

The Field Theory of Specific Heat

Yu. V. Gusev

*Lebedev Research Center in Physics, Leninskii Prospekt 53, Moscow 119991, Russia;
Max Planck Institute for Gravitational Physics (Albert Einstein
Institute), Am Mühlenberg 1, D-14476 Golm, Germany
E-mail: yuri.v.gussev@gmail.com*

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Abstract. Finite temperature quantum field theory in the heat kernel method is used to study the heat capacity of condensed matter. The lattice heat is treated à la P. Debye as energy of the elastic (sound) waves. The dimensionless functional of free energy is re-derived with a cut-off parameter and used to obtain the specific heat of crystal lattices. The new dimensionless thermodynamical variable is formed as Planck’s inverse temperature divided by the lattice constant. The dimensionless constant, universal for the class of crystal lattices, which determines the low temperature region of molar specific heat, is introduced and tested with the data for diamond lattice crystals. The low temperature asymptotics of specific heat is found to be the fourth power in temperature instead of the cubic power law of the Debye theory. Experimental data for the carbon group elements (silicon, germanium) and other materials decisively confirm the quartic law. The true low temperature regime of specific heat is defined by the surface heat, therefore, it depends on the geometrical characteristics of the body, while the absolute zero temperature limit is geometrically forbidden. The limit on the growth of specific heat at temperatures close to critical points, known as the Dulong–Petit law, appears from the lattice constant cut-off. Its value depends on the lattice type and it is the same for materials with the same crystal lattice. The Dulong–Petit values of compounds are equal to those of elements with the same crystal lattice type, if one mole of solid state matter were taken as the Avogadro number of the composing atoms. Thus, the Neumann–Kopp law is valid only in some special cases.

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1. QUANTUM FIELD THEORY FOR CONDENSED MATTER

When developing the physical theory of condensed matter, e.g., solid state matter, one usually starts with the atomistic view of matter, which consists of particles, e.g., atoms (ions) of the lattice and electrons [1, 2]. However, particles and quasiparticles in the physical theory are employed only at intermediate stages, while the final expressions are certain static functions, which describe integral properties of condensed matter systems, such as the heat capacity, electric conductivity, etc. One usually does not intend to and cannot describe the behavior of individual particles. Furthermore, one normally starts with a system of non-interacting constituents, e.g., independent oscillators of Einstein [3, 1] or free electron gas of Drude [4, 1], and later builds in interactions between them to develop eventually physics of ‘strongly interacting’ (correlated) systems. Building a theory in this way follows the historical path of physics development and, therefore, relies on thermodynamics and statistical mechanics of *gases*. However, physical properties of solid and liquid matter are very different from those of gases. Indeed, a condensed matter system can be defined as a system of particles that form a physical *continuum*. In fact, the view on condensed matter as a continuous medium is well developed in such classic branches of physics as elasticity theory [5–7] and hydrodynamics [8]. These are phenomenological theories, which are not concerned with particle compositions of condensed matter systems, but they are capable of describing the properties of matter by summarizing them as physical laws. Elasticity theory describes mechanical phenomena of solid state matter, yet its mathematical apparatus can be used for the theory of thermal phenomena, as was first proposed by Debye [9].

Temperature is a key variable of any thermal theory. Statistical thermodynamics [2] was developed as physics of gas, which is viewed as a collection of massive particles moving in free space. Correspondingly, this physical theory used classical mechanics as its foundation. In statistical physics, temperature is an emergent characteristic of a large number of particles. It appeared possible to use *mechanics* of particles (the system’s constituents) to find a *statistical* distribution of their kinetic energies (velocities), which corresponds to an observed temperature. This was done first by Maxwell

[10]. Since the physical nature of temperature in a condensed matter system, which presents the medium in a bounded space, is different, this procedure cannot work. In the quantum theory of matter temperature is introduced as an external (axiomatic) parameter. This is also the approach of the present work, but it is implemented in the geometrical language, since we believe that thermal and electronic properties of condensed matter could be better described the methods of field theory and geometry.

In statistical mechanics, in order to derive macroscopic thermal quantities, the number of particles is taken to infinity, while the volume occupied by particles is taken to infinity as well [2]. Both the limits are unphysical, but the sought physical quantities are derived finite. In this limit, the influence of a system's boundaries on its physical properties is infinitesimal and cannot be studied. However, finite size effects, e.g., in heat conductivity and heat capacity, are observed, usually at low temperatures. For some condensed matter systems under certain conditions, effects of the body's geometrical characteristics can be the leading ones. The Schwinger–DeWitt (geometric) formalism for quantum field theory (QFT) [11, 12] that we use naturally incorporates boundary effects due to its mathematical foundation, the heat kernel.

We will use the finite temperature QFT [13] to develop a theory of specific heats of crystal lattices that may also be applicable to other forms of condensed matter. Let us first recall its basic ideas. Since any condensed matter system exists within a certain three-dimensional domain, and its behavior in time is not usually studied, the field theory can be defined in the Euclidean four-dimensional spacetime, i.e., the spacetime metric's signature is not Minkowskian, but Euclidean (no time coordinate is singled out). The physical time is imaginary, and it is distinguished from other spacetime dimensions only by its closed topology, S^1 . The orbit's length of the closed Euclidean time is expressed via the fundamental physical constants as the Planck's inverse temperature,

$$\beta = \frac{\hbar v}{k_B T}, \quad (1)$$

where k_B is Boltzmann's constant and \hbar is the reduced Planck constant. Note that, in contrast to the definition in [13], there is no calibration coefficient in (1.1) because temperature T , or β for that matter, is not an independent variable in the present setting. The characteristic velocity, v , enters the definition (1). The electronic component of heat it is assumed to be the speed of light, while for the elastic (acoustic) component, contributed by the crystal lattice, it is the velocity of elastic (sound) waves.

In the Schwinger–DeWitt quantum field theory, the Laplace operator,

$$\square = g^{\mu\nu} \nabla_\mu \nabla_\nu, \quad (2)$$

defines a particular field model [14]. It is constructed of the covariant derivatives, which may contain the metric (gravity) and gauge field (e.g., electromagnetic) connections. For the theory of specific heat, gauge fields and gravity are not relevant, and the Laplacian (2) is trivially the second order partial derivatives. For the study of electronic properties, electromagnetic fields cannot be neglected, in particular, they should be important for the electronic specific heat.

The kernel of the heat equation [11, 12, 14],

$$\left(\frac{\partial}{\partial s} - \square^x \right) K(s|x, x') = 0, \quad K(s|x, x')|_{s \rightarrow 0} = \delta(x, x'), \quad (3)$$

is expressed via the proper time parameter, s . The trace of the kernel in a compact three-dimensional manifold with boundary is [13],

$$\text{Tr} K(s) \equiv \int d^3x K(s|x, x) = \frac{1}{(4\pi s)^{3/2}} \mathcal{V} + \frac{1}{(4\pi s)} \mathcal{S}, \quad (4)$$

where \mathcal{V} is the volume and \mathcal{S} is the boundary's area of the bounded domain of manifold \mathbb{R}^3 . This expression is valid at arbitrary proper time. For reasons explained in Section 2.D, we omit the boundary ('surface') term and keep only the volume ('bulk') term of this expression.

Let us compute the free energy functional, defined in the usual way [13], but with the positive lower limit of the proper time integral. This is the standard QFT regularization used to remove the ultraviolet divergences [14]. Our integral is finite, but the lower limit appears due to the wavelength cut-off caused by the discreteness of the lattice. Because the length square, \tilde{a}^2 , is proportional to the proper time, s , which parameterizes the geodesic [11, 14], we introduce the integral's lower limit as (the numerical coefficient is chosen to simplify the expressions below)

$$-F_{\tilde{a}}^{\beta} \equiv \tilde{A} \int_{\tilde{a}^2/4}^{\infty} \frac{ds}{s} \text{Tr}K^{\beta}(s). \quad (5)$$

An observable quantity, such as specific heat, must certainly be independent of the regulator (cut-off parameter), and in Section 2.B, we show that indeed it is. The overall numerical coefficient \tilde{A} is to be calibrated by experiments. We substitute the three-dimensional heat kernel trace (4) into the thermal (3+1)-dimensional expression [13],

$$\text{Tr}K^{\beta}(s) = \frac{\beta}{(4\pi s)^{1/2}} \sum_{n=1}^{\infty} e^{-\frac{\beta^2 n^2}{4s}} \text{Tr}K(s). \quad (6)$$

After applying the change of variables, $y = \beta^2/(4s)$, free energy (5) looks like

$$-F_{\tilde{a}}^{\beta} = \frac{\tilde{A}}{\pi^2} \frac{\mathcal{V}}{\beta^3} \sum_{n=1}^{\infty} \int_0^{\alpha^2} dy y e^{-yn^2}. \quad (7)$$

It is only different from the previously studied expression [13] by the integral's upper limit, which is expressed as a new *dimensionless* variable,

$$\alpha \equiv \frac{\beta}{\tilde{a}} = \frac{\hbar v}{\tilde{a} k_B T}. \quad (8)$$

The computed expression (7) has the final form,

$$-F^{\alpha} = \frac{\tilde{A}}{\pi^2} \frac{\mathcal{V}}{\tilde{a}^3} \sum_{n=1}^{\infty} \frac{1}{n^4 \alpha^3} \left(1 - \exp(-\alpha^2 n^2) - n^2 \alpha^2 \exp(-\alpha^2 n^2) \right). \quad (9)$$

This sum's first term is the zeta function, $\zeta(4) = \pi^4/90$. The two other terms cannot be analytically computed.

The new upper index of the functional F^{α} indicates a change in the physical understanding of free energy. We declare the dimensionless variable α be *the thermal variable for condensed matter systems*, i.e., field theory models with short wavelength cut-off that supersedes old variables, the absolute temperature, T (Kelvin), and Planck's inverse temperature, β (meter). Indeed, it is natural that the dimensionless functional depends on the dimensionless variable; the theory could be called conformal (or scale free) in the popular language.

Following the line of [13], we take the derivative of (9) over the variable α to obtain

$$\frac{\partial F^{\alpha}}{\partial \alpha} = \tilde{A} \frac{3}{\pi^2} \frac{\mathcal{V}}{\tilde{a}^3} \Theta(\alpha), \quad (10)$$

where the notation for the dimensionless thermal sum is introduced,

$$\Theta(\alpha) = \sum_{n=1}^{\infty} \frac{1}{n^4 \alpha^4} \left\{ 1 - \exp(-\alpha^2 n^2) - n^2 \alpha^2 \exp(-\alpha^2 n^2) - \frac{2}{3} n^4 \alpha^4 \exp(-\alpha^2 n^2) \right\}. \quad (11)$$

We conjecture that $\Theta(\alpha)$ is a *universal* function of temperature scaling for condensed matter systems. The plot of $\Theta(\alpha)$, computed in Maple for the finite sum $n = 400$, is shown in Fig. 1.

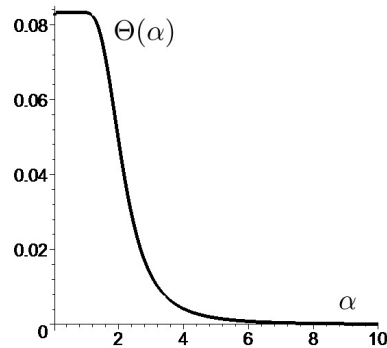


Fig. 1. Function $\Theta(\alpha)$ for the finite sum, $n = 400$.

The maximum value of this quantity is found to be

$$\Theta_{\max} \approx 8.33 \cdot 10^{-2}. \quad (12)$$

It might be convenient to redefine (11) by 10^2 especially because it usually has a rather large dimensionful factor, (29), see Section 3.B. Three other terms of the sum have good behaviors in asymptotics, $\alpha \rightarrow 0$ ('high temperature') and $\alpha \rightarrow \infty$ ('low temperature'). The limit $T = 0$ is topologically forbidden since it would be equivalent to the open manifold, \mathbb{R}^1 , [13]. Even though a numerical estimate for the expression (10) becomes negative, when α goes to zero (note, the plot in Fig. 1 is from $\alpha = 0.05$), its intermediate *asymptotics* is positive constant for any infinitesimal value of α , when the sum's upper limit tends to infinity. In fact, the leftmost bound of $\Theta(\alpha)$ is irrelevant, since in the regime, $\beta \ll a$ (the thermal wavelength of sound is much less than the lattice cut-off), the theory breaks down.

The expression (10) is valid at any values of its variables. We consider now expansions of this functional in its dimensionless thermal variable. The 'low temperature' asymptotics is easily found,

$$\frac{\partial F^\alpha}{\partial \alpha} = \tilde{A} \frac{\pi^2}{30} \frac{\mathcal{V}}{\tilde{a}^3} \frac{1}{\alpha^4}, \quad \alpha \rightarrow \infty. \quad (13)$$

The 'high temperature' asymptotics can be explored numerically. The maximum value of $\Theta(\alpha)$ gives us the constant term,

$$\frac{\partial F^\alpha}{\partial \alpha} = \tilde{A} \Theta_{\max} \frac{3}{\pi^2} \frac{\mathcal{V}}{\tilde{a}^3}, \quad \alpha \rightarrow 0. \quad (14)$$

These simple derivations are quite general and can hopefully be used for different problems of thermal physics.

2. THE FIELD THEORY OF SPECIFIC HEAT

A. From Elasticity Theory to the Heat Kernel

Let us apply this formalism to the physics of lattice heat of solid state matter. The theory we want to build can be viewed as a modified completion of the theory of specific heat of Peter Josef William Debye [9]. One century after its creation, his theory is still widely used in practice. The key idea of Debye is that the lattice heat is energy of the standing sound waves in a solid body. The sound waves are elastic waves [7], therefore, the velocity of sound in a solid body (crystal lattice), which is typically of the order of 10^3 m/s, enters Planck's inverse temperature (1) and correspondingly the α -variable (8). This velocity's magnitude lets us leave aside the electronic contribution, because it is separated from the lattice heat by the factor, $v/c \approx 10^{-5}$, taken to some power.

Free energy of finite temperature QFT (9) is applicable to this problem because the operator of the equations of elastic (sound) waves has the required form, Eq. (2). Indeed, let the three-dimensional vector of displacement, u , be a field. Two equations for the longitudinal and transverse elastic waves have the same form [5],

$$\frac{1}{v^2} \frac{\partial^2}{\partial t^2} u(x, t) = \Delta u(x, t). \quad (15)$$

The velocities of propagation of these waves are different and can be also expressed through the elasticity parameters [5], which show that longitudinal velocities are always greater than transverse ones. The sound velocities can be also expressed through the elements of the elastic stiffness tensor (the elastic constants or moduli), c_{ij} , and the matter density, ρ , [6]. There are, in general, three different velocities (one longitudinal and two transverse) for each principal crystallographic direction, for the cubic crystal lattices, which we consider as a simple example of this formalism. Due to the cubic lattice symmetries, there are only three independent elastic constants, c_{11}, c_{12}, c_{44} [6]. They determine velocities of the plane waves incident to the surface $\{100\}$ (we use the notation of [17]),

$$v_1 = \left(\frac{c_{11}}{\rho} \right)^{1/2}, \quad v_2 = \left(\frac{c_{44}}{\rho} \right)^{1/2}, \quad (16)$$

to the surface $\{110\}$,

$$v_3 = \left(\frac{c_{11} + c_{12} + 2c_{44}}{2\rho} \right)^{1/2}, \quad v_4 = \left(\frac{c_{44}}{\rho} \right)^{1/2}, \quad v_5 = \left(\frac{c_{11} - c_{12}}{2\rho} \right)^{1/2}. \quad (17)$$

For the transverse wave v_2 , both polarizations have the same velocity. We accept the elasticity theory's assumption that sound waves with different velocities are independent [1] and, therefore, they present independent contributions to the free energy. One can find sound velocities from the known elastic moduli c_{ij} , but in practice, the velocities are experimentally determined using the ultrasound techniques, and the elastic moduli are derived. These high precision measurements were made by McSkimin and Andreatch, Jr., for some relevant solids: diamond [16], silicon [15], germanium [17], and gallium arsenide [18] (where all the values are tabulated). The third-order elastic moduli were also measured [18], they introduce nonlinearity into the wave equations.

The solutions for standing sound waves are obtained via the wave equations [19]. This is done with the help of the expansion over modes that are counted by the frequency, a variable reciprocal to time, but in the context of our problem, the wavelength is an appropriate variable. However, in a physical theory of heat, we do really not need actual solutions of differential equations. We want to obtain the total energy of sound waves as a function of temperature, i.e., to find a scalar function of one argument (with fixed geometrical characteristics of a body), then time (or frequency) is a redundant variable. The heat kernel method allows us to obtain the trace of the heat kernel, which serves as a mathematical prototype for free energy, directly, by skipping explicit solutions of the field (wave) equations. Thus, the usual derivations of the heat trace asymptotics from the Laplacian's discrete spectrum can be avoided, if we seek solving physics problems in the field theory.

Since this computation is done in spacetime with imaginary time, we first go from the wave equations (15) to the equivalent Laplace equations. The spacetime metric changes its signature from Lorentzian to Euclidean, which means that the left-hand side of (15) gains the minus sign. In QFT literature [11, 12], this is commonly referred to as the Wick rotation. Thereby, we now have a Laplace equation with the *four-dimensional* operator,

$$\square = \frac{1}{v^2} \frac{\partial^2}{\partial t^2} + \Delta. \quad (18)$$

Then, instead of solving the Laplace equation, we solve the corresponding heat equation (3). In this way we reduce the mathematical problem of the Debye theory to the standard problem of the Schwinger–DeWitt QFT. Its operator (2) has the simplest form, where there are no internal degrees of freedom (no matrix structure [14]), no potential term, and no connection in the covariant derivatives: these are just partial derivatives. The Laplace operator (18) allows the separation of variables and thus the computation of the heat kernel as the standard thermal sum (6).

Finite temperature QFT, modified for condensed matter physics in Section 1, gives the volume contribution (7) for each independent velocity. The boundary contribution is defined by its own surface wave velocity, v_s . The total free energy is a sum of all these terms,

$$F_{\text{total}} = \sum_i F^{\alpha_i}[\mathcal{V}] + F^{\alpha_s}[\mathcal{S}]. \quad (19)$$

For cubic lattices, the sum spans over nine α_i , as the transverse wave contributions from the waves incident to the surfaces $\{100\}$ and $\{111\}$ double. The boundary contribution of the surface elastic waves, the Love or Rayleigh waves [7], may be neglected so far because it has an order of magnitude smaller [13] in the experiments that we consider below.

The significant restriction is that sound velocities should be independent of temperature. This condition was experimentally examined for the carbon group elements [15–17]. For example, it was found that the sound velocities in diamonds in the temperature range, -195.8°C to $+50^\circ\text{C}$, change relatively as little as 10^{-5} . This is a good confirmation of the condition $v(T) = \text{const}$. Further experiments were done [20] for germanium and silicon in the temperature range, $25\text{K} < T < 70\text{K}$, and the relative changes in the longitudinal sound velocities were found to be about 10^{-4} , with germanium showing the higher change. Experiments at temperatures beyond this range, which are important for the low temperature regime, were not done. Nevertheless, the obtained results gives us hope that the relative changes of velocities beyond the investigated range are also small.

The phase velocity of plane waves is used in the derivations of elasticity theory [1, 21]. In the heat kernel method, the *measured* velocity enters the Laplacian (2) and correspondingly the α -variable, (8). Therefore, it is the velocity of energy transfer, i.e., the group velocity. This fact emphasizes the phenomenological nature of the proposed theory. There are many more issues with

the use of elastic waves in thermal physics [1] that require further development of the basic ideas outlined here.

B. Molar Specific Heat

In Section 1, we derived the dimensionless derivative (10); let us now propose the *scaling hypothesis*: the scaling of a physical observable, e.g., heat capacity, with the change of the physical variable, e.g., thermodynamic temperature, is the same as scaling of the corresponding dimensionless functional, e.g., $\partial F^\alpha/\partial\alpha$, with the change of the dimensionless variable, when it is expressed with the help of the fundamental physical constants. It is a postulate that will allow us to avoid solving the measurement problem.

Therefore, in order to obtain a physical observable of the proper physical dimensionality, JK^{-1} , from the derived mathematical expression (10), we multiply it by Boltzmann's constant,

$$C_V \equiv k_B \frac{\partial F^\alpha}{\partial \alpha}, \tag{20}$$

where C_V is the heat capacity at the constant volume. We obtain

$$C_V = \tilde{A}k_B \frac{3}{\pi^2} \frac{\mathcal{V}}{\tilde{a}^3} \Theta(\alpha), \tag{21}$$

where the volume \mathcal{V} is fixed by the mathematics used, Section 1. However, in experiments, the heat capacity should be measured at fixed pressure to avoid changing the elastic properties of the crystal due to the additional strain [17]. Thus, we take the experimental values for C_P . It is the heat capacity *per mole* that is derived here anyway. We do not treat the thermal expansion here, which could probably account for the higher temperature behavior close to the critical points.

In order to translate the expression (20) to the normally used molar (atomic) specific heat, C_M , we should divide C_V by the amount of substance, n (mol), contained in the given volume. The molar quantity, n , can be found, with help of the Avogadro constant, N_A , if we know the number of atoms N , as $n = N/N_A$. The number N can be determined from the system's volume, if know the volume of a lattice unit cell, V , and the number of atoms per cell, m , as $N = m\mathcal{V}/V$. The lattice unit cell's volume is defined by the lattice constants that correspond to the crystallographic lattice. For cubic lattices [1, 22, 6], there is a single lattice constant, a , so, $V = a^3$. Finally, the amount of substance is

$$n = \frac{\mathcal{V}m}{a^3 N_A}. \tag{22}$$

When Eq. (20) is divided by (22), the molar specific heat (or just the specific heat) becomes

$$C_M = C_V \frac{a^3 N_A}{\mathcal{V}m} = \tilde{A}k_B N_A \frac{3}{\pi^2} \frac{a^3}{m\tilde{a}^3} \Theta(\alpha). \tag{23}$$

This expression still depends on the unknown cut-off constant, \tilde{a} . However, \tilde{a} is the length, which defines the limit of validity of the elastic model, so it can be declared proportional to the lattice constant,

$$\tilde{a} = Ba. \tag{24}$$

This gives us another calibration constant, B . As mentioned, we could introduce it into Planck's inverse temperature (1), but because temperature comes only as the combination (1.8), it does not matter if we assign an uncertainty to \tilde{a} . The overall combination of the calibration constants can be denoted, $A \equiv \tilde{A}/B^3$. Thus, as expected, we arrive at the regulator-free quantity,

$$C_M = Ak_B N_A \frac{3}{\pi^2} \frac{1}{m} \Theta(\alpha), \tag{25}$$

with

$$\alpha = \frac{\hbar v}{Bk_B a T}, \tag{26}$$

which should be calibrated by experimental data in order to determine the parameters A and B . These two calibration constants define the scaling of specific heat, C_M . The constant A sets up a vertical scale, while the constant B scales up C_M horizontally.

The formula for the specific heat (25) is dimensionless, except for the molar gas constant, which is the only expected combination of fundamental physical constants, $R = k_B N_A$, that could make up the right dimensionality of specific heat. The expression for C_M depends on the velocities of sound, v , and temperature, T , that enter (26). The sound velocities, in turn, are defined by the elastic constants and by the density of matter. So, despite its simplicity, Eq. (25) embodies all

elastic characteristics of crystalline bodies, yet, its functional behavior is described by the universal thermal sum $\Theta(\alpha)$, Eq. (11) of the single variable, α .

The ‘low temperature’ asymptotics of the α -derivative (13) generates the term, cf. [13],

$$C_M = Ak_B N_A \frac{\pi^2}{30} \frac{1}{m} \frac{1}{\alpha^4}, \quad \alpha \rightarrow \infty, \quad (27)$$

because it is a limit of the vanishing lattice constant, i.e., ideal (smooth) medium. The ‘high temperature’ asymptotics (14) provides, via the $\Theta(\alpha)$ maximum value (12), the constant term independent of α ,

$$C_M = Ak_B N_A \Theta_{\max} \frac{3}{\pi^2} \frac{1}{m}, \quad \alpha \rightarrow 0. \quad (28)$$

The above expressions (25)–(28) are valid for cubic lattices, whose velocities are (16)–(17). For other types of lattices, the final derivations should be redone starting from (22). This asymptotics can be also written in the form

$$C_M = \mathcal{R} \Theta_{\max}, \quad \alpha \rightarrow 0. \quad (29)$$

In this form, it lets us obtain the solid state equivalent of the molar gas constant, \mathcal{R} , which is different for different lattices. This factor can be used in the main equation (25) instead of the complex combination.

Even with the known elastic moduli (or velocities), we still have to calibrate the theory. But after the main equations of the theory is derived, in principle, we can forget about elasticity theory. We could declare the variables α_i be the ratios of thermodynamic temperature and some characteristic temperatures, T_i ,

$$\alpha_i \equiv T_i/T. \quad (30)$$

In such a form, the theory would be more similar to the Debye theory, Appendix A. However, this procedure would introduce many calibrating parameters in place of just one, B .

C. High Temperature Limit of Specific Heat, or About the Dulong–Petit Law

In 1819, the French natural philosophers Pierre Louis Dulong and Alexis Thérèse Petit published [23] the discovery that now bears their names. Petit and Dulong measured how fast solid bodies cooled down in low pressure air and found that the specific heat capacities of the bodies were inversely proportional to the atomic weights of the bodies’ chemical elements [1, 24]. Therefore, the Dulong–Petit law states that the product of the molar mass, M , with the specific heat, C_V , of mono-atomic solid bodies, i.e., the molar specific heat, C_M , is approximately constant,

$$C_M = MC_V \approx 25 \text{ J}/(\text{mol} \cdot \text{K}) \approx 6 \text{ cal}/(\text{mol} \cdot \text{K}). \quad (31)$$

The Dulong–Petit law was important not only in physics, but also in chemistry, where it helped Dmitry Mendeleev to discover the periodic table of chemical elements [24]. Mendeleev used the Dulong–Petit law to correct wrong atomic weights of three elements (cesium, uranium, and indium) by making new measurements of their specific heats.

Almost a century later, after the Avogadro constant, N_A , was introduced, Albert Einstein [3] used Boltzmann’s equipartition theorem to propose that the molar specific heat is universally equal to

$$3R = 3k_B N_A \approx 24.943 \text{ Jmol}^{-1}\text{K}^{-1}. \quad (32)$$

He attempted to explain this empirical rule (31) as the classical limit of a theory based on Planck’s quantum hypothesis which was new at that time. The Dulong–Petit law in the form (32) was later re-derived in the Debye theory [9], and it eventually became a dogma of solid state physics [1] and thermochemistry [25]. However, this law does not hold strictly, and the Dulong–Petit (DP) values vary widely [1]. In many cases, such variations arise from insufficient experimental data, as room temperature, assumed to be the high temperature regime for the Dulong–Petit law, is certainly not high enough for most substances. As is seen from the comprehensive analysis of numerous high temperature experiments, specific heats, e.g., for iron and silicon [26], do not become constant, but keep slowly increasing to the melting point. Thus, the critical points should provide the DP values of specific heats.

The $\alpha \rightarrow 0$ asymptotics (28) derived in this field theory formalism corresponds to the Dulong–Petit limit. In finite temperature QFT for condensed matter, the Dulong–Petit limit emerges from

the minimum length proportional to the lattice constants that cuts off the range of short wavelengths, when the field theory ceases to be valid. In other words, the approximation of condensed matter as continuous medium fails, when the elastic wavelengths become comparable to the average distance between the nodes of lattice.

The Dulong–Petit limit is a constant independent of temperature and elastic properties of the lattice, but not of its crystallographic type. This high temperature limit depends on the number of points in a unit cell, m , and the relative volume of the unit cell (one for cubic lattices). It should also depend on the total number of velocities of a lattice contributing to free energy (19). This means that *the Dulong–Petit limit should be the same for all substances that crystallize to the same lattice type*.

The Avogadro constant and the Boltzmann’s constant enter the Dulong–Petit limit, because it is the only possible combination of fundamental physical constants with the right dimensionality for specific heat. Therefore, we argue that proportionality of the Dulong–Petit limit (31) to the molar gas constant (2.18) follows trivially from dimensional analysis, while *its numerical factor close to 3 is merely a coincidence*. The number three has never been well measured, and its appearance seems to be due to the magic of whole numbers that influenced theoretical developments. All the reasonings proposed as its proofs are based on a discrete model of independent oscillators [1, 3, 9], which apparently fails to correctly describe specific heat for other temperature ranges. However, we could expect that statistical physics, based on the new mathematics being developed by Victor Maslov [27] should produce a correct version of the discrete theory for the lattice specific heat.

D. Finite Size Effects

Free energy in the finite temperature QFT based on the heat kernel (4) contains two terms defined by geometrical invariants of the compact domain, volume and area of the boundary [13]. We focus in this work only on the volume (‘bulk’) term since it gives the leading order contribution in experiments that we want to consider. Let us sketch the reason for discarding the boundary term.

With a system’s effective size [13], defined as the ratio of the body’s volume to its boundary’s area, $r = \mathcal{V}/\mathcal{S}$, the acoustic kappa-factor is determined by the sound velocity, $v \propto 10^3$ m/s,

$$\kappa_a \propto \hbar v/k_B \approx 1.1 \cdot 10^{-9} \text{ K/m}. \quad (33)$$

It shows that the threshold for the appearance of the boundary (finite size) effects in the lattice specific heat is many orders of magnitude higher than in thermal radiation phenomena, where $\kappa \approx 3.3 \times 10^{-4}$ K/m, [28]. Assuming an experimental uncertainty is 1%, we expect that the finite size effects at low temperatures, e.g., $1 < T < 10$ K, could appear only in systems of a nanometer size, i.e., with $r \propto 10^{-9}$ m. In the specific heat experiments with ‘macroscopic’ samples, [29–31], the finite size effects can be seen only at sub-Kelvin temperatures. In general, the true low temperature asymptotics, $\beta \gg r$, depends on the shape and the surface curvatures of the condensed matter system, as well as on its material. Therefore, a universal low temperature asymptotics of the free energy (and of the specific heat) does not exist. Detailed analysis of finite size effects in the heat capacity certainly deserves a special study motivated by the recent experimental quest in nanotechnology.

E. Specific Heat of Compounds, or About the Neumann–Kopp Law

The properties of specific heats of compounds (multi-atomic substances) have been studied in the 19th century by German physicist Franz Ernst Neumann and German chemist Hermann Franz Moritz Kopp. They formulated the rule (in their independent works separated by a time interval) asserting the specific heat of a chemical compound is equal to the sum of specific heats of its constituents. As every empirical law, the Neumann–Kopp rule does not hold strictly. When this rule was derived, the ambient conditions were considered to be sufficient to reach the Dulong–Petit limit, but they are not. A vast number of new compounds were discovered and studied. Extensive data of modern measurements show that many compounds do not obey the Neumann–Kopp rule, for example, the overview of solid binary antimonides [32] states that *“the Neumann–Kopp law is not a suitable substitute for experimentally obtained values of antimonide heat capacities.”* It is likely that this is the case for other classes of compounds.

In general, the Neumann–Kopp rule would give an n -times bigger specific heat for an n -atomic compound, only if the Dulong–Petit law were exact and held at ‘ambient conditions’; this is not the case. Let us have a fresh look at this rule from the point of view of the geometrical formalism,

where the heat capacity of a crystal is defined by its volume, the number of sound velocities, and by the crystal characteristics. This means that specific heats of elements that compose a compound must be irrelevant.

The Neumann–Kopp rule for specific heats of crystal matter has been established, because it uses the definition of the amount of substance (mole) of solid state matter derived for gaseous matter. Thus, one mole of an n -atomic compound contains n -times more constituents (atoms as the lattice nodes) than its composing elements in a solid state contain. If the composing elements crystallize to the same type of lattice as the compound, then the Neumann–Kopp rule would be exact. This is, of course, a special case, but many common substances have similar specific heats under some commonly used conditions (the Dulong–Petit law). It is clear that, for many more substances, which were discovered and studied since the 19th century, under general conditions, the Neumann–Kopp rule is false.

We suggest that one mole of crystal matter should *not* be equal to N_A molecules, but rather to the Avogadro number of atoms (or ions) as true constituents of the crystal lattice. Indeed, separate molecules of a chemical compound do not exist in a crystal. Instead, the whole crystal lattice can be viewed as one large molecule of a compound, whose atoms occupy positions at the lattice nodes. Therefore, we suggest to correct tabulated specific heats for n -atomic compounds by dividing their values by n . As an example, we will consider two-atomic compounds with the *zinc-blende* lattice, since it is a cubic lattice of the diamond type for two-atomic materials. We argue that the corrected Dulong–Petit limit of such substances is equal to the one for the carbon group elements with the diamond lattice.

3. EXPERIMENTS. SPECIFIC HEAT OF THE DIAMOND LATTICE

A. The Group IV Elements

In order to examine the presented theoretical ideas, let us consider experimental determinations of specific heats of some solid substances. We will do the statistical analysis of available data for the elements from group IV (carbon group) of the periodic table of chemical elements that crystallize to the diamond type cubic lattice. They include diamond (carbon, C), silicon (Si), germanium (Ge), and gray tin (α -Sn). These are α -forms (diamond lattice) of Si and Ge, but their β -forms with tetragonal lattices exist under certain pressures [33]. The properties of gray tin are little measured, so we try to make some predictions.

In 1950s, Morrison with collaborators at chemical laboratories of the National Research Council of Canada performed precise measurements of specific heats of many crystal solids at a wide range of temperatures. These were traditional measurements done with calorimeters. For some of these solids, Morrison's experiments remain state of the art today, because no attempts were made to repeat them with higher precision. Morrison's group measured specific heats of natural diamonds [29] and pure, commercially grown, single crystals of silicon and germanium [30]. They published full tables of the original experimental data together with the analysis. Among the three data sets available for the carbon group elements, the data for germanium and silicon [30] are the best. Probably this is because the diamonds used in the study were natural, thus, with uncontrolled defects and impurities. We use the germanium data as an instance of the diamond lattice although the silicon data are as good and produce the same physical results. All measurement data were converted to the SI units $\text{J mol}^{-1} \text{K}^{-1}$.

Table 1. Properties of the carbon group elements and GaAs

material	a	c_{11}	c_{12}	c_{44}	ρ	v_5	T_0	θ	T_{cr}	C_{DP}
diamond	3.567	1079	124.0	576.0	3.5156	11.659	173.3	1.44	3900	27.5
α -Si	5.431	165.78	63.937	79.625	3.3291	4.6739	39.4	1.67	1685	29.16
α -Ge	5.657	128.53	48.26	66.80	5.3256	2.7459	21.4	1.73	1210	28.76
α -Sn	6.4892	66.7	36.5	30.2	5.7710	1.618*	11.0*	1.73*	286	29.1*
GaAs	5.6533	118.77	53.72	59.44	5.3175	2.4732	20.0	1.67	1513	29.08*

The number of atoms per unit cell, m , of the diamond lattice is eight [1]. The velocities of sound in crystals of the carbon group elements were measured in [15–17]. The derived elastic constants are given according to these papers in the units of GPa , in Table 1, as a more concise and equivalent representation. The elastic constants of gray tin were indirectly derived from neutron scattering experiments [34], the standard technique to determine frequencies of crystals; these values are accepted in the later references like [36]. The lattice constants, a , in Ångstrom, 10^{-10} m, are from

the reference book [36]. The densities, ρ , also from [36], are expressed in the commonly used units of g/cm^3 . The lowest velocities of sound, v_5 , in units of 10^3 m/s , are also given (it is computed for α -tin). Critical temperatures, T_{cr} , are the sublimation temperature for diamond [35], the melting points of Si and Ge [36], and the $\alpha \rightarrow \beta$ lattice transition (its reverse is the ‘tin pest’ effect [33]) for α -tin. The low- T characteristic temperature, T_0 , is explained below. The values not directly measured yet (predicted) are marked by the asterisk sign. The elastic moduli for GaAs are from [18]. Its highest specific heat, given in [37], is corrected by the factor $1/2$. Some of the basic properties of these and other semiconductors are also available online at the Ioffe Institute [38].

B. The Dulong–Petit Values

We need to know the high temperature limit (the Dulong–Petit value) of specific heat of the carbon group elements with diamond lattice (or any other elements with this lattice) for calibrating the model. At the same time, we check the hypothesis that the Dulong–Petit values of all such elements are the same as suggested by Eq. (28).

The Dulong–Petit value for diamond is the most difficult to obtain, because its $\Theta(\alpha)$ spreads wide, thus, its low temperature regime is high, $T < 170\text{K}$. The only reliable number is $C_{\text{DP}} = 22.10 \text{ J}/(\text{mol K})$ at 1100K in [39], but its temperature is too low for the anomalous thermal behavior of diamond. Two more numbers, 24.7 and $26.3 \text{ J}/(\text{mol K})$, at 1800 and 3000K respectively, are given in the reference book on carbon [35], but their original source is not clear. Since the monotonic growth of specific heats is almost linear, we made an extrapolation to the critical (sublimation) temperature 3900K to get $C_{\text{DP}} \approx 27.5 \text{ J}/(\text{mol K})$. The reliably measured DP limit of diamond is apparently not known.

The DP value for silicon, $29.199 \text{ J}/(\text{mol K})$ at its melting point is taken from the reference book [40]. Reference [41] cites the book [42] for the recommended polynomial fit, which gives $29.114 \text{ J}/(\text{mol K})$. We take their average as C_{DP} .

The specific heat of germanium near the melting point is given in the reference book [40]: $C_{\text{DP}} = 28.756 \text{ J}/(\text{mol K})$. It lets us fix the overall constant of the model, (29), for the diamond lattices:

$$\mathcal{R} \approx 345 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (34)$$

The Dulong–Petit value of gray tin could be measured at rather low temperatures. Its critical temperature is marked by transition to β -Sn. We found the α -Sn specific heat $0.278 \text{ J}/(\text{g K})$ at 100K from the reference book [36], which translates to $33.00 \text{ J}/(\text{mol K})$. However, it is not measured, but obtained indirectly the elastic constants. It is clearly higher than the other C_{DP} values in the table. According to the proposed model, we conjecture that the true value of the Dulong–Petit limit of specific heat of gray tin is the same as the one for silicon and germanium, namely, approximately $29 \text{ J}/(\text{mol K})$.

Summarizing, it is likely, when experimental inconsistencies are cleared up, that the lattice specific heats of the group IV elements with the diamond lattice will be the same. This value is close to $29 \text{ J mol}^{-1} \text{ K}^{-1}$ and is certainly away from the presumed exact value (32). We will further check if this statement is true for *any* substance with diamond lattice.

C. Low Temperature Asymptotics

Let us explore the low temperature asymptotics of specific heats. It is common in the literature [1] to plot the data not for specific heat, but for the implied (effective) Debye temperature (43). It is experimentally known that the effective Debye temperature is not constant, as it should be if the Debye theory were correct, instead it exhibits some complex behavior, especially at low temperature [1, 45, 30, 31]. We use a similar combination, $T(R/C_M)^{1/3}$, because it clearly distinguishes different temperature regimes at low temperatures. The gas constant merely allows us to have the units of Kelvin on both axes, while numerical values on the vertical axis are irrelevant. The resulting graph for germanium in Fig. 2 resembles typical curves for the Debye temperatures [30, 31].

Because we assume that the low temperature behavior of specific heat is T^4 , we interpret the descending branch of this graph as the power law $T^{-1/3}$. Temperature at the minimum value of this graph, denoted by T_0 , indicates the limit of the low temperature regime. It is the characteristic temperature for any given material. For germanium, the characteristic temperature is $T_0 = 21.4 \text{ K}$. Characteristic temperatures for diamond and silicon are given in Table 1. The region of low tem-

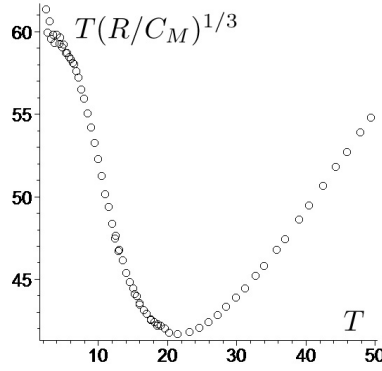


Fig. 2. Finding the low temperature regime of Ge.

peratures for specific heat is limited from below as well, because the relative contribution of the surface heat grows in addition to the experimental uncertainty, which shows up in these data.

Let us show that the characteristic temperature of a condensed matter system that specifies the condition $\alpha \gg 1$, also gives a universal heat capacity constant. Skipping the unessential calibration parameter, the explicit form of the low- T asymptotics is,

$$\frac{\hbar v}{k_B T a} \gg 1. \quad (35)$$

We take the lowest velocity of sound, v_5 , since it gives the leading contribution at low temperatures. The threshold for this condition to hold is given by the characteristic temperature, T_0 . We conjecture that the left-hand side of (35), taken at this temperature, is a dimensionless constant, which is the same for all materials with the same type of crystal lattice,

$$\theta = \frac{\hbar v_5}{k_B T_0 a}. \quad (36)$$

The values of θ are given in Table 1, which shows that they are indeed very close, with the diamond's value somewhat apart. Let us take now the computed sound velocity, v_5 , for α -tin to derive T_0 for gray tin from this constant (36), taken to be equal to 1.73:

$$\alpha\text{-Sn} : T_0 = \frac{\hbar v_5}{k_B \theta a} \approx 11.0 \text{ K}. \quad (37)$$

This is a testable *prediction* for future determinations of the specific heat of single crystals of gray tin.

Let us now test the T^4 -hypothesis (27) vs. the Debye cubic law (42) statistically and graphically, without calibrating the full theory, because we need this for the second calibration parameter. We take the obtained low temperature range, $T = 4.364, \dots, 20.233$ K, and fit its specific heat data with two testing functions, aT^4 and bT^3 . The resulting least-square fits obtained by Maple are $a = 6.297 \times 10^{-6} \text{ J}/(\text{mol} \cdot \text{K}^5)$ and $b = 9.085 \cdot 10^{-5} \text{ J}/(\text{mol} \cdot \text{K}^4)$. The chi-square statistics for both hypotheses do *not* reject either, i.e., both laws are statistically allowed. However, the χ^2 -statistic for the cubic law is 0.162 vs. 0.002 for the quartic function, with both p-values equal to one; this shows is that the T^4 -function is favored.

More apparent evidence can be seen when the two obtained fits are plotted together with the measured data in a popular graph, C_M/T vs. T^2 , Fig. 3, often used to demonstrate the validity of the Debye cubic law [1, 30, 31]. It is obvious that, in the selected temperature range, the specific heat of germanium does *not* obey the cubic law.

Another popular graph in the solid state physics literature is C_M/T^3 vs. T , Fig. 4. This graph looks even more compelling, since the observed data are nowhere close to a constant (horizontal line) expected from the Debye T^3 -law. Instead, they can be approximated by a linear function (obtained above by fitting the original data, not this scaled data), which means that we have a

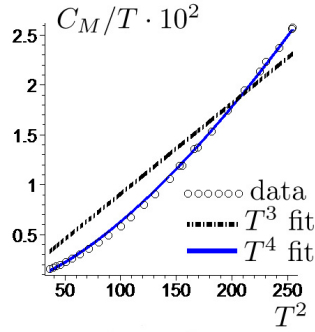


Fig. 3. Testing the low-T hypotheses for Ge. I.

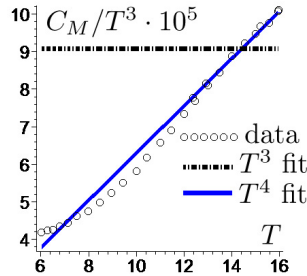


Fig. 4. Testing the low-T hypotheses for Ge. II.

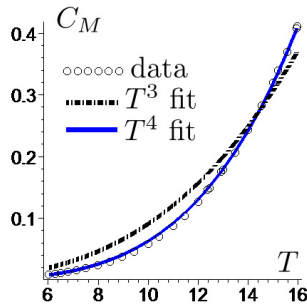


Fig. 5. Testing the low-T hypotheses for Ge. III.

T^4 -law. Note that this fits the assumption $C_M = 0$ at $T = 0$, which is excluded in the geometrical formalism, is only a reasonable approximation here, since C_M is infinitesimal (but never zero due to surface heat) at $T < 1$ K.

The results of the power law fits and the χ^2 -statistics as well as the graphs made for the silicon data [30] are qualitatively the same, they confirm the quartic power law.

The diamond data [29] gave inconclusive results, both power laws are equally bad at approximating the low-T specific heat. The reason could be not only the anomalously big region of low temperatures, but also the presence of impurities and defects in natural diamonds (or catalytic atoms in synthetic diamonds, see the Discussion).

In general, it is difficult to make a selection of the two tested power laws using original (not scaled) data. However, this is not in the case for germanium, as seen from Fig. 5.

However, in the solid state physics literature, such fits are done not to the cubic law, but to the extended polynomial, $C_M = aT^3 + bT^5 + cT^7$. Various arguments were given for its introduction, but its two higher power coefficients usually have low or no statistical significance. Probably, because of the use of such extended polynomials and because of the firm belief in the Debye cubic law, its validity has not been questioned, even though experimental data contradicting to it are abundant.

D. Specific Heat of Gallium Arsenide

The ideas about the Kopp–Neumann rule for multi-atomic substances presuppose that compounds have the same properties as elements if their crystal lattice types are the same. In the diamond lattice of a two-atomic compound (zinc-blende lattice), half of its atoms belong to each composing element [1, 22]. Many semiconductors crystallize to the zinc-blende lattices [38], thus, their properties are well measured [43].

Let us take gallium arsenide, GaAs, as an example. According to the conjecture of Section 2.E, the Dulong–Petit limit of GaAs should be the same as the DP value of any of the carbon group elements with the diamond lattice, if we would take one mole of its *atoms*, not molecules. Indeed, this is true within experimental uncertainty: the GaAs specific heat given at 1500 K in [37] is $C_{DP} = 58.17/2 = 29.08 \text{ J}/(\text{mol}\cdot\text{K})$.

We can also look at the low temperature asymptotics of the GaAs specific heat. The study [44] provides the sufficient number of data points for specific heat of gallium arsenide. Using it, we made a plot of the type of Fig. 2 that determined the low temperature region as $T_0 = 20.0 \text{ K}$, which produced the θ -constant as 1.67, confirming its universal nature. Further statistical and graphical analysis performed according to the described above procedures gave the same conclusions as for the group IV elements: *the low temperature asymptotics of the GaAs specific heat is a T^4 -function*.

Therefore, we can conclude that the conjecture about the similarity of thermal characteristics of compounds and elements with the same lattice type holds. In fact, their elastic properties are also similar, as they should be. In particular, gallium arsenide resembles germanium, as is seen from Table 1. Such a similarity was noted first in [18], and it is likely the fundamental reason for a near coincidence of characteristics of the considered specific heats.

4. SUMMARY

The chief applications of finite temperature quantum field theory lie in condensed matter physics. As a first element of this program, we have implemented the idea of Debye about lattice heat as energy of sound waves in elastic bodies. The proposed thermodynamics of solid state matter presents the theory of specific heat formulated in the field theory language, without reference to Planck’s distribution and quantum oscillators. The summary follows.

- (1) Thermodynamics of condensed matter is a theory different from classical thermodynamics of gases.
- (2) The dimensionless combination of thermodynamic temperature and the lattice constant is a proper thermal variable in condensed matter physics.
- (3) The dimensionless functional of free energy is defined by the sound velocities, lattice constants, crystallographic type and geometrical characteristics of the condensed matter system.
- (4) The measurement postulate is expressed as a scaling hypothesis.
- (5) The specific heat of any condensed matter system is determined by the universal thermal sum of the new thermodynamic variable.
- (6) The specific heat near a critical point (the Dulong–Petit vale) is the same for all substances with the same type of crystal lattice. The Dulong–Petit limit appears due to the lattice cell size cut-off.
- (7) One mole of an n-atomic compound, in crystal form, should be equal to the Avogadro number of its atoms. The Neumann–Kopp law holds only in special cases due to the old definition of the solid matter mole.
- (8) The lattice specific heat at low temperatures is the T^4 law, not the Debye T^3 law. The experimental data of the Morrison group and some other data decisively confirm the quartic law. Other power laws may appear due to the electronic, surface, and polycrystalline properties of solid matter.
- (9) Universal thermal asymptotics of a solid body towards the absolute zero temperature do not exist, because they depend on the body’s shape and material.

5. DISCUSSION

The central object of spectral geometry [46] is the trace of the heat kernel. Its leading (under the ‘high-temperature’ conditions [13]) terms are expressed by two geometrical invariants of the system’s domain, its volume and the boundary’s area, (4). This theorem of mathematical physics has been re-derived by various methods starting from the pioneering works of P. Debye [9] and H.

Weyl [47]. The heat kernel removes the need to study actual spectra of condensed matter systems. The spectrum of lattice frequencies, as studied in neutron scattering experiments and in phonon theory, may be complex, nevertheless, its heat kernel trace is always proportional to the system's volume, (4).

We need to know the function's values at two temperature points in order to finally fix it for a specific class of materials, e.g., diamond lattice crystals. Thus, the model should be calibrated anew for every type of crystal lattice, which means there is an own thermodynamics for every crystallographic type. This is not surprising at all. Classic thermodynamics was developed as the physics of rarefied gases, and the universal feature of gas is its homogeneity. In contrast, solid state matter is inhomogeneous and anisotropic, i.e., it possesses internal scales along different directions. These geometrical properties determine the thermodynamics of condensed matter systems.

We have not completed the full calibration of this model. In the low temperature regime, the model has a simple power behavior, which is defined by the lowest velocity of sound. However, as seen from the $\Theta(\alpha)$ behavior, Fig. 1, the one-velocity model can only be correct in the low temperature limit. According to the assumption about the total free energy (2.5), the sum over all allowed velocities should be performed. However, the naive sum without independent weights, i.e., with equal weights, $\mathcal{R}/9$, does not match the full data set. Obviously, by varying weights in the sum, we could fit the data well, but this is an artificial procedure that would multiply the number of calibration parameters. This means we have to acquire more information about physics of elastic waves to finish this work.

Experimental testing of this model has only begun. The data for natural [29] and synthetic [49] diamonds do not confirm the quartic law. Instead, both power laws are statistically allowed, but they are equally bad at describing the natural diamonds data, while the Debye cubic law is selected for the synthetic diamonds. However, diamond is the single thermophysical anomaly among all substances in the Nature; more precise measurements are needed. Furthermore, available data sets for metals, copper (Cu) [44] and aluminum (Al) [50], show T^3 behavior at low temperatures when treated with the algorithms above. Whether this is a property of metals with electronic heat contribution or a characteristic of polycrystalline solids, which apparently formed the used ingots, should be examined. At the same time we can observe the T^4 -power law in the specific heat data of some two-atomic compounds: gallium antimonide, GaSb [44], silver chloride, AgCl [51]. The critical experimental analysis and the development of the theory should be continued.

Physical properties of polycrystalline bodies are different from those of single crystals. A polycrystalline body can be considered as a composite of grains (domains) of single ideal crystals joined by their common faces (boundaries). Therefore, it is reasonable to assume that each grain has its own volume free energy as well as its own surface free energy, while the contributions from the edges and vertices of the grains could be significant. We know that the contribution of a boundary may exceed the volume one in the 'low temperature' regime [13]. Thus, the total heat capacity of polycrystalline bodies may be complex.

In his work [3], Einstein introduced the quantum hypothesis of M. Planck to condensed matter theory. It has been admitted that this innovative approach was not correct in the method and the result. The Einstein theory seemingly produced the Dulong–Petit law, but not the low temperature asymptotics. We have argued that the DP limit could not also be derived this way. The non-success was caused by the use of mechanistic methods, inherited through statistical mechanics (oscillators and the equipartition theorem), in an entirely new realm of physics. In this early work, Einstein did not get rid of classical mechanics altogether, but later, he criticized *the mechanical view* of physics and advocated dispensing with it [52]. Debye chose the right approach, but Planck's empirical formula [53] remained the only way to connect elasticity theory and thermal physics.

The dynamical theory of crystal lattices developed for specific heat by Max Born and Theodore von Karman [1, 55] was originally close to the Debye theory [54] in its use of elasticity theory. In modern textbooks, the Born–von Karman theory is regarded as a first principles theory based on quantum mechanics. The obvious and often criticized fault of this theory is its periodic (cyclic) boundary conditions (the Born–von Karman boundary conditions), which define the condensed matter system's space as compact without a boundary. Thus, this theory cannot deal with boundary effects at all. Furthermore, it is important to realize that the topology of the Born–von Karman theory's space is non-trivial. Its boundary conditions effectively replace the topology of the open space, \mathbb{R}^3 by the topology of the three-dimensional torus, $\mathbb{S}^1 \times \mathbb{S}^1 \times \mathbb{S}^1$. This makes it a different mathematical problem, whose solutions are also different from those of the original problem. The

comparisons of the Born theory predictions with experimental data were done [21] and they demonstrated that the Born theory had failed to agree with the experimental data available at that time. Later experimental studies, e.g., [39], also cited significant disagreements of measured specific heats with theoretical results of the Born-von Karman theory.

Another theory of the lattice specific heat is a phenomenological theory of Chandrasekara Venkata Raman [56]. His theory of the crystal lattice dynamics was based on the frequencies of a basic block of atoms, e.g., in the diamond lattice [57], and it is apparently better than the Born theory in describing diamond's properties [39]. However, this model is not working well at low temperatures [39]. The likely reason is that, in this regime, the theory should take into account the system's spatial domain as a whole, i.e., the full lattice with its boundary, and the discreteness of its frequencies spectrum.

Dissatisfaction with the Debye theory brought up attempts to improve its agreement with experiment by introducing more parameters to fit the empirical equations to the observation data. Sometimes large discrepancies between the Debye theory and experiments are assigned to peculiar properties of a specific state of matter, such as glass [58]. However, the shape of the low-temperature graphs in [58] looks similar to Fig. 4. Thus, this could likely be a consequence of the universal power law (27), which makes its appearance in many instances of condensed matter.

Diamond is one of the most experimentally studied crystals. It has fascinated people and researchers for a long time, [3, 56, 29, 49]. Diamond is indeed a thermal anomaly among elements, and it proved its character again by refusing to reveal its low temperature power law. The belief in the anomalously low Dulong–Petit limit of diamond [1] was false since its specific heat maximum is simply reached at very high temperatures. Diamond's remarkable thermal properties are explained by its unusual elastic characteristics. Namely, the high velocities of sound and the dense lattice provide the anomalously large combination v/a in (26), which spreads the functions $\Theta(\alpha)$ along the temperature axis. Thus, the diamond has the longest range of low temperatures. We believe the parameters in Table 1 found in experiments should be different if ideal diamond crystals were available for measurement. Neither natural, nor currently produced synthetic (due to the used technology) diamonds can be satisfactory. In particular, the DP value should be the same as for other entries, about 29.1 J/(mol K), and the θ -parameter be equal to 1.7. The importance of carbon for the technology of high temperature resistant materials gives the hope that these numbers will be verified soon.

It is derived in statistical mechanics that the specific heat and the heat conductivity are intrinsically related. Therefore, instead of direct determinations, the heat conductivity is often measured, while the specific heat is implied from the Fourier's thermal conductivity equation [1]. Since we have not derived thermal conductivity in the present formalism yet, we have focused only on the calorimeter measurements. For this reason, we place the discussion of specific heat of solid argon [60, 61], the textbook's topic, Chap. 5 of [1], to Appendix B.

To our great surprise, basic thermal and elastic properties of α -tin, in single crystals, have not been studied yet (at least, we failed to find such studies and data). Neither specific heat, nor sound velocities were directly measured in gray tin. The technique for producing single crystals of α -tin is described in [59]. Now these crystals await an experimentalist to have their properties measured.

A special statement about experimental data is in order. It is regretful that starting from around 1980s, many reports on physics experiments stopped including essential measurement data in their publications. Instead, data are analyzed by experimental teams, sometimes in collaboration with theoreticians, and a result of such an analysis is presented. If data are presented, it is done in plots, which makes them useless for other researchers. This situation creates a serious danger to physics as an experimental science by removing access to valuable information that should belong to the whole science community. Appendix C of this paper reproduces the specific heat data for germanium [30], that were obtained at the publicly funded laboratories of National Research Council of Canada. Let us mention that the results of another great work of Morrison's group [31] were essentially lost, since we failed to recover its full data, deposited at the Royal Society (U.K.) archives, despite the efforts of both countries' agencies.

When the present work was done and the paper was written, we discovered the comprehensive series of works of Roland Pässler, e.g., [62, 63]. In these works, a new model for the description of specific heats over an entire range of measured temperatures is developed. The model contains several characteristic temperatures and fits the data with the sums of exponential functions, whose arguments are quadratic in the temperature. The fact that [30] is used to calibrate the model further

emphasizes the crucial role of experimental data for theory development. A careful comparison is required, but it is already clear that the empirical representation derived by Pässler is similar in some aspects to the axiomatics proposal above.

Thermodynamics was created as physics of gaseous state of matter, and its main practical application was the development of heat engines. Therefore, in its original form, classical thermodynamics is limited to the range of physical phenomena it can describe, and its extension to continuous medium requires further development. Thermodynamics is incomplete until a body's *boundaries* are included into the physical theory. In classical thermodynamics, boundaries are present, but only implicitly as a means to keep volume finite and to transfer heat energy from gas to external media and conversely. Thermodynamics with boundaries included *explicitly* arises from the finite temperature quantum field theory.

The opening paragraphs of the paper by James Clerk Maxwell 'On the dynamical theory of gases' [10], read: "*Theories of the constitution of bodies suppose them either to be continuous and homogeneous, or to be composed of a finite number of distinct particles or molecules.*

In certain applications of mathematics to physical questions, it is convenient to suppose bodies homogeneous in order to make the quantity of matter in each differential element a function of the co-ordinates, but I am not aware that any theory of this kind has been proposed to account for the different properties of bodies. Indeed the properties of a body supposed to be a uniform plenum may be affirmed dogmatically, but cannot be explained mathematically."

The present work is only a first step towards the mathematical theory of 'homogeneous bodies', i.e., the field theory of condensed matter. Let us hope it will motivate some critical development in condensed matter physics.

APPENDIX A: REVIEW OF THE DEBYE THEORY

The generating functional of the Debye theory is not dimensionless, but is energy (J) [9]. The Debye theory contains one calibration parameter, the Debye temperature, T_D , which gives the dimensionless variable of the theory,

$$\tau \equiv T_D/T. \quad (38)$$

The scaling function of the Debye theory has the form

$$D(\tau) = \frac{3}{\tau^3} \int_0^\tau dx \frac{x^4 e^x}{(e^x - 1)^2}, \quad (39)$$

which gives the specific heat as

$$C_D = 3k_B N_A D(\tau). \quad (40)$$

The overall factor of the Debye specific heat is fixed by the belief in the exact Dulong–Petit law,

$$C_D = 3k_B N_A, \quad \tau \rightarrow 0. \quad (41)$$

The low temperature asymptotics

$$C_D = (12\pi^4/5)k_B N_A/\tau^3, \quad \tau \rightarrow \infty. \quad (42)$$

and C_D is zero at $T = 0$.

The Debye temperature is an experimentally determined constant for every material. It is found from the low-T limit of the specific heat (42) as

$$T_D = (12\pi^4/5)^{1/3} T(R/C_M)^{1/3}. \quad (43)$$

The Debye temperature is related to the elasticity constants through the sound velocities [9, 45, 1],

$$T_D = (\hbar v_m/k_B)(6\pi^2 N/\mathcal{V})^{1/3}. \quad (44)$$

The general deficiency of the Debye theory is its single characteristic temperature that could not be physically realistic for describing specific heats, as is recognized in the literature. With one Debye temperature, there can be only one velocity. It is the average velocity v_m of the longitudinal and transverse velocities,

$$v_m = \left(1/3(1/v_l^3 + 2/v_t^3)\right)^{-1/3}. \quad (45)$$

In fact, at low temperatures, this expression is equivalent to using the transverse velocity: v_t is typically 1.5–2.0 times smaller than v_l , so, $v_m \propto v_t$. This fact may explain why the values of the implied Debye temperature (43) and the elastic Debye temperature (44) are so close.

It is described in the literature [45, 1], that the Debye theory of specific heat works relatively well at temperatures below $T < T_D/50$ and above $T > T_D/2$, with different values for the Debye temperature in each range. Thus, it does not work for the large and important range of temperatures. Above, we have argued that the Debye theory also fails to work at the high and low temperature asymptotics.

The reason for the poor performance of the Debye theory is its two intrinsic problems. First, in order to deal with the divergence of total energy in the high frequency limit, the continuous medium model based on elasticity theory was replaced by the discrete model of quantum oscillators, which were identified with the lattice nodes [1, 9]. Here Debye used Einstein's idea [3] in order to explain the Dulong–Petit law by postulating that the number of quantum oscillators is equal to the number of lattice nodes of a crystal lattice, N . Then he equated the total energy of these oscillators, which were found according to the equipartition theorem, to the total energy of elastic standing waves, in the volume \mathcal{V} , up to certain maximum frequency, ν_{\max} . From elasticity theory he derived that the *total* energy of elastic the waves is proportional to the third power of this maximal frequency [9],

$$3N = \nu_{\max}^3 \mathcal{V} F, \quad (46)$$

where F is given by the elasticity parameters. This equation enforces the fixed upper limit of a body's elastic spectrum. The maximum value ν_{\max} obtained from (46) serves as the upper cut-off of the frequency integral.

However, this explanation could not have been acceptable, because Debye theory is a field model, while the discrete model of a crystal lattice presents an alternative description of the same physical phenomena. This creates a mix-up of two entirely different formalisms, and the resulting hybrid theory is not self-consistent. Second, in his derivation of specific heat, Debye computed an integral of the density of eigenstates over frequency. Thereby, he replaced the discrete modes by a continuous variable. However, in the low temperature regime (42), the deviation from the true discrete distribution inside a compact domain can be significant. In fact, this substitution procedure in general is ambiguous and serves as a cause of confusion.

APPENDIX B. SPECIFIC HEAT OF SOLID ARGON

The popular solid state physics textbook of Charles Kittel [1] gives a graphic proof of the T^3 law by plotting the specific heat of solid argon vs. T^3 , Fig. 9, p. 125. The figure is given with no reference, but the names of experimental data's authors let us trace its published source, which is the work of Leonard Finegold and Norman Phillips [60]. These experiments were done, at temperatures between 0.4 and 12K, with the heat pulse technique, i.e., by determining the speed of heat propagation in matter, as different from the calorimeter measurements. Besides the crystal lattice of solid argon is face-centered cubic, not the diamond one as in the examples above. However, due to significance given to this plot in the literature, we still analyzed these references and the specific heat data for solid argon.

Using the data of [60], the graph of C_M vs. T^3 , similar to Fig. 9 of Chap. 5 in the textbook [1], can be plotted, and it does look like, at the first glance, as a straight line. However, this figure is really deceiving, because the use of such a scale on the horizontal axis does not reveal the data's power law. This apparently straight line is determined by a few points at higher temperatures $7\text{K} < T < 11\text{K}$, while nothing quantitative can be concluded about the majority of data points in the few Kelvin region of interest.

We performed on these data the same analysis as done for the carbon group elements, and the conclusions are the same. If the statistical analysis is done with the raw data, $C_M(T)$, it confirms the quartic law at lower temperatures, but the cubic law is not statistically excluded. Using the plot, $T(R/C_M)^{1/3}$ vs. T , Fig. 6, the characteristic temperature of solid argon is found, $T_0 = 8.0\text{K}$.

If we draw the graph, plotted by Finegold and Phillips [60], C_M/T^3 vs. T , we do not get a horizontal line (constant) expected from the T^3 -law, so neither Finegold and Phillips did.

The graph, Fig. 7 (Fig. 2 of [60]), varies significantly, as does the krypton data plot [60]. The data points below 1.5 K should be excluded due to apparent experimental uncertainties. In the remaining range of temperatures, 1.5 to 8 K, this graph is almost a linear function, $C_M/T^3 = aT$, which implies the T^4 power law in the data for solid argon (as well as for solid krypton).

These experimental data are similar to and improve on the results of Morrison's group [61], as compared in [60]. The experimentalists, being unable to explain these discrepancies with the theory,

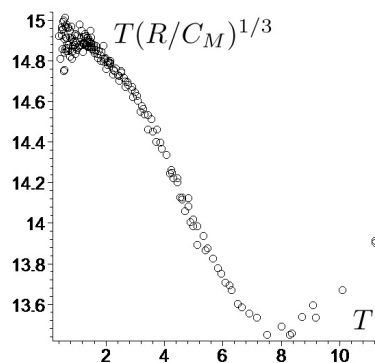


Fig. 6. Low temperature region for specific heat of solid argon, [60].

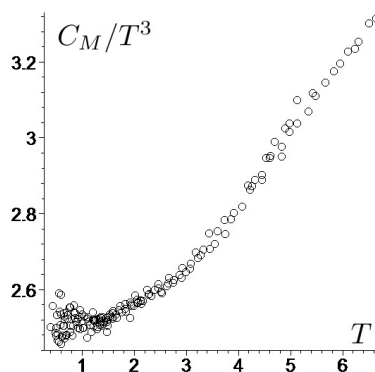


Fig. 7. Power law for the specific heat of solid argon, [60].

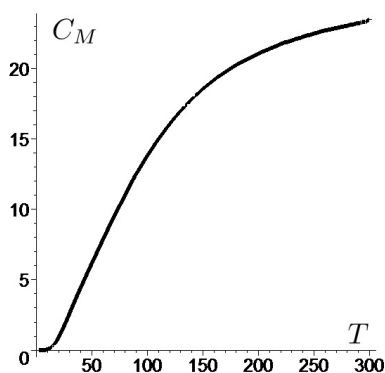


Fig. 8. Specific heat of germanium, [30].

concluded their paper by calling in 1969 for better theories [60]: “*whereas some years ago the theories were more advanced than the experimental data available, now the need is for a better understanding of the interatomic forces as well as for improved anharmonic theories.*” The old experimental data are still quite sufficient for modern use, but instead of building a tower of improvements upon the old theory we suggest to explore different theoretical ideas.

APPENDIX C. SPECIFIC HEAT OF GERMANIUM, [30]

In Table 2, the temperature is given in the units of Kelvin, and the specific heat of germanium is converted from calories of the original table to Joules of the SI system, $\text{J mol}^{-1} \text{K}^{-1}$.

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Table 2. Specific heat of germanium, [30].

T	C_M	T	C_M	T	C_M	T	C_M	T	C_M
2.461	0.000537	13.008	0.1784	40.46	4.548	95.46	13.242	200.02	21.062
2.675	0.0007389	13.478	0.2069	42.43	4.8869	97.17	13.456	203.54	21.192
2.971	0.0009778	14.002	0.2439	44.29	5.1882	98.76	13.665	207.02	21.301
3.175	0.001259	14.536	0.2831	45.89	5.4894	100.27	13.845	210.49	21.418
3.481	0.001639	15.002	0.3200	47.87	5.8283	103.23	14.192	213.92	21.527
3.713	0.002040	15.192	0.3394	49.37	6.0793	106.87	14.652	217.34	21.644
3.961	0.002411	15.579	0.3693	51.90	6.5145	110.39	15.046	222.82	21.836
4.364	0.00332	15.945	0.4081	53.59	6.7864	113.82	15.406	226.53	21.891
4.471	0.003499	15.961	0.4112	55.63	7.1254	117.17	15.765	230.21	21.991
4.814	0.004506	16.578	0.4715	57.15	7.3848	120.44	16.104	233.87	22.117
4.963	0.004895	16.979	0.5151	59.02	7.6986	123.84	16.435	237.50	22.171
5.283	0.006050	17.579	0.5866	60.39	7.9287	127.36	16.761	241.11	22.280
5.503	0.006845	17.588	0.5853	62.35	8.2592	130.81	17.067	244.70	22.380
5.774	0.008012	18.051	0.6418	63.76	8.4893	134.18	17.364	246.4	22.380
6.024	0.009155	18.493	0.7008	65.81	8.8324	135.93	17.481	249.98	22.485
6.284	0.01051	18.628	0.7117	67.30	9.0751	139.22	17.761	253.51	22.552
6.506	0.01172	19.041	0.7640	69.22	9.3680	142.42	18.025	257.02	22.656
6.784	0.01359	19.632	0.8481	70.73	9.5939	145.75	18.255	262.81	22.748
7.131	0.01609	20.233	0.9439	72.54	9.8868	149.23	18.523	268.85	22.849
7.51	0.01953	21.449	1.1334	74.07	10.130	152.66	18.723	272.84	22.920
7.974	0.02409	23.186	1.4192	76.00	10.422	156.05	18.949	276.81	22.987
8.465	0.03021	24.548	1.6527	77.45	10.653	159.39	19.150	280.72	23.054
8.948	0.03745	25.86	1.8845	79.38	10.950	162.69	19.372	280.90	23.075
9.434	0.04619	27.22	2.1313	81.09	11.217	166.06	19.531	284.80	23.117
10.006	0.05820	28.46	2.356	82.75	11.477	169.50	19.715	286.55	23.167
10.442	0.07025	29.87	2.6221	84.36	11.719	172.90	19.887	288.66	23.205
11.015	0.08799	31.16	2.8614	85.97	11.962	176.26	20.067	292.38	23.251
11.458	0.1037	32.68	3.1418	87.50	12.180	178.49	20.184	292.48	23.263
12.011	0.1272	33.91	3.3677	89.06	12.439	183.82	20.418	296.23	23.351
12.366	0.1469	35.72	3.7020	90.70	12.615	189.31	20.631	296.24	23.313
12.471	0.1489	36.93	3.9229	92.22	12.791	192.91	20.782	300.01	23.468
12.902	0.1752	39.00	4.2928	93.98	13.054	196.48	20.916	300.05	23.430

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