential, to calculate the characteristic temperature is not a simple matter. For example, consider some atoms in a harmonic potential $U(r) = \frac{1}{2}m\omega^2 r^2$. We can easily calculate the specific heat per atom $c_v = (3\omega^2/T^2)\exp(-\omega/T)/[1 - \exp(-\omega/T)]^2$ [14]. Here we have set $\hbar = 1$. We know $c_v = 3$ if $T \gg \omega$ and this is the classical case. Thus we can set $T_c = \omega$ (in full $T_c = \hbar\omega/k_B$).

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[5] In fact, here we just consider the energies in the first Brillouin zone. If considering $E_\kappa = E_{-\kappa}$ and $E_\kappa = E_{\kappa+\mathbf{G}_j}$, we need to multiply by a constant before the partition function $\mathcal{Z}$ in the expression of the free energy.
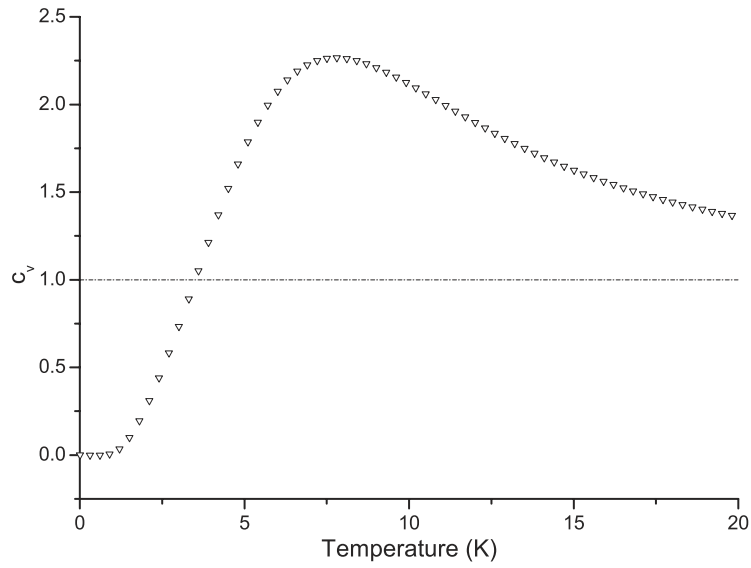
**Figure 5.** The specific heats (triangles) per atom $c_v$ of Ne inside a (20, 20) nanotube at low temperatures.
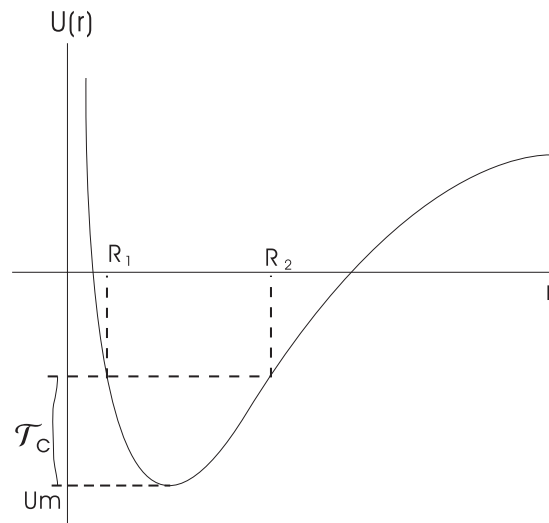


**Figure 6.** A potential and its characteristic temperature. $U_m$ is the minimum of the potential and $\mathcal{T}_c$ is the characteristic temperature. The parameters $R_1$ and $R_2$ satisfy $U(R_1) = U(R_2) = U_m + \mathcal{T}_c$.

The above discussion suggests that $\mathcal{T}_c$ depends on the potential. We propose a rough method to obtain $\mathcal{T}_c$ which is the least root of the following equation:

$$
\begin{aligned}
U_m + \mathcal{T}_c &= U(R_1) = U(R_2) \\
R_2 - R_1 &= h/\sqrt{2\pi m \mathcal{T}_c}.
\end{aligned}
\tag{17}
$$

The physical meanings of parameters in equation (17) are shown in figure 6.
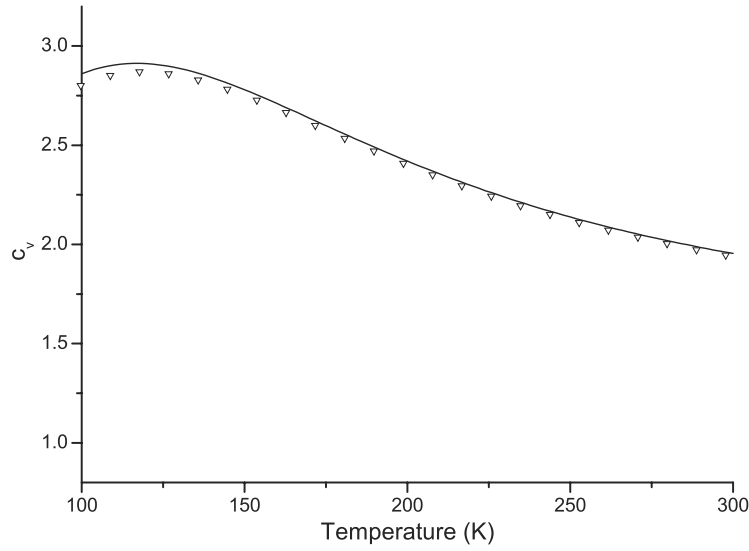
**Figure 7.** The specific heats per atom $c_v$ of Ne inside a (20, 20) nanotube at high temperatures. The triangles are the results of OS without considering the $\theta, z$ effect and the solid curve is that of CSM with the $\theta, z$ effect.

For the potential $U(r) = \frac{1}{2}m\omega^2 r^2$ in the above example, $U_m = 0$, $R_1 = -R_2$, $R_2 - R_1 = 2R_2$, using equation (17) we arrive at $\mathcal{T}_c = \frac{\sqrt{\pi}}{2}\omega \sim \omega$ (the full form is $\mathcal{T}_c = \frac{\sqrt{\pi}\hbar\omega}{2k_B} \sim \hbar\omega/k_B$). For a (20, 20) nanotube, the approximate potential is $U(r) = 4\varepsilon[(\frac{\tilde{\sigma}}{\rho-r})^{10} - (\frac{\tilde{\sigma}}{\rho-r})^4]$, with $\rho = 13.56$ Å, $\varepsilon = 390$ K, and $\tilde{\sigma} = 2.63$ Å. We can numerically solve equation (17) and give $\mathcal{T}_c \approx 60$ K. If $\mathcal{T} \gg \mathcal{T}_c$ (e.g. $\mathcal{T} > 3\mathcal{T}_c = 180$ K), the classical case is expected and CSM is valid. But CSM cannot be used if $\mathcal{T} \sim \mathcal{T}_c$ (e.g. $\mathcal{T} < 2\mathcal{T}_c = 120$ K), especially $\mathcal{T} < \mathcal{T}_c = 60$ K.

In figure 4 we give results obtained from OS and CSM. The information shown in figure 4 agrees with our rough estimate of $\mathcal{T}_c$ very well. Therefore, using the CMS is insufficient. It is necessary to consider the quantum mechanics. In other words, quantum mechanics must be used when studying the behaviours of gases on the nanometre scale.

## 8. Discussion and conclusion

We notice that the potential $U$ is a function of $(r, \theta, z)$ and $U(r, \theta + 2\pi j_1/N, z + j_1\tau + j_2T) = U(r, \theta, z)$, where $N$, $\tau$ and $T$ are parameters of a carbon nanotube, and $j_1$ and $j_2$ are two integers. Under this symmetry, we must use a generalized Bloch theorem (see appendix) to find the eigenvalues of the Schrödinger equation. We can also obtain the secular equation of energies. Although we have 16 Pentium IV computers, the data and computing time exceed our computers' capability if we calculate the specific heat with temperature varying from 0 to 400 K. But, fortunately, we find that the variation of potential with $\theta, z$ is less than 30 K, much smaller than that with $r$. In section 5, we neglect the effect of the variation of potential with $\theta, z$. Indeed, this effect can be neglected under high temperature in terms of intuition. At high temperature, the values of $c_v$ approach that calculated from CSM. We show them in figure 7, in which the triangles are values neglecting the effect of $\theta, z$ and the line is the result calculated from CSM considering the effect of $\theta, z$. It suggests our intuition is reliable.

We know the effect of $\theta, z$ is important under low temperature. In section 6, we consider this effect in detail. Because the shape of $U$ is very sharp and deep with $r$, the particles are confined in the bottom of $U(r)$ at low temperature. Thus we can consider the effect of $\theta, z$ but neglect the effect of $r$ at low temperature.

Therefore, we believe that we have grasped the main factors under high and low temperature and our qualitative conclusions are reliable.

The interactions (including the contribution from the polarization of the pi electrons) between Ne and C atoms are intermolecular forces, van der Waals type interactions. For theoretical study, the simplest form of van der Waals force is the Lennard-Jones potential. We believe that the final results based on the Lennard-Jones potential are qualitatively reasonable. Maybe, many researchers [7, 8] use it for the same reasons. Indeed, the more detailed study needs to consider the Gay–Berne potential [19] or other complex potentials. We are considering overcoming this difficult problem by using numerical simulations.

It is necessary to notice that we just consider dilute Ne and the interactions between Ne atoms are naturally neglected. Therefore, we do not describe the phase transition of Ne in SWNTs. If we intend to deal with the phase transition, we must include the interactions between Ne atoms and use the methods of quantum field theory, such as the renormalization group approach [20], etc.

In conclusion, we calculate the specific heat of Ne in (20, 20) SWNTs at low and high temperature and find the dimensional crossover of thermal behaviour in this system. Especially, the dilute Ne gas exhibits a 2D behaviour at low temperature or 2D lattice behaviour at ultra-low temperature. The simple physical picture is that all atoms are confined on a shell below a critical temperature.

## Acknowledgments

## Appendix. Generalized Bloch theorem

In section 5, we calculate the specific heat neglecting the effect of $\theta, z$; and in section 6, in fact, we neglect the effect of $r$. In other words, we do not obtain the specific heats in a consistent way from low to high temperature. Indeed, the potential $U$ is a function of $(r, \theta, z)$ and satisfies $U(r, \theta + 2\pi j_1/N, z + j_1\tau + j_2 T) = U(r, \theta, z)$, where $j_1$ and $j_2$ are two integers. If a potential satisfies this condition, it is called spiral symmetric. Under this spiral symmetry, we must use a generalized Bloch theorem to find the eigenvalues of Schrödinger equation and then calculate the specific heat in a consistent way [21].

Above all, we go over traditional translational symmetry and Bloch's theorem [22].

The Hamiltonian of a system with translational symmetry is expressed as

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r}); \qquad V(\mathbf{r} + \mathbf{R}_j) = V(\mathbf{r}), \tag{18}$$

where $\mathbf{R}_j = n_{j1}\mathbf{a}_1 + n_{j2}\mathbf{a}_2 + n_{j3}\mathbf{a}_3$ and $n_{j1}, n_{j2}$ and $n_{j3}$ are integers.

Define translational operators $\mathcal{J}(\mathbf{R}_j)$, which act on a function $f(\mathbf{r})$ as

$$\mathcal{J}(\mathbf{R}_j)f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}_j). \tag{19}$$

It follows that

$$\mathcal{J}(\mathbf{R}_j)\mathcal{J}(\mathbf{R}_l) = \mathcal{J}(\mathbf{R}_l + \mathbf{R}_j) = \mathcal{J}(\mathbf{R}_j + \mathbf{R}_l) = \mathcal{J}(\mathbf{R}_l)\mathcal{J}(\mathbf{R}_j), \tag{20}$$

and

$$\mathcal{J}(\mathbf{R}_j)Hf(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\mathcal{J}(\mathbf{R}_j)\nabla^2 f(\mathbf{r}) + \mathcal{J}(\mathbf{R}_j)V(\mathbf{r})f(\mathbf{r})$$

$$= -\frac{\hbar^2}{2\mu}\nabla^2 \mathcal{J}(\mathbf{R}_j)f(\mathbf{r}) + V(\mathbf{r}+\mathbf{R}_j)f(\mathbf{r}+\mathbf{R}_j)$$

$$= \left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]f(\mathbf{r}+\mathbf{R}_j) = H\mathcal{J}(\mathbf{R}_j)f(\mathbf{r}). \tag{21}$$

Therefore $\{\mathcal{J}(\mathbf{R}_j), H\}$ is the set of conserved quantities. In this case, an eigenfunction of the Hamiltonian must be an eigenfunction of the translational operators, i.e., $\mathcal{J}(\mathbf{R}_j)\psi(\mathbf{r}) = \psi(\mathbf{r}+\mathbf{R}_j) = \lambda(\mathbf{R}_j)\psi(\mathbf{r})$ if $H\psi(\mathbf{r}) = E\psi(\mathbf{r})$. Furthermore, the electron density must be periodic, i.e., $|\psi(\mathbf{r}+\mathbf{R}_j)|^2 = |\psi(\mathbf{r})|^2$. It follows that

$$|\lambda(\mathbf{R}_j)|^2 = 1. \tag{22}$$

But from equation (20), we know

$$\lambda(\mathbf{R}_j)\lambda(\mathbf{R}_l) = \lambda(\mathbf{R}_j + \mathbf{R}_l). \tag{23}$$

The solution of equation (23) under the constraint equation (22) is $\lambda(\mathbf{R}_j) = e^{i\boldsymbol{\kappa}\cdot\mathbf{R}_j}$. Thus we have Bloch's theorem:

$$\psi(\mathbf{r}+\mathbf{R}_j) = e^{i\boldsymbol{\kappa}\cdot\mathbf{R}_j}\psi(\mathbf{r}). \tag{24}$$

Next, we will turn to the spiral symmetry and generalize the Bloch theorem. The Hamiltonian with the spiral symmetry in cylindrical coordinates is expressed

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{\partial}{r\partial r} + \frac{\partial^2}{r^2\partial\theta^2} + \frac{\partial^2}{\partial z^2}\right) + V(r,\theta,z), \tag{25}$$

$$V(r,\theta,z) = V(r,\theta+j_1\vartheta, z+j_1\tau+j_2T), \tag{26}$$

where $\vartheta = 2\pi/N, N\tau = MT, N, M \in \mathbb{N}, j_1, j_2 \in \mathbb{Z}$. Define vectors $\mathbf{r} = (\theta, z)$ and $\mathbf{R}_j = (j_1\vartheta, j_1\tau+j_2T)$ in the space $[0, 2\pi) \times \mathbb{R}$, and operators $\mathcal{J}(\mathbf{R}_j)$ which act on a function $f(r;\mathbf{r})$ as $\mathcal{J}(\mathbf{R}_j)f(r;\mathbf{r}) = f(r;\mathbf{r}+\mathbf{R}_j)$. It follows that $\mathcal{J}(\mathbf{R}_j)\mathcal{J}(\mathbf{R}_l) = \mathcal{J}(\mathbf{R}_l + \mathbf{R}_j) = \mathcal{J}(\mathbf{R}_j + \mathbf{R}_l) = \mathcal{J}(\mathbf{R}_l)\mathcal{J}(\mathbf{R}_j)$ and $\mathcal{J}(\mathbf{R}_j)V(r;\mathbf{r}) = V(r;\mathbf{r})\mathcal{J}(\mathbf{R}_j)$. Otherwise,

$$\mathcal{J}(\mathbf{R}_j)\left(\frac{\partial^2}{r^2\partial\theta^2} + \frac{\partial^2}{\partial z^2}\right)f(r;\mathbf{r}) = \left(\frac{\partial^2}{r^2\partial\theta^2} + \frac{\partial^2}{\partial z^2}\right)\mathcal{J}(\mathbf{R}_j)f(r;\mathbf{r}). \tag{27}$$

Thus

$$\mathcal{J}(\mathbf{R}_j)H = H\mathcal{J}(\mathbf{R}_j). \tag{28}$$

We can obtain a generalized Bloch theorem analogizing the method to obtain the traditional Bloch theorem:

$$\psi(r;\mathbf{r}+\mathbf{R}_j) = e^{i\boldsymbol{\kappa}\cdot\mathbf{R}_j}\psi(r;\mathbf{r}), \tag{29}$$

where $\boldsymbol{\kappa} = (l,\kappa), l = 0, 1, \ldots, N-1, 0 \leqslant \kappa < 2\pi/T$.

If we set $\boldsymbol{\alpha}_1 = (\vartheta, \tau), \boldsymbol{\alpha}_2 = (0, T), \boldsymbol{\beta}_1 = (N, 0), \boldsymbol{\beta}_2 = (-\tau N/T, 2\pi/T)$ and $\mathbf{G_j} = j_1\boldsymbol{\beta}_1 + j_2\boldsymbol{\beta}_2 = (j_1 N - j_2 N\tau/T, 2\pi j_2/T)$, then we can expand the wavefunction as the superposition of planar waves:

$$\psi(r;\mathbf{r}) = \sum_{\mathbf{j}} C_{\mathbf{j}}\varphi(r)e^{i(\boldsymbol{\kappa}+\mathbf{G_j})\cdot\mathbf{r}}. \tag{30}$$

In cylindrical coordinates, equations (29) and (30) are expressed

$$\psi\left(r, \theta + \frac{2\pi j_1}{N}, z + j_1\tau + j_2 T\right) = \exp\left(i\left[\frac{2\pi l j_1}{N} + \kappa(j_1\tau + j_2 T)\right]\right)\psi(r, \theta, z), \tag{31}$$

$$\psi_{l\kappa}(r, \theta, z) = \sum_{j_1 j_2} C_{j_1 j_2}\varphi_{l\kappa}(r)\exp(i[(l + j_1 N - j_2 N\tau/T)\theta + (\kappa + 2\pi j_2/T)z]). \tag{32}$$

Expanding $\varphi_{l\kappa}(r)$ with normalized orthogonal basis $\{\chi_{nl\kappa}(r), n \in \mathbb{N}\}$ we obtain the secular equation from equation (32) and the Schrödinger equation

$$\det[(\mathcal{H}_{m_1 m_2 j_1 j_2 nn'} - E_{nl\kappa}\delta_{j_1 m_1}\delta_{j_2 m_2}\delta_{nn'})] = 0, \tag{33}$$

where

$$\mathcal{H}_{j_1 j_2 m_1 m_2 nn'} = \mathcal{T}_{j_1 j_2 nn'}\delta_{j_1 m_1}\delta_{j_2 m_2} + \mathcal{U}_{j_1 j_2 m_1 m_2 nn'},$$

$$\mathcal{T}_{j_1 j_2 nn'} = -\frac{\hbar^2}{2\mu}\int_0^\rho \chi_{nl\kappa}(r)\left[\frac{d^2}{dr^2} + \frac{d}{rdr} - \frac{(l + j_1 N - \frac{j_2 N\tau}{T})^2}{r^2} - \left(\kappa + \frac{2\pi j_2}{T}\right)^2\right]\chi_{n'l\kappa}(r)r\,dr,$$

and

$$\mathcal{U}_{j_1 j_2 m_1 m_2 nn'} = \frac{N}{2\pi T}\int_0^{2\pi} d\theta \int_0^T dz \int_0^\rho r\,dr\,\chi_{nl\kappa}(r)U(r, \theta, z)\chi_{n'l\kappa}(r)$$

$$\times \exp\left(i\left[(j_1 - m_1) - \frac{(j_2 - m_2)\tau}{T}\right]N\theta + \frac{i2\pi(j_2 - m_2)z}{T}\right).$$

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